

Research Progress in Methane Storage Using the Metal-Organic Frameworks

Jialin Li*

School of Material Science and Engineering, Shanghai University, Shanghai, China

* Corresponding Author Email: hait@shu.edu.cn

Abstract. The improvement of social production and social technology in recent times has led to a gradual increase in the worldwide energy demand. In addition to the issue of shortage, burning fossil fuels like traditional oil produces a significant quantity of greenhouse emissions, which contribute to global climate change. In today's world, natural gas is an essential clean energy source. These days, liquefied natural gas (LNG), adsorbed natural gas (ANG), and compressed natural gas (CNG) are the most widely utilized storage techniques. ANG is the most promising method since it offers advantages over other approaches, including room temperature storage, safety, dependability, efficiency, and environmental protection. The most popular adsorbent materials at the moment are metal-organic frameworks (MOFs), which are characterized by a high specific surface area and porosity, a topological structure and pore size that can be adjusted, strong solvent stability, and heat stability. For this reason, the structural traits and techniques of the production of MOFs are first summarized in this article. The methane adsorption process was then clarified. Ultimately, the use of MOFs in methane storage was highlighted to offer some guidance for the advancement of MOFs as adsorbent materials in the future.

Keywords: MOFs, synthetic method, adsorption, methane storage.

1. Introduction

The energy sources that we have been using have changed over the past several years. One such change is the widespread use of natural gas, which is an essential part of fossil fuels [1]. Natural gas has long been viewed as a new-generation energy commodity to replace some of the conventional fuels because of its plentiful supplies and reduced carbon emissions when compared to other fossil fuels like oil. But the main ingredient in natural gas, methane, also plays a significant role in the emissions of greenhouse gases. The International Energy Agency (IEA) reports that methane emissions are above 70 million tons per year worldwide, which is a hugely detrimental amount. Moreover, methane has a low energy density as a gas, at about 0.036 MJ/mol [2]. Thus, there are still several important obstacles in the way of methane storage.

Adsorbed natural gas (ANG) is rapidly taking the place of compressed natural gas (CNG), which was the main technique employed initially. Adsorbed natural gas (ANG) differs greatly from conventional compressed natural gas (CNG) in that it functions over a pressure range of around 5 bar to 60 bar, exhibiting greater gas adsorption. It's important to remember that ANG maintains an appropriate working temperature range of around -40 °C to 85 °C while simultaneously lowering manufacturing costs and increasing safety [3]. Adsorbent selection has changed throughout time. Zeolites were first used, but their tiny surface area made them unsuitable for contemporary needs [2]. Activated carbon was subsequently used, providing a greater surface area than zeolites, but with functional design restrictions [2]. Over time, attention began to turn to the materials used in MOFs. These disadvantages have been somewhat mitigated by the MOFs, an effective gas storage adsorbent. It has several benefits, the most important of which are that its qualities can be customized and its pores can be tuned. According to specific research, the ligands' length affects certain of their characteristics, and ligand characteristics are connected to the MOFs' deliverable capability [3]. Thus, the gas storage capacity of the MOFs can be increased by modifying the pores and creating the functional groups. At the same time, the manufacturing costs can be kept below \$10/kg, and the

materials have a usable cycle life of more than 100 cycles, satisfying the practical needs of the applications [3].

Therefore, this paper primarily explores various aspects, including the structure and the preparation of the MOFs, the adsorption mechanisms, and the storage applications, providing some reference for the future methane storage potential of the MOFs.

2. Structure and Synthesis of MOFs

2.1. Characteristics of the Metal Ions

Because metal ions in MOFs have a variety of oxidation states, they will display distinct properties [2]. For example, the intrinsic instability of monovalent metal ions in metal-organic frameworks (MOFs) necessitates bonding with ligands containing nitrogen elements to enhance their stability. Conversely, although divalent metal ions are generally stable, they may occasionally have problems due to weak binding strengths. The performance of the overall structure becomes steady when the oxidation state advances to trivalent or tetravalent, although the development of the MOFs crystals will eventually be slightly hindered.

2.2. Characteristics of the Organic Ligands

In addition to the varied features exhibited by the metal ions, the various kinds of organic ligands also exhibit unique characteristics [2]. To start, nearly all metal ions may form bonds with carboxylates, such as carboxylic acids. Their negative charge balances the metal ions' positive charge, creating a comparatively stable structure. It will be difficult to determine the exact structure of the modes, though, because of their varied coordination. However, similar to pyridine, it forms weak connections with the metal ions while coordinating with them in an obvious way. Furthermore, because it is uncharged, other components are needed to counterbalance the positive charge that the metal ions carry. Additionally, azoles and carboxylates exhibit a straightforward and stable binding process with metal ions. On the other hand, the combination of carboxylates and pyridine as ligands takes advantage of both of these properties, achieving charge balance and satisfying multi-nuclear coordination simultaneously.

2.3. Pathways for the MOFs' Synthesis

As for the MOF materials' synthesis, it aims for suitable single crystal sizes, a convenient and time-saving process, and efficient large-scale production based on an environmentally friendly basis [3]. Currently, there are various pathways for MOFs synthesis, and each of them with some unique characteristics, so this paper just focuses on introducing some of the commonly used methods.

2.3.1 Solvothermal method

This process usually entails combining the metal salts with the organic ligands in a particular solvent and letting them react in an environment with high pressure and temperature for a few days. The growth of single crystals is aided by both high temperature and pressure, and by adjusting the reaction conditions, MOFs that satisfy experimental requirements can be produced. However, the disadvantages of this process are that it requires a lot of energy and has lengthy reaction times.

2.3.2 Ordinary solution method

The difference between this method and solvothermal synthesis is that low temperature and stirring are used in place of high temperature and high pressure. This makes the method more energy-efficient and convenient to use, but it also results in much lower stability in the synthesized MOFs and more difficult characterization.

2.3.3 Solid-phase reaction method

In this method, metal oxides or metal hydroxides are mixed and heated to synthesize the new MOFs, its uniqueness lies in its reduced reliance on the effects of the solvent, achieving a yield that

is close to 100% while controlling the operational costs, in addition, the MOFs synthesized through this method also show the excellent adsorption capabilities.

2.3.4 Diffusion method

This method involves dissolving the reactants in the same or different solutions and synthesizing the MOFs through the diffusion reactions between the two fluids in the medium, the problem is that this method requires a longer time, making it more suitable for some small-scale preparations.

2.3.5 Microwave method

Using this method allows for the rapid synthesis of the MOFs, and it can produce smaller particles with excellent selectivity and adsorption properties at the same time.

2.3.6 Electrochemical method

The principle of this method is through the dissolution of the cathodic that provides the required metal ions of the reaction, during this method, it eliminates the need for the separate use of metal salts, thus the whole synthesis process is much simpler and more time-efficient.

2.3.7 Sonochemistry method

This technique uses sonochemistry to synthesize MOFs. It is quick and produces products with a certain degree of selectivity. However, it is noteworthy that because the method involves localized heating, the MOFs that are produced might not last as long as the other materials.

Important to remember is that after synthesis, MOFs usually lack some of the requisite functional groups, which is why post-synthesis modifications are unquestionably required [2]. This entails altering the MOFs while maintaining their original structure following the synthesis procedure. The precise techniques include heating or vacuuming the unsaturated metal sites and eliminating some of the ligands that are prone to detachment. Ultimately, these adjustments improve the MOFs' performance and guarantee that they satisfy the required parameters.

3. Mechanism and Influencing Factors of Methane Adsorption

3.1. Mechanism of Methane Adsorption

The primary reason for the MOFs' capacity to adsorb gas molecules is their open metal sites. The underlying mechanism of this adsorption is based on Coulomb forces, where the adsorption capacity is dictated by the material's geometric shape in addition to the affinity between the adsorbate and adsorbent. Furthermore, the existence of potential metal sites is important for this process [2]. Van der Waals forces are strengthened when gas molecules come into contact with multiple surfaces; additionally, the quantity of potential metal sites increases as the number of open metal sites does, further enhancing the adsorption capacity of MOFs.

According to the current requirements set forth by the U.S. Department of Energy (DOE), the volumetric adsorption of the MOFs should achieve $263 \text{ cm}^3/\text{cm}^3$ while the gravimetric adsorption of them should reach 0.5 g/g . Before delving into the discussion of methane storage using MOFs, it is essential to clarify the following conceptions:

- (1) Excess adsorption: the amount of gas adsorbed on the surface of the material.
- (2) Absolute adsorption: the amount of gas adsorbed on the surface of the material in the absence of the gas-solid interactions.
- (3) Total adsorption: the sum of the excess adsorption and the amount of gas in the material's pores.

These concepts play a crucial role in assessing the MOFs' capacity for methane storage, ensuring compliance with the volumetric adsorption as well as the gravimetric adsorption requirements outlined by DOE.

When assessing the methane storage capacity of the MOFs, it is crucial to consider their corresponding working capacity, which refers to the difference between the maximum storage pressure and the release pressure [4]. In addition, some indicators such as volumetric adsorption and

gravimetric adsorption also need to be clarified, where volumetric adsorption refers to the gas volume that a unit volume of the material can adsorb, similarly, gravimetric adsorption refers to the gas mass that a unit mass of the material can adsorb.

After clarifying the basic conceptions mentioned above, methane storage capacity can be discussed from the perspectives of rigid and flexible MOFs [5]. Among the rigid MOF materials, USTA-76 stands out with an impressive storage capacity, which is composed of copper and 5,5'-(pyrimidine-2,5-diyl) diisophthalic acid linkers, achieving the gas adsorption of $197 \text{ cm}^3/\text{cm}^3$. Besides, ZJNU-50 (Cu+5,5'-(benzene,1,4-diyl-ethyne-1,2-diyl) diisophthalic acid) and MAF-38 (Zn+4-(1H-pyrazol-4-yl) pyridine+1,3,5-benzenetricarboxylic acid) also exhibit high methane storage capacities, reaching $184 \text{ cm}^3/\text{cm}^3$ and $197 \text{ cm}^3/\text{cm}^3$ respectively. As for the range of the flexible MOF materials, the MOF synthesized from cobalt and 1,4-benzenedipyrazole demonstrates volumetric adsorption that is similar to USTA-76, reaching $197 \text{ cm}^3/\text{cm}^3$. But currently what is notable is that a new MOF material, Al-soc-MOF-1, which is synthesized by the coordination of Al with 3,3',5,5'-tetrakis (4-carboxyphenyl) -p-terphenyl linkers, surpasses the DOE target with the methane storage capacities that exceeding $263 \text{ cm}^3/\text{cm}^3$ and 0.5 g/g under the conditions of 298 K and 80 bar.

3.2. Influencing Factors of Methane Adsorption

One of the most important metrics for assessing the MOFs' effectiveness is their adsorption efficiency. A deeper comprehension of the variables affecting the gas adsorption's desorption efficiency is necessary to improve the MOFs' ability to store gas.

Several investigations have revealed that several factors affect the specific adsorption efficiency, including:

First off, gas adsorption is an exothermic process. As a result, as the outside temperature drops, the adsorption reaction changes to follow the direction of the exothermic reaction, which promotes adsorption and increases the MOFs' ability to store gas [2].

Secondly, research on gases is inherently tied to collision theory, and according to this theory, as the pressure of the gas increases, the collisions between the gas molecules become more intense, consequently, the probability of gas molecules entering the MOFs rises, thereby increasing the gas storage capacity of the MOFs [2]. However, there is a practical limit to the pressure increase due to the associated higher costs, safety concerns, and spatial constraints.

Furthermore, the BET surface area and porosity are also important variables affecting the MOFs' gas adsorption performance. The MOFs give greater room for gas molecule adsorption as the BET surface area rises, increasing the gas storage capacity. Similar to this, an increase in the MOFs' porosity results in more space being accessible for gas storage, which raises the gas storage capacity. It is crucial that the MOFs' density may drop and their ability to store gas may be affected when the BET surface area rises above a particular point [6].

Indeed, when calculating the gas storage capacity of MOFs, people often treat them as perfect crystals, overlooking their real defects. For example, the presence of gaps can lead to a lower actual density of the MOFs, and this decrease in density can result in a reduction in the gas adsorption efficiency [4].

In addition to the factors mentioned above, the arrangement of the atoms and the nature of the functional groups also impact the gas storage capacity of the MOFs to varying degrees [6]. The former affects the mechanical and durability properties of the MOFs, while the specificity and functionalization of the latter alter the selectivity of the MOFs. All these factors ultimately influence the gas adsorption efficiency to varying extents.

Some recent studies also found that under conditions of higher porosity and lower ambient temperatures, the exposed metal sites of the MOFs increase, enhancing their gas transport capability [2].

Therefore, to improve the gas storage efficiency of the MOFs, it is necessary to compress the gas without affecting its adsorption, thereby increasing the final energy density. Additionally, controlling

the size of the crystals is crucial, for instance, the MOFs produced by suppressing mixed crystal sizes lead to increased packing density, resulting in a higher gas adsorption efficiency [2].

4. Applications of the MOFs In CH₄ Storage

The MOFs have emerged as promising materials for methane storage due to their unique structural characteristics and tunable properties [7]. Methane, as a clean and abundant energy source, presents challenges in terms of storage and transportation, and the MOFs, offer a high surface area and adjustable pore size, making them ideal candidates for methane adsorption. The key advantage of the MOFs in methane storage lies in their exceptional surface area, which allows for significant gas adsorption. The porous nature of the MOFs provides ample sites for methane molecules to adhere, forming stable host-guest interactions, and additionally, the framework's tunable nature allows for customization of the pore size and geometry, optimizing the material for methane adsorption.

One prominent example is the use of a famous MOF—BUT-107 [8], this MOF exhibits a large surface area and well-defined channels, facilitating efficient methane adsorption, the strong interactions between the metal nodes and methane molecules also enhance the material's storage capacity and the stability as well. Moreover, some researchers have been exploring the incorporation of the functional groups within the MOFs to enhance their methane storage performance, for the introduction of specific functional moieties can improve the selectivity and the affinity of the MOFs for methane, leading to higher storage capacities and better cycling stability. The MOFs also offer some advantages in terms of reversibility and recyclability, essential factors for practical applications. The adsorption-desorption process in the MOFs is generally reversible, allowing for the release of the stored methane under controlled conditions, this feature is crucial for the development of efficient methane storage systems that can be readily integrated into various applications, including vehicles and stationary storage.

According to the latest research findings, some MOFs, such as HKUST-1, exhibit a high capacity of 28.1 wt% at 300 K and 25 MPa [9], while Al Nia MOFs have a gas adsorption capacity of 33.6 wt% at 300 K or 50 MPa [8]. Regarding the material structure, as the BET surface area of MOF materials increases, gas adsorption also increases. However, the rate of increase decreases with increasing pressure and eventually approaches a constant value [2]. From the perspective of adsorption conditions, as physical adsorption is an exothermic process, reducing the ambient temperature under high pressure can increase gas adsorption to a certain extent, but this may lead to a decrease in its working capacity [2]. In addition, doping other metal centers in MOFs can improve their storage capacity. Wang et al. prepared a series of flexible MOFs by doping metal Co in X-dia-1-Ni. The opening pressure of flexible MOFs doped with Co on carbon dioxide and methane increases, and it also increases with the increase of Co content [10]. As for the current situation, MOFs face some challenges in meeting the dual requirements of volume adsorption and weight adsorption simultaneously. In other words, the focus should be on improving the working capacity and unadsorbed volume of MOFs, while maintaining their original gas adsorption capacity, to reduce their density while maintaining their inherent gas adsorption capacity.

The MOFs represent a cutting-edge solution for methane storage, addressing the challenges associated with this clean energy source. Their tunable structures, high surface areas, and functionalization possibilities make them versatile materials for optimizing methane adsorption and release [11]. As research in this field continues, the MOFs hold great promise for revolutionizing methane storage technologies and contributing to a more sustainable energy landscape.

5. Conclusion

A long-standing worry is that the growing depletion of coal and petroleum hydrocarbon supplies would provide substantial barriers to sustained economic and social progress. As the primary component of hydrocarbon resources, methane is seen to be the best substitute for coal and oil due to

its plentiful supplies. Methane has a volumetric energy density that is essentially one-thousandth that of conventional fuels. High-pressure storage and liquefaction storage are typically the two primary ways used to store methane. Although these two technologies are currently the most popular, the process of storing methane requires a large amount of energy and poses safety risks. Therefore, using porous materials as adsorbents is one of the current research directions, as they can store methane more safely and effectively. Because of their superior performance in several areas, MOFs are now the most promising materials as methane adsorbents. The primary purpose of this article is to provide an overview of the present state of use for MOFs as a practical methane storage solution.

MOFs have numerous benefits, but they also confront several significant obstacles that require immediate attention. First off, there is currently minimal study on the properties of methane adsorption at low pressure, even though a huge number of MOFs have been designed to store methane under high pressure. Consequently, further investigation is required to enhance MOF methane adsorption at room temperature and low pressure. Second, as they will influence the final adsorption performance, parameters like material porosity, open metal sites, functional groups, etc. should be taken into account concurrently when producing MOFs. There is still a long way to go before MOFs are widely used. This necessitates taking into account the material's purity, recyclability, cost of production, and other factors. Furthermore, the primary emphasis of current research is on the extraction of methane from various gasses. The rate at which single-component methane adsorbs has not been thoroughly studied. To maximize the energy exchange between methane and MOFs, it is imperative to optimize both its structure and performance. Lastly, as big data analysis and artificial intelligence are being used extensively, future studies may potentially include these techniques in the structural design of MOFs. Combining them allows for the fast and precise selection of appropriate MOFs as well as the optimization of the MOF synthesis process. As research progresses, MOFs, a novel class of adsorbent materials, will help advance the global energy and materials sectors.

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