Application of metal-organic frameworks in natural gas storage

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Abstract. In recent years, fossil energy sources have been diminishing as global energy demand grows. The combustion of traditional petroleum fuels also produces large amounts of greenhouse gases, contributing to global warming. Natural gas has attracted widespread attention as a relatively cleaner and cheaper energy source. The main component of natural gas is methane. However, due to the poor safety of methane under standard conditions, its application in practical storage and transmission is greatly limited. To use methane fuel routinely, the development of a safe, low-cost, and efficient methane storage strategy is an urgent issue. Metal-organic skeletons (MOFs), as a new class of efficient adsorption and separation materials, have received great attention in the field of gas storage due to their high specific surface area, designability, and size tunability. In this paper, the basic characteristics of MOFs are first introduced. Then, the mechanism of methane adsorption by MOFs is explained and its main influencing factors are summarized. Finally, this paper also proposes relevant modification strategies to improve the ability of MOFs to store methane.

Keywords: MOFs, natural gas, storage.

1. Introduction

The world's energy consumption is rising exponentially as a result of the rapid advancements in science, technology, and society production. Many air pollutants, such as CO2, SO2, and nitrogen oxides, are released during its burning as a primary industrial fuel energy source. These pollutants exacerbate global warming and the greenhouse effect. Therefore, finding renewable energy sources to replace conventional fuels generated from petroleum is crucial to lowering carbon emissions.

Natural gas has emerged as a significant and promising fuel when compared to other fossil fuels because of its many benefits, including its high hydrogen-to-carbon ratio, plentiful content in nature, purity, and renewability. However, natural gas's poor volume energy storage density prevents it from being used in vehicle transportation under real-world conditions, even at compression pressures of up to 25 kPa. For instance, to attain the extremely high pressure needed for natural gas liquefaction, sophisticated and costly multi-stage compressors must be used. This leads to high consumption costs, an unnecessary amount of space being occupied in storage tanks, and subpar safety performance. To use methane as a conventional fuel, more appropriate ways of storing the gas must be developed. An optimal approach for achieving better energy density at lower pressures (e.g., 3.5-6.5 kPa) and room temperature is gas storage (ANG) [1]. The development of effective adsorption materials is essential to ANG technology's success. But the adsorption capabilities of conventional materials like carbon, mesoporous silica, and zeolite are lower [2].

Because of its enormous specific surface area, easily modifiable pore size and pore structure, and ease of functional modification, MOFs have been thoroughly researched for their methane storage capacity. This article mainly introduces the basic characteristics of MOFs, including the characteristics of metal ion centers and organic ligands. Secondly, the mechanism of methane adsorption was elucidated and the reasons affecting methane adsorption rate were summarized. Finally, strategies for enhancing the methane adsorption efficiency of MOFs were summarized.

2. Characteristics of MOFs

2.1. Metal Ions

The metal ions that are most often utilized in the production of MOFs are divalent (Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, etc.) [3]. These metals are somewhat stable and have a reasonable hardness. They are not as strong as covalent connections with ligands of nitrogen and oxygen. Trivalent or tetravalent metal ions (Al^{3+}, Fe^{3+}, Cr^{3+}, Zr^{4+}, etc.) may be used to create very stable MOFs, have tight covalent interactions with oxygen-containing ligands, and have great polarization ability; Large single crystals are difficult to form because high-valent metal ions tend to combine with water to generate oxides and hydroxides, which somewhat impede crystal development.

2.2. Organic Ligands

As per the MOFs specification, ligands need to be organic compounds possessing multiterminal coordination capabilities and at least two coordination functional groups. MOFs' primary organic ligands include pyridines, azoles, carboxyl groups, and a combination of pyridines and carboxylates.

2.2.1 Carboxyl ligand

Any common metal ion may bond with carboxylate, a hard base, especially trivalent and tetravalent metal ions. MOFs are more stable when negatively charged carboxylic acid radicals neutralize the positive charge of metal ions. However, a lot of carboxylate coordination patterns are erratic and difficult to control.

2.2.2 Pyridine ligands

Another ligand that's frequently employed in MOF synthesis is pyridine. The coordination mode is really easy to understand since the nitrogen atom in the pyridine ligand is in the sp^2 hybrid state and has a single pair of electrons. Nevertheless, pyridine's poor ability to coordinate with the majority of metal ions and the fact that its ligands are uncharged imply that the other elements must counteract the positive charge of the metal ions. It is noteworthy that end-cap ligands with two teeth and one tooth can be found in some multinuclear metal clusters. As a result, a combination of two ligands or carboxylate can be joined with the pyridine functional group.

2.2.3 Azole ligands

Imidazoles, pyrazoles, triazoles, and other azole ligands enjoy the benefits of both carboxyl and pyridine ligands. The produced MOFs are much more stable due to the simple and uncomplicated coordination mode and the attachment of the nitrogen atom to the hydrogen atom, which permits the removal of protons to create a strong alkaline anionic multiterminal ligand.

3. MOFs for Methane Storage

3.1. Mechanism of Methane Adsorption

Coordinatatively unsaturated metal ions (CUS) and increased Van der Waals potential pockets are the two primary locations for methane adsorption on MOFs from the perspective of the methane-MOF interaction. Adsorption isotherms for several MOFs and adsorbents were proposed by Dietzel, proving the presence of these two primary adsorption sites [4]. Methane can directly connect to the metal ions of the structure through electrostatic interactions at CUS, often referred to as open metal sites (OMS). Conversely, the elevated Van der Waals potential pocket is mostly associated with the aperture, where the contact is somewhat weaker. In moderate weather, this difference is more noticeable. According to one research, when dispersive interactions were specifically taken into account, the CH_4 molecule's affinity for the basic N-site of the pyridazine ring Lewis was approximately 10% greater than that on the phenyl ring. Therefore, it may be deduced that higher CH_4 absorption at high pressures is also due to a stronger van der Waals interaction in addition to the "dynamic" pyridazine ring. MOFs adsorption isotherms typically follow a Type I trend, reaching saturation at high pressure. The structural and compositional advantages of MOFs provide a unique platform for the storage of natural gas. The extremely high specific surface area of MOFs can increase the usable capacity, the abundant active sites can provide different kinds of strong binding sites for natural gas, and the molecular polarization of CH_4 further increases the bulk density of stored CH_4.

3.2. Factors Affecting Methane Adsorption

3.2.1 Electrostatic interaction

Typically, MOFs and CH_4 interact electrostatically at the framework's unsaturated metal sites (OMS).M-MOF-74 absorbs a notably greater amount of CH_4 due to the high-density OMS functioning as a strong CH_4 interaction site. Ni-MOF-74 had the greatest ability to adsorb CH_4 among them. The main reasons for this are that OMS and Ni^{2+} ions have the highest electrostatic interaction with CH_4 and the strongest polarization, respectively. The high CH_4 adsorption heat of 20.6 kJ/mol (at zero loading) for Ni-MOF-74 is consistent with this [5]. Therefore, to increase the CH_4 adsorption capabilities, the electrostatic interactions of the sites within MOFs should be improved.

3.2.2 Flexibility of the framework

Two MOFs, Co(bdp) and Fe(bdp), were created by the self-assembly of bdp_2-(H_2bdp = 1,4-benzenedimethyl (4'-pyrazole)) and Co^{2+}/Fe^{2+} by Long et al. in 2015 [7]. At ambient temperature and pressures near 1-1.5 kPa, there is a significant drop in the adsorption isotherms of MOFs. At 298 K, the pressure dropped from 6.5 kPa to 0.5 kPa, releasing more than 96% of the adsorbed methane. This unusual adsorption behaviour is attributed to the flexibility of the material framework of both MOFs.

3.2.3 Van der Waals interaction

The locations where the CH_4 molecule interacts with the framework through van der Waals interactions are typically where MOFs and methane interact. Pore size and shape can alter the strength of the van der Waals contact between the CH_4 molecule and the framework. Eddaoudi et al. (2015) reported on Al-soc-MoF-1, a metal-organic framework material for methane storage. $Al_3O(OOC)_6$ cluster and a TCPT linker (H4TCPT = 3,3",5,5"-tetrakis(4-carboxyphenyl)-p-terphenyl) were built to form Al-soc-MOF-1. Al-soc-MOF-1 has a methane mass adsorption of 0.42 g/g at 298 K and 6.5 kPa. Figure 1 illustrates the methane mass working capacity of Al-soc MOF-1 at 298 K and 0.55-6.5 kPa, which is 0.37 g/g for methane mass adsorption. The van der Waals contacts between the methane molecules and the framework may be weak because of the ultra-high working capacity of Al-soc-MOF-1 [6]. Van der Waals interactions are the predominant force in methane storage, as evidenced by the giant canonical system complex Monte Carlo technique (GCMC).

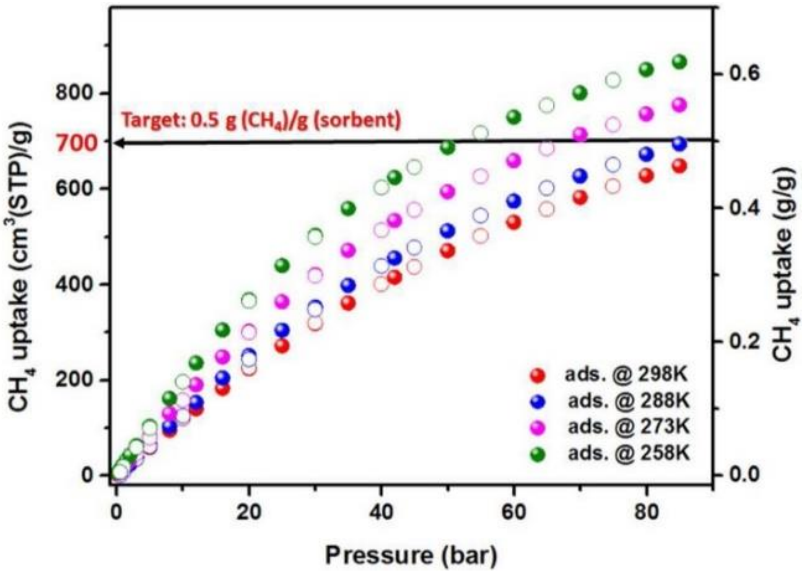

Fig. 1 CH_4 adsorption isotherms of Al-soc-MOF-1 at different temperatures [6].

4. Strategies for Increasing Methane Storage Capacity in MOFs

4.1. Porosity and Internal Surface Area

A study has documented the correlation between the total methane adsorption capacity at 100 pressure and pore volume. As illustrated in Fig. 2a, both at 298 K and 273 K, the gravimetric total adsorption exhibits an upward trend with the increase of pore volume. Notably, at 298K, NU-1501-Fe33 (0.52 g g^{-1}) and NU-1501-Al33 (0.54 g g^{-1}), which possess a large pore volume (~2.9 cm^3 g^{-1}), are capable of meeting the Department of Energy's (DOE) gravimetric target. Furthermore, when the storage temperature is lowered to nearly freezing at 270K, the adsorption capacity experiences a significant boost. In contrast to the consistent rise of gravimetric adsorption capacity with pore volume, the volumetric total adsorption capacity slightly decreases as pore volume increases due to the combined effect of higher gravimetric adsorption and lower crystal density (as shown in Fig. 2b). Similarly, a reduction in storage temperature leads to an enhancement in volumetric adsorption capacity, akin to the behavior observed in gravimetric adsorption [8].

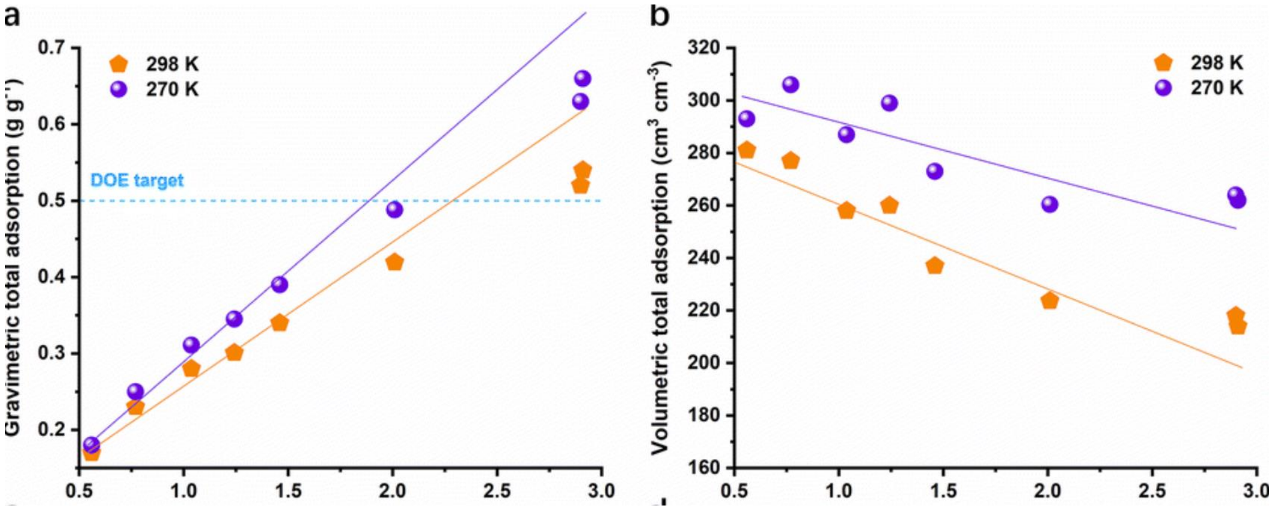

Fig. 2 (a) Gravity adsorption and (b) volumetric adsorption of methane at 100 bar [8].

4.2. Functional Group Modification

The structure of organic ligands of MOFs can be regulated by two methods, namely the synthesis method and the introduction of functional groups. Through this method, different organic ligands form different backbone structures, which can make the MOFs have different physicochemical properties, to obtain the target product that can complete the target.

To enhance gas storage capacity and improve the efficiency of CO_2 separation, the functionalization of MOFs plays a crucial role in modifying the interaction between the guest molecules and the MOF framework. There are primarily three methods for synthesizing functional MOFs. The first approach involves the assembly of MOFs using pre-functionalized organic linkers. This method allows for the integration of specific functional groups into the MOF structure during its synthesis. The second method, commonly adopted by most MOF research groups, involves the elimination of unstable coordination solvent molecules to create unsaturated metal centers or open metal sites. This process results in the formation of functional MOFs with enhanced adsorption properties. The third and increasingly popular strategy, known as post-synthetic modification (PSM), has emerged in the past decade. PSM involves several techniques to introduce functionality into pre-existing MOFs [9].

4.3. Structural Design

In two distinct experiments, the first one involved the preparation of HKUST and its modified versions, HKUST-N and HKUST-Ca, via the solvothermal synthesis method. X-ray diffraction (XRD) analysis revealed that these materials exhibited the same structural characteristics as the previously reported HKUST-1. Nonetheless, noticeable changes were observed in their textural and surface properties due to the addition of NH_4OH and $Ca(NO_3)_2$ during synthesis. Despite significant variations in surface area, all materials demonstrated a comparable CO_2 adsorption capacity, achieving an impressive 12 mol/kg at 50 bar and 303 K [10]. In the second experiment, the post-synthetic transmetalation product, MFU-4l-Li, was found to possess enhanced gas storage properties compared to its isoreticular analog, MFU-4l. The combination of optimal porosity and pore geometry rendered MFU-4l-Li a promising candidate for use as a porous adsorbent in the storage and delivery of methane and hydrogen. This material boasted high deliverable capacities under conditions relevant to onboard storage systems in vehicles. Furthermore, its robust framework could be almost fully activated under mild heat and vacuum conditions, maintaining stability even upon exposure to air. These findings further establish its potential for successful practical applications [11].

5. Conclusion

MOFs are a potential material for methane storage because of their huge specific surface area, changeable pore size, and designable pore surface. Methane is a clean, renewable energy source that can replace conventional petroleum-based fuels. Numerous research studies have demonstrated that discovering MOFs with strong frame flexibility, increasing the number of electrostatic phase/interaction sites, and modifying the size and shape of the pores to boost the van der Waals forces may all be used to examine the methane storage capacity of MOFs. Although some progress has been made so far, MOFs need to be further investigated as novel materials for methane storage. On the one hand, most of the studies on methane adsorption by MOFs have been conducted under high-pressure conditions, and the adsorption characteristics of methane storage under low-pressure conditions should be thoroughly investigated. The ability of MOFs to adsorb methane under low pressure can be considered to be improved by optimizing the structure, functional group modification, and surface modification. Secondly, it is necessary to develop and design new metal-organic skeleton composites to meet the storage needs of different gases. Finally, considering the large-scale application, it should be considered how to improve the filling efficiency of MOFs particles, reduce the cost, and improve the reuse rate.

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