

Design of Metal-Organic Frameworks with High Low-pressure Adsorption Performance of CO₂

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Abstract. Reducing the concentration of carbon dioxide (CO₂) in the atmosphere has momentous significance for alleviating global warming and protecting human health. Attractively, metal-organic frameworks (MOFs), as a novel class of porous materials, have held enormous potential in the field of CO₂ adsorption in virtue of their unique features such as ultrahigh specific surface area, adjustable channels, and high-density active sites. Considering that the CO₂ capture in practical applications is often performed at low pressure, it is more practical to design and develop MOFs with high low-pressure CO₂ adsorption performance. In this contribution, the strategies for improving low-pressure CO₂ adsorption performance of MOFs have been introduced and compared, and the relationship between the structure and adsorption capacity of MOFs as CO₂ adsorbents has been analyzed.

1. Introduction

Carbon dioxide (CO₂), one of the primary greenhouse gases, has made enormous contribution to more and more severe global warming, posing a daunting threat to sustainable development of the world. Reducing the emission and lowering the concentration of atmospheric CO₂ have been regarded as one of the most pressing environmental issues at present. In addition, the capture of CO₂ in confined spaces and the adsorptive separation of CO₂ from CH₄ for natural gas upgrading are both of essential significance to the manufacture and living of our society. Consequently, it's exceedingly imperative to design and fabricate advanced materials with high performance for selective adsorption and separation of CO₂. Metal-organic frameworks (MOFs), as a class of emerging crystalline porous materials, are self-assembled by the bonding of inorganic metal ions with organic ligands and have aroused great concern and interest from researchers [1-4]. On account of their large specific surface area, high porosity, tailorable pore structures and highly dispersed active sites, MOFs have been widely applied in many fields [5-7]. Remarkably, selective adsorption and separation of gas mixture, especially CO₂ from other gases, has been one of the most intriguing research areas in the applications of MOFs over past two decades, which could be demonstrated by the number of publications presented in Figure 1 [8-10].



Since Yaghi and co-workers [11] first attested the viability of CO₂ sorption in MOF-2 in 1998, tremendous efforts have been made to explore new MOFs for efficient adsorption of CO₂. For instance, the research group synthesized MOF-177 in 2005 and found that the MOFs exhibited a CO₂ adsorptive capacity of 1470 mg/g at room temperature and 35 bar, equivalent to 9 times its own volume when there was no other adsorbent [12]. Subsequently, they claimed that the CO₂ uptake values in MOF-200 and MOF-210 were both 2400 mg/g at 298 K and 50 bar, far more than that of other MOFs ever reported, ascribed to their ultrahigh specific surface areas [13]. Similarly, Hupp's group [14] obtained NU-100 with a specific surface area of 6143 m²/g via De novo synthesis and the sorption experiments manifested that the material had a storage capacity of 2315 mg/g for CO₂ at room temperature and 40 bars.

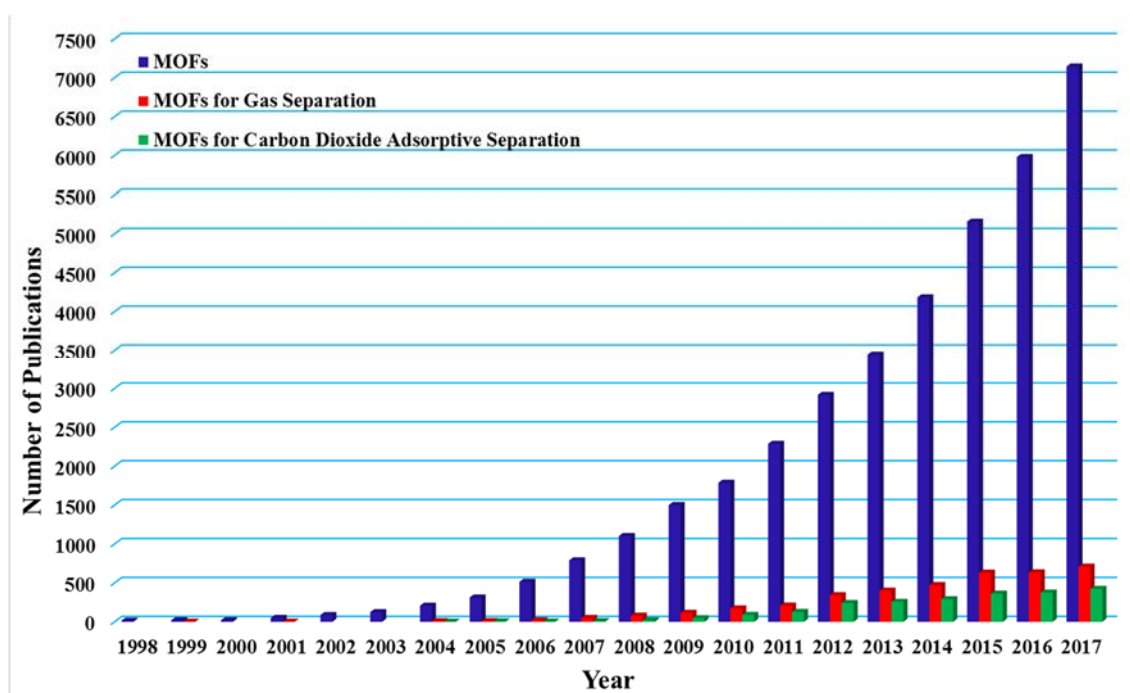


Figure 1. Distribution of publications on MOFs and their application in gas adsorptive separation from 1998 to 2017.

As is well known, the larger the specific surface area of MOFs, the stronger their ability to capture CO₂. However, taking actual applications into account, the adsorption and separation of CO₂ is generally conducted in a low-pressure multi-component gas system, thus the adsorption property of MOFs for CO₂ may be markedly influenced when exposed to multi-component gaseous mixture under dynamic conditions. Hence, investigating CO₂ adsorption performance of MOFs at low pressure is a much more meaningful topic.

2. Strategies to improve low-pressure adsorptive capability of CO₂ in MOFs

2.1. Adjustment of pore structures

In comparison with high pressure, the interaction between MOFs and CO₂ at low pressure is relatively weaker, rendering low-pressure CO₂ adsorption capacity of MOFs poorer. Studies have shown that the adsorption capability of CO₂ on MOFs at low pressure is related to the adsorption heat [15, 16]. Fortunately, the introduction of new metal centers with smaller radius can decrease the pore size of MOFs to some extent, thereby increasing CO₂ adsorption heat of MOFs. For example, Lau et al. [17] revealed that the CO₂ uptake of UiO-66(Zr) increased by 81% with a 10 kJ/mol enhancement in isosteric adsorption heat via post-synthetic exchange with Ti(IV) ions over the wide range from low pressure to

ordinary pressure at 273 K. the contrastive experiments interestingly indicated that enhanced performance of CO₂ uptake could be attributed to smaller pore size in Ti-exchanged UiO-66 (Figure 2). Alternatively, the fabrication of interpenetrating structures can be an effective option for MOFs to boost their adsorption capability of CO₂ at low pressure. For instance, Kim and coworkers [18] synthesized catenated CuTATB-60 and non-catenated CuTATB-30 by a controllable sonochemical method. The experimental results showed that the adsorption value of the as-obtained CuTATB-60 for CO₂ could reach 189 mg/g, which was higher than that of CuTATB-30 (156 mg/g). Besides, CuTATB-60 also exerted an exceptional selectivity of CO₂ over N₂ (>20:1) at normal temperature and pressure, testifying that the catenated structures in CuTATB-60 played a key role in CO₂ adsorption.

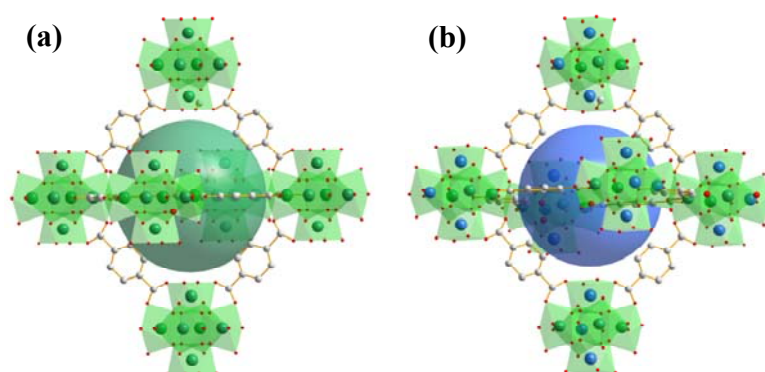


Figure 2. Structures of (a) UiO-66 and (b) Ti-exchanged UiO-66.

2.2. Introduction of coordinatively unsaturated metal sites into MOFs

In principle, coordinatively unsaturated metal sites in the structure of MOFs bring about strong interaction between MOFs and CO₂, endowing MOFs with outstanding CO₂ adsorption performance at low pressure. Previous work [19, 20] have manifested that metal sites with unsaturated coordination mode in MOFs could be obtained by removing coordinated certain molecules like solvent and ligands with poor coordination ability. Yaghi et al. [21] reported that Mg-MOF-74 with coordinatively unsaturated magnesium ions, as shown in Figure 3, could adsorb 8.9 wt. % CO₂, equal to 0.44 mol of CO₂ molecules per metal ion, while its structural analog Zn-MOF-74 adsorbed merely 0.35 wt. % of CO₂, which implied different metal ions played different roles in determining CO₂ adsorption performance of MOFs. Furthermore, they attributed the exceptional capacity of Mg-MOF-74 to the interaction between CO₂ molecules and the open metal ions in the structure of Mg-MOF-74. Analogously, Wang and co-workers [22] fabricated a novel Co(II)-based MOF, {[Co₂(tzpa)(OH)(H₂O)₂] · DMF}_n, employing tetrazolyl-carboxyl as bifunctional ligand followed by the removal of coordinated water molecules. The gas sorption experiments suggested that the Co(II)-based MOF displayed an excellent CO₂/CH₄ selectivity of 31.8 for the mixtures containing 50% CO₂ at room temperature and atmosphere pressure. X-ray crystallographic measurements suggested that multiple coordinatively unsaturated metal centers in the as-prepared MOF created by removing coordinated water molecules acted as active Lewis acid sites, resulting in eminent adsorption property and prominent selectivity for CO₂.

As a matter of fact, the presence of moisture is inevitable in the mixture of CO₂ and other gases, which poses a major obstacle to the CO₂ adsorption performance of MOFs. For this reason, it is of practical significance to develop moisture-resistant MOFs as high-efficiency CO₂ adsorbents. For example, UTSA-16 was synthesized by Masala et al. [23] and activated under high vacuum. The experimental statistics illustrated that the CO₂ working capacity (0.94 ± 0.04 mol /kg) of UTSA-16 in humid conditions was only slightly lower than that of dry conditions (1.30 ± 0.02 mol/kg), which demonstrated that high-density coordinatively unsaturated metal centers were more likely to interact with CO₂ than water, making the as-obtained MOF a promising candidate for efficient CO₂ capture even under wet operating conditions.

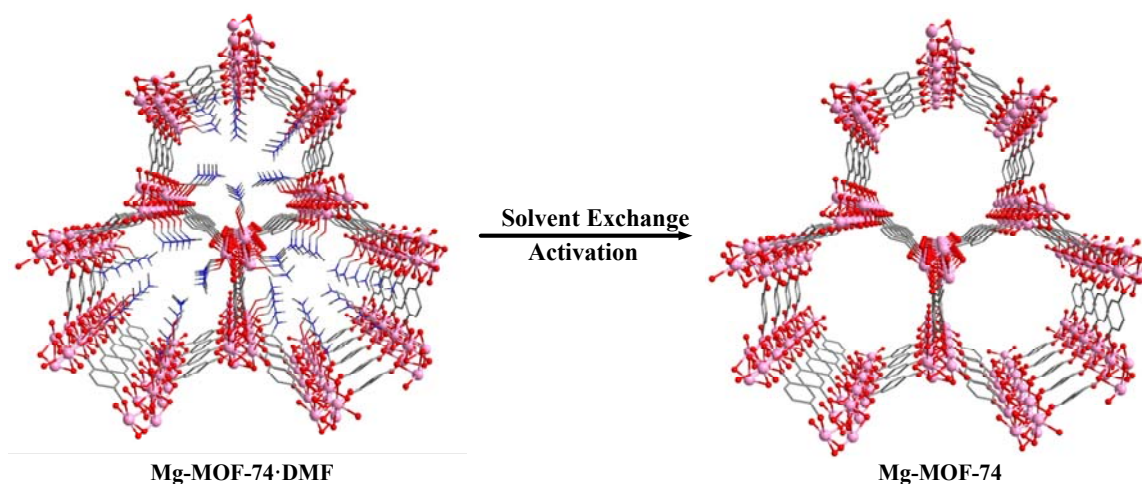


Figure 3. Formation of Mg-MOF-74 with open magnesium sites via a solvent exchange route.

2.3. Functionalization of MOFs with Lewis base

As is noted, when Lewis base such as nitrogenous groups of amines is introduced into the structure of MOFs, the interaction between the local dipole of the nitrogenous groups and the quadrupole moment of CO_2 molecule will induce the dispersion force and electrostatic force between MOFs and CO_2 , consequently enhancing the CO_2 adsorption capability of MOFs [24-26]. For example, Milner et al. [27] successfully prepared 2,2-dimethyl-1,3-diaminopropane-grafted $\text{Mg}_2(\text{dobpdc})$ (Figure 4) by means of post modification. The experimental data suggested that the diamine-functionalized MOF could uptake 90% CO_2 from coal flue gas at 313 K at about 15 mbar and the adsorption between CO_2 and amine functionalized MOF was responsible for the exceptionally high CO_2 uptake from dilute streams.

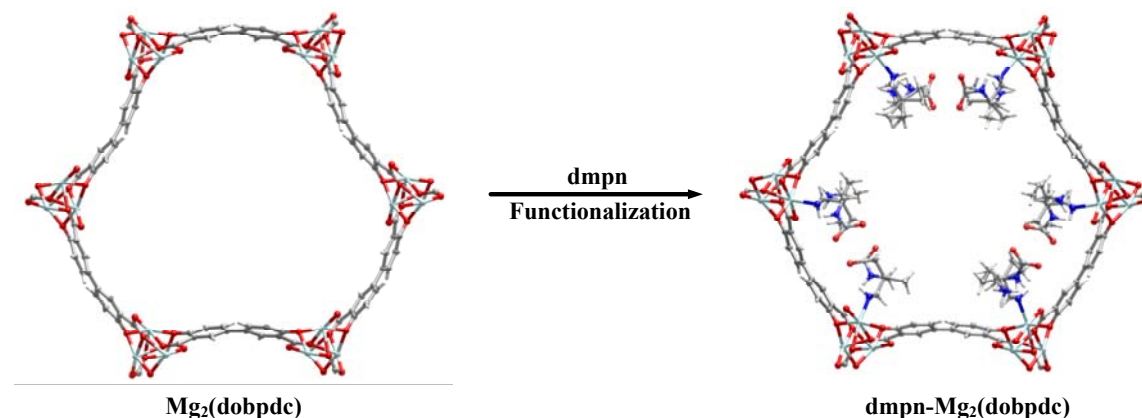


Figure 4. Functionalization of $\text{Mg}(\text{dobpdc})$ with 2,2-dimethyl-1,3-diaminopropane (dmpn).

3. Conclusion

With the urgent demand for energy-saving separation techniques, the exploration of new adsorbents for CO_2 is therefore gaining big momentum, of which MOFs have shown great potentialities and wide prospects owing to their unique properties. Studying the adsorptive separation performance of MOFs for CO_2 under actual production and living conditions, in particular at low pressure, is of vital significance for promoting MOFs from the laboratory scale to the practical use. Several useful strategies on how to effectively improve the low-pressure CO_2 adsorption performance of MOFs have been developed, including the adjustment of pore structures, the introduction of coordinatively unsaturated

metal sites into MOFs and the functionalization of MOFs with Lewis base. Although some progress has been made in the field of low-pressure adsorptive separation of CO₂ in MOFs, intense efforts still need to be made to further improve its performance and promote its industrial application. Moreover, the development of reliable approaches to achieve MOFs with high stability and reproducibility for CO₂ adsorption remains an arduous mission.

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