

Research on Metal-organic Frameworks for CO₂ Capture

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Abstract. Metal-organic frameworks are a new class of hybrid materials emerged in the two decades. Due to its porous structures, it is potential in the CO₂ adsorption area. In this paper, we summarize the advance in metal-organic frameworks for CO₂ capture in the five years.

Introduction

Metal-organic frameworks (MOFs), also known as coordination polymers, are novel family of porous materials constructed by coordinate bonds between organic ligands and metal atoms or metal clusters. Owing to their ultra large surface area and porosity, high crystallinity with well-defined pore properties and easily tunable structure and chemical functionality, MOFs are attracting increasing attention in the field of CO₂ adsorption and separation over the past two decades.

At high pressure condition, it appears that the strong positive correlation between CO₂ adsorption capacity and the surface area owing to the efficient packing and close approach of the guest molecules on the pore surface. For example, MOF-210 with a specific area of 6420 cm² has 16.9 mmol/g of CO₂ adsorption capacity at 50 bar and 298 K[1]. The CO₂ adsorption capacity of MOF-177 with a specific area of 4500 m² reach 13.8 mmol/g at 50 bar and 298 K. However, the CO₂ uptake decrease dramatically with the pressure, e.g. the CO₂ uptake of MOF-177 is 1.48 mmol/g at 1 bar and 298 K[2]. It is demonstrated that the CO₂ uptake of MOFs is related to the heat of adsorption at lower-pressure (<1.2 bar) condition. According to the equipment of plant, the bulk of the flue gas is composed of N₂ and other minor components, such as H₂O, O₂, CO, NO_x, SO_x and so on. For post-combustion CO₂ capture, the lower partial pressure of CO₂ (P_{CO₂}≈0.15 bar) leads to a smaller CO₂ adsorption capacity. Besides, the temperature of flue gas is between 40 and 60 °C. Higher temperature also results a lower CO₂ adsorption capacity in MOFs. Therefore, the requirement of new-generation MOF-based adsorbent should satisfy the following requirements: a high selectivity for CO₂ over other flue gas components, high adsorption uptake, lower regeneration energy consumption, long-term stability under the flue gas condition, and high adsorption rate. The CO₂ affinity to the pore surface of MOFs is crucial parameter to enhance the adsorption selectivity and capacity yet minimize the regeneration energy. Current strategies to enhancing the CO₂ affinity in MOFs include ligand functionalization, insertion of metal ions, framework interpenetration and incorporation of open metal sites.

Ligand Functionalization

The Incorporation of Basic Nitrogen-Containing Organic Group. The incorporation of basic nitrogen-containing organic group into MOFs is crucial for improving the CO₂ adsorption selectivity and capacity. The dispersion and electrostatic forces resulting from the interaction of the quadrupole moment of CO₂ with localized dipoles generated by heteroatom incorporation are typically responsible for the enhanced CO₂ adsorption. The increased amount of CO₂ adsorption is determined by the nature of functional groups. To date, the most studied nitrogen-functionalized ligands are heterocycle derivatives, aromatic amine derivatives, and alkylamine. There are two methods employed to incorporate nitrogen-containing groups into MOFs. One is pre-synthesis

functionalization, namely, modifying the ligands with functional groups prior to the formation of MOFs. He *et al.* has done a lot of work to synthesize a series of MOFs with functionalized nitrogen-containing group[9, 12]. They designed a bent diisophthalate ligand functionalized with aminopyrimidine group and synthesized a porous **ZJNU-54** via a solvothermal method. In this process, both amine group and the Lewis basic pyrimidine-ring nitrogen sites in the organic ligand are incorporated in MOFs, thus this strategy can greatly improve the selectivity of CO₂. The CO₂ uptake of **ZJNU-54** is 120 and 189 cm³ (STP) g⁻¹ at 295 K and 278 K at 1 atm, and the selectivity of CO₂ with respect to CH₄ is 6.1 at 298 K and 1 atm. The reason why **ZJNU-54** exhibits a higher uptake of CO₂ than CH₄ is difference in the isosteric heat of adsorption. The value of isosteric heat of adsorption for CO₂ and CH₄ at low coverage are 24.7 and 16.8 kJ mol⁻¹, suggesting that CO₂ is adsorbed more strongly in **ZJNU-54** than CH₄. Another strategy is post-synthesis method, that is, to chemically modify MOFs after the formation of MOFs crystals. Choi *et al.*[13] have modified Mg/DOBDC by functionalization of its open metal coordination sites with ethylene diamine (ED) to introduce pendent amines into the MOFs micropores. The result of theoretical calculation demonstrated that 1 ED molecule was added to each unit cell. The adsorption capacity from simulated ambient air (400 ppm CO₂) reached 1.51 mmol/g, which is higher than that of the parent Mg/DOBDC MOF. Besides, the adsorbent provides excellent stability over successive cycles.

The Incorporation of Other Polar Groups. Biswas *et al.* [14] has introduced six different functional groups (electron withdrawing, -Cl, -Br, -CF₃; electron donating, -CH₃, -OH, -OCH₃) into the parent MIL-47 (V^{IV}) framework to evaluate the effect of such organic functionalities on the sorption property. The largest CO₂ uptake (mmol g⁻¹) of MIL-47-X compounds at 1 bar is MIL-47(V^{IV})-OCH₃ (5.9), which is higher than that of parent MIL-47(V^{IV}) (4.4). *ab initio* DFT calculations reveal two driving forces for the enhanced CO₂ affinity of the MIL-47(V^{IV})-OCH₃: (i) the presence of the substituents increases the adsorption enthalpy of CO₂ and (ii) the mildly collapsed structure of the framework allows a CO₂ molecule to interact simultaneously with all surrounding linkers and substituents. Recently, Huang *et al.*[8] have designed a keton-functionalized MOF with open Cu^{II} sites pointing toward the cage center. The framework exhibits exceptionally high CO₂ (46.7 wt% at 273 K and 1 bar) and displays a high selectivity of CO₂ adsorption over N₂ at 298 K, which is the highest reported value under the same experimental conditions. Usage of fluorinated links to improve the Q_{st} value in MOFs has caught researcher's attention in recent years. Banerjee *et al.*[15] have designed three isostructural MOFs from isonicotinic acid (INA) and its fluorinated analogue 3-fluoro-isonicotinic acid (FINA) along with Co^{II} as the metal center. The CO₂ adsorption results show that the fluorinated MOFs have a higher CO₂ uptake (3.09 mmol g⁻¹).

Insertion of Metal Ions. Electrostatic force can be introduced into MOFs through the insertion of metal ions. The presence of extra metal ions can increase the electrostatic interaction with CO₂ and act as additional adsorption sites[11]. Besides, the Q_{st} value of CO₂ adsorption should be increased to a certain degree that minimized the energy penalty for regeneration. Yeganegi *et al.* have done theoretical study on the effect of lithium cation on the adsorption and separation of CO₂, CH₄, and H₂ on a Zn₂(NDC)₂(diPyNI). The results indicated that the selectivity of CO₂/H₂ on MOF was higher than that of CO₂/CH₄ at room temperature and pressure up to 50 bar[16]. Thus, Li⁺ doping is a possible way for making effective MOFs for gas storage and separation. Suh. *et al.* have done much study on various metal ions. They impregnated Li⁺, Mg²⁺, Ca²⁺, Co²⁺, and Ni²⁺ in the channels of SNU-100, and the Q_{st} value of CO₂ adsorption in the MOF to the range of 37.4-34.5 kJ mol⁻¹ as well as the adsorption selectivity of CO₂ over N₂ to 40.4-31.0 kJ mol⁻¹ at room temperature[11]. Among various metal ions, the Ca²⁺ ions seems to be the best for increasing the isosteric heat of CO₂ adsorption. The Q_{st} value of CO₂ adsorption for metal-doping MOFs is always lower than that of amine-functionalized MOFs. e. g. the isosteric heat of adsorption for mmen-Mg₂(dobpdc) approached a value of 71 kJ mol⁻¹[17].

Incorporation of Open Metal Sites.

Open metal sites in the MOFs can provide coordination bonding sites for CO₂ molecules[18]. e. g. the initial isosteric heat of adsorption is 39 kJ mol⁻¹ for Mg-MOF-74. Hence, it is expected that

removal of CO₂ from the MOF will require less energy in the separation process. The exceptional high uptake of Mg-MOF-74 for CO₂ may be attributed to the strong interactions between the oxygen lone pair orbitals of CO₂ with the coordinately unsaturated metal cations[19]. Nowadays, the most researched MOFs with open metal sites are HKUST-1[20], MIL-101 series[21], and MOF-74 series[7]. The open metal sites are typically obtained by incorporating solvent molecules as terminal ligands, which can be readily removed following desolvation at elevated temperatures or under vacuum. Recently, Huang *et al.* have synthesized a polar ketone-functionalized metal-organic framework with exposed metal sites showing a high CO₂ adsorption performance (46.7 wt % at 273 K and 1 bar), which exceeds MOF-74 that known as CO₂ adsorbents with the highest CO₂ adsorption at lower pressure. The results suggest that implanting polar ketone groups into a multidentate ligand could throw certain light on designing and preparing novel MOFs with high performance in the research of gas adsorption[8].

Conclusion

For post-combustion CO₂ capture, the CO₂ adsorption capacities of some MOFs with unsaturated metal sites or amino functional group usually reach 3 mmol•g⁻¹. This is because interaction between CO₂ molecules and the skeleton of MOFs. The focus of application for this material is to make more functional materials. Design and synthesis of composite material with the versatility, modifying and optimizing the hole cavity of MOFs and controlling their chemical stability and reactivity are the three approaches to design a more suitable for the separation of the flue gas environment CO₂/N₂ mixtures of CO₂ adsorbent.

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