

Applications of Metal-Organic Frameworks in Methane Storage

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Abstract. Metal-organic frameworks (MOFs) are a type of porous materials that are receiving a lot of attention for their application potential in gas storage and separation. Methane storage, in particular, is an active area of research due to its significance as a vital component of natural gas, which is used for heating, transportation, and electricity generation. MOFs offer a promising solution to the challenge of efficiently storing and transporting methane because of their enormous surface area and variable pore sizes, which can facilitate efficient and reversible methane adsorption. The development of MOFs for methane storage has the potential to revolutionize the energy industry by enabling more efficient and cost-effective storage and transportation of natural gas, thereby reducing greenhouse gas emissions and promoting the use of cleaner energy sources. New MOF materials are being created and characterized as part of this field's research., and the study of their adsorption properties uses both experimental and computational techniques as well as the understanding the underlying mechanisms that govern methane adsorption in these materials. Key areas of investigation include measuring methane uptake and selectivity, as well as studying the thermodynamics and kinetics of the adsorption process.

Keywords: Metal-organic frameworks, Natural gas storage, Methane storage.

1. Introduction

MOFs are composed of metal ions or clusters linked together by organic ligands to form a 3D network structure with well-defined pores and channels. These materials have exceptional surface area and porosity, which makes them ideal candidates for gas storage applications [1]. Methane storage involves the study of storing methane efficiently and safely, with the goal of finding solutions for the transportation and use of natural gas as a fuel. Methane offers a relative high energy density compared to other fuels, which means it can produce lots of energy per unit of fuel, making it very suitable as fuels. Furthermore, methane is a potent greenhouse gas and an important climate change agent, so finding ways to store it securely is crucial for reducing emissions and mitigating climate change. Thus, due to the low density and high volatility of methane, it is challenging to be stored or transported. However, MOFs offer a potential solution to this problem, as they can adsorb large amounts of methane in their porous structures. Many different MOFs have been studied for methane storage, including MOFs based on metals such as copper, zinc, and nickel, as well as a range of organic ligands [2].

Moreover, Experimental techniques such as gas sorption measurements, thermogravimetric analysis, and infrared spectroscopy have been used to characterize the adsorption behavior of MOFs towards methane. Computational methods, such as molecular simulations and density functional theory calculations, also held employment in order to gain insight into the interactions between methane and MOFs at the molecular level [3].

An overview of current developments in the development of MOFs for methane storage is provided in this review paper, including the design and synthesis of new MOFs with optimized structures and properties, as well as their evaluation for methane storage under different conditions. Strategies for enhancing methane uptake, improving desorption kinetics, and overcoming the limitations of MOFs in real-world applications are also discussed.

2. Fundamentals of MOFs

2.1. Classification of MOFs

MOFs, a novel class of porous inorganic-organic hybrid materials with regular and tunable structure, are formed of metal ions or clusters (secondary building units) with bridged organic ligands by self-assembly, which usually possess one-, two- or three-dimensional structures and belongs to the category of coordination-type polymeric materials. An enormous number of MOFs can be obtained through different combination of this elements. Based on the different organic ligands employed in the synthesis process of MOFs, the metal organic frameworks materials can be divided into 1) MOFs containing carboxylic acid ligands, 2) MOFs containing nitrogenous heterocyclic ligands, and 3) MOFs containing nitrogenous heterocyclic and carboxylic acid mixed ligands [4]. Additionally, MOF materials can be categorized into ZIFs, MILs, IRMOFs, PCNs, etc. based on the same frame structure or similar properties of metal organic frameworks. Researchers mainly classify MOFs by the structure and the difference of metal ions in the synthesis process of metal organic frameworks.

2.2. Synthesis and Characterization of MOFs

2.2.1. Synthesis

For MOFs synthesis, a large number of synthesis methods could be achieved, among which, the solvothermal method is a frequently-used ideal synthesis method. The original mixture is reacted to obtain MOF compounds in a self-pressure closed high-pressure reactor at the certain temperature with water or liquid organic matter as solvent. Through this method, MOF microcrystalline products can be easily obtained under pressurized conditions, generally with high thermal stability. Reaction time, reaction temperature, the stirring speed and the metal/ligand molar ratio all could affect the morphology of the product.

Ultrasonic synthesis is the preparation of MOFs by using high-energy ultrasound (20 kHz-15 MHz) to synthesize mixed solutions of metal salts and organic ligands at different ultrasonic power, ultrasonic time and temperature. This method depends on the formation, growth and collapse of short-lived bubbles in the liquid and generates acoustic cavitation at high temperature (5000°C) and pressure (50 atm) and extremely fast heating and cooling rates [5].

Mechanical synthesis is to use mechanical energy to achieving chemical complexation between metal salt and organic ligand. When metal salt and organic ligand are ground in mechanical ball milling system, intramolecular bond is broken and new chemical bond is formed, which accelerates the formation process of MOFs in high yield with no solvent or its small amount [6]. Both ultrasonic synthesis and mechanical synthesis can quickly synthesize MOFs, with simple operation and large amount of preparation. In addition, electrochemical synthesis, microwave-assisted method, layer-by-layer growth method, liquid phase diffusion method, spray drying method and other methods also have been applied in the synthesis of MOFs [7,8].

2.2.2. Characterization

The choice of analysis method for MOFs mainly takes into account the periodic structure, sensitivity to heat, and large pore surface area etc. The high specific surface area and porosity are the most critical properties of metal organic frameworks. The classical Brunauer-Emmett-Teller (BET) method, which was developed from the Langmuir theory for polymolecular (multilayer) adsorption, is used to determine the specific surface area of MOFs. Because of the periodic structure of MOFs, X-Ray Diffraction (XRD) is the most used analysis technique. Considering the actual pore size and crystallization result, the Powder X-Ray Diffraction is often used at room temperature, which could explain the structural variations between the identical MOF materials produced using various synthetic methods. Thermal stability is another essential characteristic for metal organic frameworks, and while heating at certain temperature, the organic solvent in the MOFs materials evaporates. Thermogravimetric analysis (TGA) is used to studying the thermal stability of MOFs directly, which

measures how the mass of sample materials changed with temperature. Recently years, X-ray absorption spectroscopy is frequently used to investigate the composition and characteristics of different catalytically active compounds as well, especially the porous materials [8].

Since the synthesis of the first metal-organic framework material MOF-5, MOF materials have made rapid and rich development. The research for Metal organic framework mainly concludes experimental research and computational simulation research. The former is about synthesis or compound by experimental method and studying the effects of MOFs prepared with different procedure, while the latter is using high-throughput screening and molecular simulation technology to design different MOFs structure or study post-processing performance. Because of the substantial specific surface area and flexible pore structure, MOF materials have a wide range of potential applications in gas storage, gas separation, drug delivery, catalysis, sensors and other many fields [8,9].

3. Methane Storage

Owing to the highest H to C ratio, methane is considered as a form of clean energy that produces less CO and CO₂, compared to other forms of fuels, methane holds the full potential in powering vehicles. There are two scopes in the natural gas storage, the capture and disposal processes [10]. Natural gas transportation and storage requires media with high adsorption and flexibility, to maximize the deliverable capacity and reducing the heating effects [11].

The recent research established MOFs and gas hydrates as potential resources for the efficient storage of natural gas. MOFs feature porous structure and ready fictionalization, enabling high storage capacity for methane and are promising adsorbents that can be applied in the transportation of natural gases. Under suitable thermodynamic conditions, clathrate hydrates, also known as gas hydrates, are crystalline compounds composed of open cages formed by hydrogen bonds, which are potential storage sites for molecules of suitable size such as methane (CH₄). To design high-capacity systems for adsorbing natural gas that well manage the thermal fluctuations during the transportation and desorption from the adsorbents, combining MOFs with gas hydrates would be a promising method in offering sites of gaseous binding and higher energy-phase transitions when handling methane.

3.1. The Application of MOFs for Methane Storage

The recent advances in methane storage and separation are highly associated with the application of MOFs as adsorbents. The design of MOFs has been of great interest to researchers and flexible metal organic framework variants are also promising media for methane storage applications. Metal ions make up the porous materials known as MOFs and clusters. With the highest surface area known, MOFs are promising materials for storing gas molecules such as methane, with their micro-porous, MOFs can be designed to accommodate for natural gas adsorption by enlarging the surface area and adjusting pore structure. In 2012, the department of energy experimentally met the gravimetric capacity goal of 0.5 gram of methane per gram of MOF material by alternating the pore metrics, linker, and the adsorption site, establishing the role of MOFs in natural gas storage. Metal organic framework Fe (bdp) (bdp²⁻ = 1,4-benzenedipyrazolate) was recognized by researchers that possess intrinsic thermal management

The amount of heat released for this MOF was 41% less than that of HKUST-1 during methane adsorption process [12]. HKUST-1 was experimented on to demonstrate a working capacity of 259 cm³ (STP)/cm³ of volume at absolute zero (273.15K) and 1ATM, illustrating a 50% increase in efficiency in comparison to other previously published experimental results and closely matches to the 2012 Department of Energy target of 263 cm³ (STP) cm⁻³ going through packing and densification processes. New MOF structures with mesoporosity and breathing properties are being researched whose adsorption capacity was largely improved, which are promising future generation of natural gas storage and transportation media [13].

3.2. HKUST-1 in Methane Storage

Some established promising metal organic frameworks include PCN-14, UTSA-20, HKUST-1, NU-125, etc. The standard volumetric methane uptake is measured to evaluate the adsorption capacity of the MOFs. Among all these material, HKUST-1 is one of the most promising MOFs with high surface area and pore volume, which performs overall adsorbing capacity for natural gas. HKUST-1 is the reference for the research on many other general MOFs. HKUST-1 is a copper-based metal organic framework with the chemical formula is $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$. Also known as MOF-199, HKUST-1 is composed of dimeric metallic units joined by benzene-1,3,5-tricarboxylate ligands. The metallic group is composed of two copper ions chelated by four carboxylate ligands, forming a conformation known as a paddle-wheel unit.

HKUST-1 for adsorbing methane has been tested on vehicles and proved to be effective. When loading the methane fast to HKUST-1, the released adsorption heat of around 15–30 kJ/mol is dissipated fast than when it is evacuated. The introduced heat increases the temperature of the gas and reducing its loading. Instead of loading the methane slowly to increase the capacity of adsorption, packing HKUST-1 inside 3D printed metal lattices largely improve the efficiency of the filling process [14].

One established method for storing methane is utilizing PCN-14, which is the MOF that demonstrates the highest adsorption capacity to date. This material has two adsorption sites for natural gas molecule and its organic ligands play a significant role in gas adsorption. Based on the progress of methane storage from PCN-14, a new material PCN-M was designed which displays a 12 percent higher storage than PCN-14, with a storing capacity of 257 V/V at 290 K and 3.5 MPa. This rational modification on the organic linker of PCN-14 paves the way for the future research on improving the methane storage capacity by alternating the design of established MOFs [15].

MIL-101(Cr) is another well-recognized MOF for CH_4 adsorption, its total volumetric uptake of methane is about $150 \text{ cm}^3/\text{cm}^3$ at 35 bar, $215 \text{ cm}^3/\text{cm}^3$ at 65 bar, and $30 \text{ cm}^3/\text{cm}^3$ at 5 bars correspondingly. To further improve the adsorption of methane gas, the novel idea of coupling ANG (adsorbed natural gas) vessel and LNG ((liquefied natural gas) re-gasification in application was proved to be efficient. Through this method, the CH_4 working capacity is largely enhanced. The parameters of operation increased to $240 \text{ cm}^3/\text{cm}^3$ between the ranges of 6 bar at 160 K to 5 bars at 298 K, and $125 \text{ cm}^3/\text{cm}^3$ between 1.2 bar at 160 K to 5 bar at 298 K.

3.3. Combining Gas Hydrates and HKUST-1 in Storing Methane

Gas hydrates, commonly known as clathrate hydrates, are water-based solids which forms a crystalline property. It can trap small molecules owing to its large surface area and hydrophobic moieties. They can trap such as methane molecules inside of the hydrate components. For natural gas storage and transportation, the established method is to uptake the natural gas in semi-batch stirred vessels with the temperature set to be 273.7 K at constant pressure. The composition of the gases and hydrates were found to evolve over time demonstrating remarkable adsorption capability. Dry water hydrates are an example of silica stabilized flowing powder that can achieve 90% saturation uptake of methane in 160 minutes. Natural gas can store be stored at $175\text{v}(\text{STP})/\text{v}$ methane at 273.2 K and 2.7 MPa, which is close to the DOE volumetric target for methane storage [13].

Improving the methane storage capacity and deliverable convenience; meeting the gravimetric and volumetric targets are the priorities in recent research in adsorbed natural gas (ANG) storage.

Combining MOFs and gas hydrates holds full potential in natural gas storage application. The highest experimented adsorption efficiency exceeds what has been previously reported using one type of material solely when setting temperature lower than 298 K and pressure higher than 65 bar. The implementation of MOFs and gas hydrates system for absorbing natural gas (ANG) is still faced with challenges such as the loss of storage capacity and the impurities of natural gas. The reduction of storage capacity can be modified by pore engineering on both materials.

When dealing with the impurities of natural gas, hydrocarbons and other molecules may be accidentally adsorbed forming a blockage of the 'active sites' of the MOFs. This can lead to a 50% reduction of the deliverable energy. This loss of efficiency can be modified by pore engineering.

4. Conclusion

In conclusion, Metal-organic frameworks have shown promising potential in methane storage applications and able to store methane at high gravimetric and volumetric densities, making them promising materials for natural gas storage and transportation. Numerous studies have demonstrated that MOFs can achieve high storage capacities and good selectivity for methane adsorption, as well as excellent stability and durability under various conditions. Moreover, advances in MOF synthesis and characterization techniques have enabled the development of new MOFs with even better performance characteristics, such as higher storage capacity and improved stability. The continued development of MOFs for methane storage holds great promise for the energy industry. Ongoing research is focused on optimizing the properties of MOFs to enhance their methane storage capacity and selectivity, as well as improving their stability and durability under practical operating conditions. There is also increasing interest in developing MOFs for other gas storage and separation applications, including carbon dioxide capture and hydrogen storage. However, several challenges remain in the commercialization of MOFs for methane storage. These include issues related to energy required for gas adsorption and desorption, scalability, reproducibility, the stability of MOFs under high-pressure methane conditions and the development of cost-effective synthesis methods. Nonetheless, research in this area continues to progress, and ongoing efforts to overcome these challenges are expected to pave the way for the widespread application of MOFs in methane storage.

Overall, the potential benefits of MOFs in methane storage, including higher storage capacity, selectivity, and stability, make them a promising avenue for the development of advanced natural gas storage technologies. With continued research and development, MOFs have the potential to play a significant role in addressing the challenges associated with the storage and utilization of natural gas as a cleaner energy source.

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