

# A Review on Carbon dioxide Capture by Metal-Organic Frameworks

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## ABSTRACT

*Efficient capture of human induced increasing carbon dioxide in the atmosphere is a great challenge at the present time from biological and environmental point of view. Metal-organic frameworks (MOFs) are one of the important groups of porous compounds able to capture of increased carbon dioxide in the atmosphere without doing much damage to the environment. Some reputed published works have been consulted to summarize recent and remarkable progress in the carbon dioxide capture from fuel, water and air using metal-organic frameworks. The effects of central metal ions, open metal sites, linkers, porosity, temperature, pressure, modification of metal-organic frameworks in adsorption, and the possible interactions between carbon dioxide and MOFs have been highlighted in the present review article.*

**Keywords:** capture, carbon dioxide, environment, metal-organic framework.

## INTRODUCTION

Metal-organic frameworks (MOFs) are compounds consisting of metal ions or clusters joined by multidentate organic ligands via coordination bonds. Here metal ions cover both transition and non-transition metals whereas multidentate organic linkers include some specific carboxylate, sulphonate, azolate, phenolate etc. compounds. The combination of particular metal ions and organic ligands gives rise to coordination compounds having suitable porosity in them and able to attract definite compounds or gases. Metal-organic frameworks are an important class of ordered solids since their discovery in 1989 by Robson [1]. MOFs can be categorized into rigid and flexible classes [2]. Rigid MOFs usually have comparatively stable and strong porous frameworks with permanent porosity, similarly to zeolites, on the other hand flexible MOFs are dynamic and soft frameworks that act in response to external parameters, such as pressure, temperature and guest molecules. This extraordinary sensitivity to external parameters affords metal-organic frameworks special properties such as pressure/temperature dependant molecular sieving, which is beyond the reach of traditional adsorbents, such as zeolites and activated carbons. MOFs can be made with exceptionally high porosity and can be synthesized by a simple mixing reaction between various metal ions and organic ligands under mild conditions. The judicious choice of organic building blocks and metal ions is the key factor in the construction of functional metal-organic frameworks.

With the rapid increase of the global population and the industrialization of more and more countries the utilization of energy is rapidly growing. Currently 85% of global demand is being supported by the burning of fossil fuels [3]. The sharply rising level of atmospheric carbon dioxide resulting from anthropogenic emissions is one of the most important green house gases responsible for global warming which on the other hand impacts on global climate, environmental concerns and world economy as well. Thus carbon capture and sequestration (CCS) technologies that efficiently capture carbon dioxide from existing emission sources will play a vital role until more significant modifications to the energy infrastructure can be realized. Metal-organic frameworks are regarded as promising candidates for the capture of green house gases especially carbon dioxide [4]. MOFs are superior to other porous materials because of their high/tunable porosity, pore functionality, various pore architectures, open metal sites and so on [5]. Therefore, recently extensive studies have been done on the adsorption/separation of carbon dioxide with MOFs. The purpose of this paper is to review some selective notable works regarding capture of increased carbon dioxide in the atmosphere due to anthropogenic activity by suitable metal-organic frameworks since its inception in 1989.

## Discussion

A well-studied series of metal-organic frameworks is M-MOF-74 [M<sub>2</sub>(2,5-DOT); 2,5-DOT = 2,5-dioxoterephthalate, M = bivalent metal ions such as magnesium [Mg(II)], zinc [Zn(II)], manganese [Mn(II)], iron [Fe(II)] and nickel [Ni(II)] [6]. Here Mg-MOF-74 has the highest uptake capacity (27.5 wt%) of carbon dioxide under standard condition at 298 K and 1 bar [7]. The usefulness of this structural aspect in Mg-

MOF-74 is marked by its high initial  $Q_{st}$  (isosteric heat of adsorption or standard enthalpy of adsorption) value of 47 kJ mol<sup>-1</sup> [8]. The use of metals of lighter atomic weight can result in higher surface areas and better carbon dioxide uptake. The identity of the metal can influence stability of the resulted framework under humid conditions. In a few cases weak coordination bonds can be formed between metals and carbon dioxide showing high binding energies and finally the polarity of the metal-organic frameworks. Carbon dioxide storage capacity in MOFs can be improved in various ways such as introducing open metal sites, increasing surface area and functionalizing organic ligands [5]. It is quite challenging to characterize effect of individual metals on carbon dioxide uptake since many MOFs contain different linkers and environments and hence have different physical and chemical uniqueness. MOFs gifted with coordinatively unsaturated metals take advantage of Lewis acidity [6]. Metal-organic frameworks with these sites exhibit relatively high heats of carbon dioxide adsorption at low pressures, thus leading to substantial selectivity and carbon dioxide uptake. The larger quadrupole moment and greater polarizability of carbon dioxide compared with nitrogen leads to a stronger electrostatic interaction with an exposed metal site and carbon dioxide.

Organic ligands in metal-organic frameworks connect metal centers or clusters to create three dimensional porous structures. A large variety organic molecule based on carboxylate, sulphonate, azolate, phosphonate etc. may be used as ligands in metal-organic frameworks. The size of the organic ligand contributes to the pore characteristics of metal-organic frameworks, since they are the main constituent of a given MOF structure. There is a competitive coordination of water molecules to the coordinatively unsaturated metal sites and is a real challenge to overcome when using MOFs with such structural features. The incorporation of hetero atoms within the backbone that possess high polarity results a great promise towards interaction with carbon dioxide [6]. Suitable example in this regard is CAU-1 [Al<sub>4</sub>(OH)<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>(BDC-NH<sub>2</sub>)<sub>3</sub>.xH<sub>2</sub>O; BDC-NH<sub>2</sub> = 2-aminoterephthalate, a framework containing aluminium hydroxide clusters linked by BDC-NH<sub>2</sub>, a moderate uptake of 15 wt% at 298 K and 1 bar was achieved with high initial  $Q_{st}$  value of 48 kJ mol<sup>-1</sup> and CO<sub>2</sub>/N<sub>2</sub> selectivity [9].

Bio-MOF-11, a porous cobalt adeninate MOF Co<sub>2</sub>(ad)<sub>2</sub>(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>.2DMF. 0.5H<sub>2</sub>O (bio-MOF-11) generated in 2010 by Rosi group [10], illustrates many physical properties with respect to CO<sub>2</sub> capture including high adsorption capacity of 4.1 mmol g<sup>-1</sup> (approximately 18 wt%) at 298 K and 1 bar CO<sub>2</sub>/N<sub>2</sub> selectivity of 75:1 at 298 K and adsorption enthalpy of 45 kJ mol<sup>-1</sup>. Rosi and co-workers compliment the exposure of multiple functional sites, amino and pyramidal nitrogen atoms exposed in the pores, to the observed adsorption enthalpies and selectivity.

An ultra porous metal-organic framework [Cu<sub>3</sub>(cdm)<sub>4</sub>] {cdm = C(CN)<sub>2</sub>(CONH<sub>2</sub>)}, which holds 0.35 nm nonintersecting channels shared with close vacant Cu<sup>II</sup> sites has been shown by Turner group [11] to exhibit selective gas uptake of CO<sub>2</sub>. The coordinated solvent molecules, uncoordinated solvent within the channels is excluded by treatment of the material with supercritical CO<sub>2</sub> to give the solvent free framework [Cu<sub>3</sub>(cdm)<sub>4</sub>]. The internal pore size is ideal for improved sorption of CO<sub>2</sub> over CH<sub>4</sub>. Here the uptake of CO<sub>2</sub> is almost twice that of CH<sub>4</sub> (46 cm<sup>3</sup> g<sup>-1</sup> vs. 25 cm<sup>3</sup> g<sup>-1</sup>) up to a pressure of 1000 mbar at 273 K. It is revealed that the interaction of CO<sub>2</sub> at two positions close to the open metal sites, aligned with the direction of the narrow channels.

In 2015 J.N. Moorthy and his coworkers [12] reported a semirigid tetraacid linker H<sub>4</sub>L functionalized with 1,2,3-triazole was reasonably designed and produced to access nitrogen-rich MOFs for selective adsorption of CO<sub>2</sub>. The cadmium MOF, that is, Cd-L, obtained by the reaction of H<sub>4</sub>L with Cd(NO<sub>3</sub>)<sub>2</sub> giving a 3D porous framework structure. The sample of Cd-L MOF was triggered by replacing the trapped solvent in the crystals with dichloromethane followed by vacuum drying at 35 °C overnight. Gas adsorption showed that Cd-L MOF allows remarkable CO<sub>2</sub> uptake to the extent of 99 and 1000 cc/g at 1 and 30 bar respectively at 0 °C. The isosteric heat ( $Q_{st}$ ) of CO<sub>2</sub> adsorption for Cd-L was calculated to be approximately 30 kJ mol<sup>-1</sup>.

Honghan Fei and his group [13] in 2016 reported a rare example of a sulfonate-based metal-organic framework [Cu(bpy)<sub>2</sub>(EDS)]<sub>n</sub> (bpy = 4,4'-bipyridine and EDS = 1,2-ethanedisulfonate) holding a prototypical primitive cubic topology built with Cu<sup>II</sup> and a mixed linker (organosulfonate and N-donor) system. The inherent highly polar, permanent porosity gives to the highest reported CO<sub>2</sub> sorption properties to date among organosulfonate-based MOFs, exceeding the notable carboxylate MOF counterpart. Large scale synthesis of this material had been successfully attained on a gram scale (> 1 g) in a single batch with a high yield. The overall structure of [Cu(bpy)<sub>2</sub>(EDS)] comprises of doubly interpenetrated nets, in which each independent net can be analyzed as cationic two-dimensional brick like layers [Cu(bpy)]<sup>2+</sup> pillared EDS (1,2-ethanedisulfonate) linkers. Due to high density and strong polarity of the sulfonate groups in [Cu(bpy)<sub>2</sub>(EDS)] would significantly enhance the attraction of carbon dioxide to have a quadrupole moment. On the basis of low-pressure CO<sub>2</sub> sorption isotherms, [Cu(bpy)<sub>2</sub>(EDS)] showed CO<sub>2</sub>

uptake of 104.2 cm<sup>3</sup>/g (297.4 mg/g) at 200 K, 47.1 cm<sup>3</sup>/g (98.6 mg/g) at 273 K, 32.4 cm<sup>3</sup>/g (62.0 mg/g) at 298 K, and 27.7 cm<sup>3</sup>/g (51.5 mg/g) at 308 K under 1 bar. The heat of adsorption ( $Q_{st}$ ) of [Cu(bpy)<sub>2</sub>(EDS)] was calculated to be 30.9 kJ/mol.

In 2017, S. Bordiga and coworkers [14] present the metal-organic framework UTSA-16 i.e., [K<sub>2</sub>Co<sub>3</sub>(cit)<sub>2</sub>] (where, cit = citrate ion) considering a hopeful material for its capacity to proficiently capture carbon dioxide in large quantities, because of the presence of open metal sites. It is here shown that [K<sub>2</sub>Co<sub>3</sub>(cit)<sub>2</sub>] is also able to desorb fully water at room temperature. This material shows both high volumetric (160 cm<sup>3</sup> cm<sup>-3</sup>) and gravimetric carbon dioxide capacities (4.2 mol kg<sup>-1</sup> at 1 bar and 298 K; 0.9 mol kg<sup>-1</sup> at 0.15 bar and 333 K) at 1 bar and 298 K. The heat involved in the adsorption ( $Q_{st}$ ) of carbon dioxide on [K<sub>2</sub>Co<sub>3</sub>(cit)<sub>2</sub>] is calculated to be 37 kJ mol<sup>-1</sup> on average.

A new 3D porous metal-organic framework, JUC-141, made by 5-aminoisophthalic acid and Cu(NO<sub>3</sub>)<sub>2</sub> has been produced successfully by G. Zhu and his co-workers [15] in 2017. Here the carboxyl groups in the ligands coordinated to copper atoms to form the classic Cu<sub>2</sub>(COO)<sub>4</sub> paddle wheels secondary building units. The amino groups in the ligand also take part in the coordination link to the dipole of the paddle wheel as pillars forms a 3D porous framework. Gas sorption studies disclose that JUC-141 holds a relatively high CO<sub>2</sub> adsorption capacity and good separation performance toward CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub>. The CO<sub>2</sub> adsorption capacities of JUC-41 were observed to be 3.57 mmol g<sup>-1</sup> and 2.29 mmol g<sup>-1</sup> at 273 and 298 K under 1 atm pressure respectively. The  $Q_{st}$  value of CO<sub>2</sub> was 27.85 kJ mol<sup>-1</sup>.

The highlighting points from the above discussion have been depicted in the following table (Table 1).

**Table 1: CO<sub>2</sub> Adsorption Capacities in Selected Metal-Organic Frameworks**

Chemical formula	Common name	Capacity (wt%)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pressure (bar)	Temperature (K)	Heat of Adsorption (kJ mol <sup>-1</sup> )	Ref
[Mg <sub>2</sub> (2,5-DOT); [2,5-DOT = 2,5-dioxoterephthalate]	Mg-MOF-74	27.5	1174	1	298	47	7, 8
Al <sub>4</sub> (OH) <sub>2</sub> (OCH <sub>3</sub> ) <sub>4</sub> (BDC-NH <sub>2</sub> ) <sub>3</sub> .xH <sub>2</sub> O; [BDC-NH <sub>2</sub> = 2-aminoterephthalate]	CAU-1	15		1	298	48	9
Co <sub>2</sub> (ad) <sub>2</sub> (CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> .2DMF.0.5H <sub>2</sub> O	Bio-MOF-11	18		1	298	45	10
[Cu <sub>3</sub> (cdm) <sub>4</sub> ]; [cdm = C(CN) <sub>2</sub> (CONH <sub>2</sub> )-]	-	9		1	273	-	11
Cd-L; [where H <sub>4</sub> L = triazole-based tetraacetic acid]	Cd-MOF	20	421	1	273	30	12
[Cu(bpy) <sub>2</sub> (EDS)] <sub>n</sub> ; [bpy = 4,4'-bipyridine and EDS = 1,2-ethanedisulfonate]	-	6.2	250-260	1	298	-	13
[K <sub>2</sub> Co <sub>3</sub> (cit) <sub>2</sub> ]; [where, cit = citrate ion]	UTSA-16	18.5		1	298	37	14
[CuL](Guest); [where H <sub>2</sub> L = 5-aminoisophthalic acid]	JUC-141	10.1	1057	1	298	27.85	15

## CONCLUSION

Maintaining the level of carbon dioxide in the atmosphere is an important factor to tackle the phenomenon of climate change for sustainable development. Traditional methods of carbon dioxide removal by certain amine compounds are facing some vital problems due to their high energy cost, corrosion, and toxicity. Metal-Organic Frameworks (MOFs) are one of the best alternatives in coming days because MOFs are comparatively environmentally friendly considering both cost and toxicity. Moreover, adsorbed carbon dioxide by MOFs may be regenerated when necessary. The objective of this review is that to find usable metal-organic frameworks to capture increased carbon dioxide in the atmosphere from burning of fossil fuels. The adsorption of carbon dioxide by any MOF depends on number of factors such as surface area, pore size, number of open metal sites, pressure, temperature etc. It is evident from the through discussion of the selected reputed published works that there is no direct correlation of adsorption of carbon dioxide by any MOF with its surface area and number of open metal sites. The selectivity of carbon dioxide adsorption in comparison to other gases present in the atmosphere such as nitrogen, water vapor, methane

etc. must also be taken into consideration. It is very difficult to comment on for the particular MOF in the present situation. It will be very appreciable if the rigidity of zeolite based metal-organic framework is changed in such a way to capture more carbon dioxide. Many metal-organic frameworks have been developed till date. But further research works and improvements are necessary to make commercially and environmentally viable metal-organic framework to capture requisite amount of carbon dioxide effectively to maintain the global temperature useful for living creatures and world economy as well.

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