

A review on modified MOFs as CO₂ adsorbents using mixed metals and functionalized linkers

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Abstract

The effects of greenhouse gases, like CO₂, are becoming more and more visible, from drastic weather changes to global sea level rise. The resultant global warming has become an environmental issue of great concern in recent years. The potential for CO₂ capture through metal-organic frameworks has been widely studied and is currently being explored as a way to reduce greenhouse gas emissions. The strong structural and electronic properties of these frameworks make them excellent candidates for capturing CO₂ due to their high porosity, tunable composition and good chemical stability. Functionalized metal organic frameworks (MOFs) are important because it allows for the development of MOF materials with properties that are tunable for many different applications. Many of these functions are gas adsorption, catalysis, and separation. Depending on the composition of the linkers and nodes, various functional groups can be introduced into the network through the organic linkers and metal nodes, resulting in MOFs with different functions. Mixed-metal MOFs are composed of several different metals. The variety of metals in a mixed-metal MOF gives the MOF many options for tailoring its properties. The resulting bimetallic MOFs are not only more thermally and chemically stable, but also can absorb more gases. The other objective of this study was to observe the effect of organic functional groups on CO₂ adsorption in MOFs. The study found that organic functional groups have a significant effect on CO₂ adsorption in MOFs.

Introduction:

The Combustion of fossil, fuels including Coal petroleum, and natural gas meets the majority of the world's energy requirements. By 2035, demand is expected to be at 778 Etta Joule [1]. Global warming is a serious issue from all over the world, and it Continues to draw a lot of attention both in and out of the scientific community [2]. One of the most significant greenhouse gases causing global warming is CO₂. Because of the excessive carbon dioxide (CO₂) emissions into the atmosphere as a result of our heavy reliance on fossil fuels, we have major environmental issues [3]. The most problematic issue in the twenty-first century. Fossil fuels, on the other hand, provide us with a tremendous quantity of energy in our everyday activities. So, we're in a dilemma, and we need to find a way to improve these two situations quickly [4]. The capture of CO₂ from the atmosphere is being considered as a possible option to control the increase in atmospheric CO₂. Carbon capture and storage (CCS) is a technology used to trap carbon dioxide (CO₂) which is generated from fossil fuel burning [5]. Liquid

ammonia absorption, membrane separation, adsorption, pressure swing adsorption, and cryogenic separation are just some of the CO₂ capture methods that are available. Amine scrubbing, also known as amine gas absorption, is a chemical process for the removal of carbon dioxide from gases by absorption on a suitable absorbent such as an amine[6].

In industrial settings like power plants, chemical absorption of amine scrub has been discovered to be a widespread approach used. The process is also known to be the most affordable and effective method for removing CO₂[5]. Although liquid ammonia absorption has a high CO₂ selectivity, it also has a number of disadvantages[7]. The main problem with amine scrubbing is that it's very expensive and requires many chemicals are used during the process to be efficient. Furthermore, amine scrubbing processes use a large amount of energy to accomplish the same results, in addition to aqueous amine solution corrosion. As a result, solid adsorption techniques have been highly suggested and explored to overcome the intrinsic problems relating with chemical absorption[3], [6].

Zeolites and activated carbon are solid materials that have been effectively studied for the capture of carbon dioxide[8],[9]. These materials have a large internal surface area and small pore sizes, which enable the adsorption of gases into the pores of zeolites and onto the surfaces of activated carbon. The storage of these gases can also be a challenge. zeolites are not so selective and are relatively insensitive to humidity and have CO₂ capture capacities that are too low for commercial application[10],[11]. This is the reason that other sorbent materials are also being developed for the capture of carbon dioxide. A promising new technology is metal-organic frameworks (MOFs). MOFs are a brand-new category of porous materials offering a vast surface area for adsorption of gases. MOFs are synthesized by using metal ions or metal clusters as nodes and organic linkers as connectors in their framework, fig.1. comparatively, metal organic frameworks (MOFs) are more diverse and offer many more potential applications than zeolites and activated carbon. MOFs can be used as catalysts, sensors, and gas storage units.

MOFs are good candidates for CO₂ capture in power plants because of their large surface area, tunable pore topologies, and high efficiency.

The following are some advantages of using MOFs to capture carbon dioxide:

1. MOFs are more easily manipulated and therefore offer more potential applications.
2. MOFs have been used to store carbon dioxide and hydrogen.
3. MOFs are more stable and therefore less likely to degrade over time.
4. MOFs have a significant capacity for carbon dioxide.
5. MOFs are very stable both thermally and chemically.
6. MOFs are more flexible and more efficient than zeolites.
7. MOFs are non-toxic and more easily recycled.
8. MOFs have a high pH stability.
9. MOFs have a high ionic strength stability.

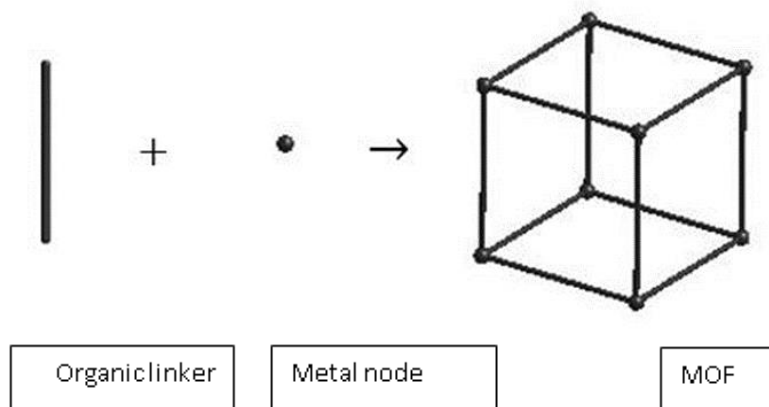


Fig. 1 Schematic drawing of metal organic frameworks.

Despite these potential applications, the use of these novel materials has been limited due to certain disadvantages such as high fabrication costs, low stability in the harsh environment such as high temperature, humidity, and difficulties in recycling or regeneration[12].

This review paper investigates MOFs as potential adsorbents for CO₂. The adsorption of CO₂ on the functionalized MOFs was studied to understand the impact of these modifications on the adsorption behavior of the MOFs. The metal-organic framework is exposed to different types of metal nodes. The linker-like material functionalization is achieved by exposing the MOF to different kinds of ligands.

CO₂ capture using MOFs adsorbents

The ability of MOFs to adsorb gases in differing chemical environments and their high porosity have been exploited to develop adsorbents for air purification, water treatment, and gas storage.

Because of the need for smarter methods that can give increased selectivity and capacity, the use of MOFs as adsorbents for gases is becoming increasingly appealing[13]. Effective adsorbents should contain main strategies such as high selectivity, capacity, regeneration, and promising kinetics of sorption of contaminants. The higher boiling point of CO₂ in (195 K) in addition to the strong dipole–dipole interactions and the high quadrupole–quadrupole interactions between CO₂ molecules and the metal cations in the MOFs. Duo to the binding energy of CO₂ molecules to metal ions being much higher than that of CO₂ molecules to other substrates, the MOFs are expected to be more promising candidates for the large-scale capture of CO₂ than conventional materials, table 1.

Table 1: MOF and MOF-composite potential for CO₂ capture[14]

MOF-Composite	Surface Area (BET), m ² /g	CO ₂ Adsorption	CO ₂ Adsorption Conditions
HCM-Cu ₃ (BTC) ₂ -1	270	2.36 mmol/g	25 ° C
CuBTC-OMC	1288	4.35 mmol/g	25 ° C, 1 bar
CuBTC-AC	1368	4.49 mmol/g	25 ° C, 1 bar
CuBTC-NC	1364	4.51 mmol/g	25 ° C, 1 bar
CuBTC/GA	1048	3.26 mmol/g	298 K, 1 bar
MWCNTs@CuBTC	727	3.26 mmol/g	ambient conditions
HS-1	1745	108.0 cm ³ /g	25 ° C, 1 bar
CuBTC	1760	5.33 mmol/g	25 ° C, 1 bar

CuBTC/GO2	1820	5.12 mmol/g	25 ° C, 1 bar
CuBTC/GO5	1520	4.79 mmol/g	25 ° C, 1 bar
CuBTC/GO10	1380	4.11 mmol/g	25 ° C, 1 bar
CuBTC	892	2.46 mmol/g	295 K, 0.12 MPa
CuBTC/GO	1010	3.09 mmol/g	295 K, 0.12 MPa
CuBTC/GO-U3	1367	4.78 mmol/g	295 K, 0.12 MPa
CuBTC	1594	3.06 mmol/g	25 ° C, 100 kPa
CuBTC@MWCNT	1150	3.4 mmol/g	25 ° C, 100 kPa
HKUST-1	1322	114.92 cm ³ /g	298 K
HKUST-1/ATP	1158	127.88 cm ³ /g	298 K
CuBTC	1580	8.02 mmol/g	273 K, 1 bar
CuBTC@1%GO	1772	8.90 mmol/g	273 K, 1 bar
CuBTC-AC-2	1381	5.35 mmol/g	298 K, 1 bar
CuBTC-AC-2	1381	8.1 mmol/g	273 K, 1 bar
Zeolite 13X	570	210 mg/g	ambient temperatures, 1bar
Zeolite 13X	616	1.77 mmol/g	293 K, 1 bar
UTSA-16	628	189 mg/g	Ambient temperatures, 1bar
UTSA-16@Co-kaolin	620	3.1 mmol/g	25 ° C, 1 bar
UTSA-16/carbon composites	211	2.0 mmol/g	room temp., 1 bar
UTSA-16(Co)-cordierite monolith	223	1.1 mmol/g	298 K, 1 bar
UTSA-16monolith containing bentonite	568	3.0 mmol/g	25 ° C, 1.1 bar
UTSA-16 727		3.5 mmol/g	25 ° C, 1.1 bar
UiO-66-BTEC	568(Langmuir surf. Area)	1.05 mmol/g	303 K, 0.99 bar
HKUST-1@GO-2	1550	8.5 mmol/g	0 ° C, atmospheric pressure
CuBTC	1305	6.39 mmol/g	273 K, 1 atm
CG-3 (CuBTC-GO-3)	1470	7.94 mmol/g	273 K, 1 atm
CG-15(CuBTC-GO-15)	500	2.97 mmol/g	273 K, 1 atm
Cu ₃ (BTC) ₂	933	2.77 mmol/g	298 K, 1 bar
Cu ₃ (BTC) ₂ /GO-l	898	3.13 mmol/g	298 K, 1 bar
Cu ₃ (BTC) ₂ /GO-m	837	3.37 mmol/g	298 K, 1 bar
Cu ₃ (BTC) ₂ /GO-h	743	2.66 mmol/g	298 K, 1 bar
Cu ₃ (BTC) ₂	1587	295 mg/g	298 K, 18 bar
CNT@Cu ₃ (BTC) ₂	1458	595 mg/g	298 K, 18 bar
HKUST-1	434	1.59 mmol/g	25 ° C, 1 bar
HKUST-1/GO	369	0.98 mmol/g	25 ° C, 1 bar
HKUST-1	1410	7.92 mmol/g	196 K, 1 bar
wt%SWCNT@HKUST-1	1714	8.75 mmol/g	196 K, 1 bar
HKUST-1	1379.87	3.55 mmol/g	25 ° C, 1 bar
HKUST-1@GO	1096.46	2.53 mmol/g	25 ° C, 1 bar

Many studies have used MOFs materials to capture carbon dioxide in gas separation applications, such as flue gas separation in thermal power plants (CO₂/N₂), natural gas

purification (CO_2/CH_4) in biogenic methane processes, syngas separation (CO_2/H_2), and so on. There are a number of great reviews that summarize the CO_2 capture capabilities of MOFs[15]. Sumida et al. evaluated the pioneering work and evaluation strategies of MOFs for CO_2 removal in detail[16]. MOF-based composite membrane systems for CO_2 separation were reviewed by Seoane et al[17]. Low-concentration CO_2 capture utilizing adsorbents such as MOFs was reviewed by Belmabkhout et al[18]. CO_2 capture and separation using MOFs was examined by Yu et al. from both a computational and experimental aspect[19].

The latest developments in gas storage and separation utilizing MOFs, as well as the desirable chemical characteristics of MOFs for various gas storage/separation situations, were highlighted by Li et al[20]. Lin et al. discussed new developments in MOFs for CO_2 selectivity from post combustion flue gas and CH_4 storage for automotive applications[21]. The most common way to achieve the binding of CO_2 molecules into MOFs is the use of functional groups that can form stronger interactions with CO_2 molecules, such as carboxylate groups, aliphatic amines, monodentate hydroxide, open metal sites on the surface of MOFs are typically used as active sites has been proven to be a promising approach[22].

Mechanisms of adsorption of gas on MOFs

Adsorptive separation mechanisms can be divided into three categories[23],[24]: including 1) the molecular sieving effect also called size exclusion separation, 2) equilibrium separation and 3) kinetics separation. The difference in diffusion is determined by the relative pore size. When investigating a separation process, the steric effect can be advantageous. It describes how each atom in a molecular structure has a defined size and takes up a specific amount of space[25]. As a result, it's known as the molecular sieving effect. Consider a steric effect-induced gas separation; certain components will be adsorbed as a result of the molecular sieving effect. Whereas other types of molecules will be blocked from entering the framework. The steric mechanism, as can be seen, is based on the incompatibility of the substrate pores' shape and size with those of the adsorbate gas molecules[23]. For instance, molecular sieving of methane and nitrogen from carbon dioxide has been successfully achieved owing to the fine-tuning of some MOF structures, which benefit from a variety of uniform pore topologies and adjustable porosities. In order to separate molecules of similar size or shape in a mixture, one must build a medium with a specified size and tune the pore size, which can be a very precise operation due to the difficulty of precisely adjusting the dimension and functioning in the majority of solid-state materials[26]. In kinetics separation, adsorption of porous materials is determined by the diffusivity of each gas component, therefore selection is intrinsically transitory[27]. The mechanism of adsorption is controlled in this case by adjusting the exposure duration; as a result, certain adsorbates of penetrate through the pores at a higher rate and become adsorbed. The aforementioned process is known as a "kinetic effect." The study of such a phenomenon is more difficult because it is based on the diffusion rate, which is influenced by a number of factors. The bulk's molecular shape and size, pore shape and size, the chemical composition of the adsorbates and adsorbents, as well as the interactions of certain adsorption sites to the adsorbate's molecules are all factors to consider[23]. The thermodynamic equilibrium effect occurs when specific components preferentially adsorb on the surface of an adsorbent due to various adsorbate surface and/or adsorbate packing interactions[23]. The components of the gas mixture can all flow within the adsorbent when its pores are big enough, resulting in equilibrium separation

(dynamic separation). Hence, in order to achieve an equilibrium-based separation, the porous material must have a large pore size that allows all of the molecules to pass through[23]. The insertion of significant interaction areas on the MOF framework creates comparable thermodynamic attractions between the gas molecules and the MOF material in equilibrium separations[28].

Modified MOFs as CO₂ adsorbents

1- Based on the functionalization of metal nodes

In recent years, MOFs have shown a growing interest as porous materials for adsorption of carbon dioxide (CO₂) due to their high surface areas, low costs, and high adsorption capacities. The strategy of mixed-metal MOFs which involve introducing multiple functionalities into a single MOF network, has received much scientific attention because MOFs with mixed-metal networks can have greater stability and better gas uptake properties than those with single-metal networks. Mixed-metal MOFs are generally composed of two or more transition metals, which are usually linked by organic linkers.

The first mixed-metal MOF (MM-MOFs) by Kim and co-workers[29]. They introduced a cubic network MOF based on Cd after soaking this Cd -MOF in Pb(NO₃)₂ liquid solution for about seven days, resulted in a full replace with no loss of crystallinity in a crystal structure. In fact, Pb²⁺ exchanged about 98 percent of Cd²⁺ in just two hours the ICP-atomic emission spectroscopy (AES) findings indicated 50 percent exchange of Pb²⁺ for Cd²⁺ in one day. The opposite process, on the other hand, took nearly three weeks. Sun et al[30] developed bimetallic MOFs with increased stability and CO₂ adsorption capability using a metal ion exchange method. To produce bimetallic Zn-1', Cu ions were largely substituted by Zn ions in Zn-1[Zn₃(L)₂(dabCO)(H₂O)].9DMF, where H₃L is [1,1':3',1''-terphenyl]-4,4'',5'-tricarboxylic acid). Cu-1, a copper(II) counterpart, was made by replacing Cu-1 with Zn ions, fig.2. Because the hybrid framework has a high level of stability, Zn-1' had a higher N₂ adsorption quantity (2063 m² g⁻¹) than Zn-1 (59 m² g⁻¹). Similar amounts of N₂ were adsorbed by Cu-1 and Cu-1'. Zn-1 uptakes of CO₂ was 52 m³ g⁻¹. For Zn-1', Cu-1 and Cu-1', CO₂ absorbed at rates of 1490, 703, and 770 m³ g⁻¹ for, respectively, at 195 K and 1 bar. The adsorption efficiencies of bimetallic Zn-1' and Cu-1' were higher than those of their analogues.

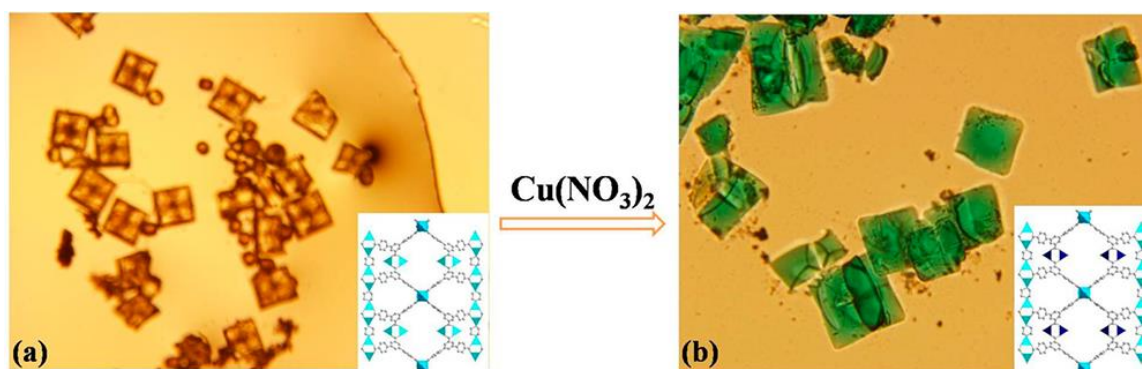


Fig. 1 Zn-1 crystal images before (a) and after (b) the metal-ion metathesis[30]

Hill et al found that by substituting Ti for Zr in UiO-66, they were able to synthesis bimetallic UiO-66 which was characterized by the smaller crystallite size and greater adsorption enthalpies, resulting in improved CO₂ uptake. As Ti replacement increased, the octahedral cages diminished by one and became considerably broader, fig.3. UiO-66(Zr100),

UiO-66(Ti32), and UiO-66(Ti56) absorb CO₂ at 273 K was 2.2, 2.3, and 4 mmol g⁻¹, respectively. Given that UiO-66(Ti100) has a theoretical increase in CO₂ gravimetric uptake of 19%, while UiO-66(Ti56) has a high CO₂ loading capacity of up to 81 percent when compared to UiO-66(Zr100), The findings indicate that efficient adsorption of CO₂ can be achieved by smaller pore sizes and the stronger adsorption characteristics of Ti(IV)[31].

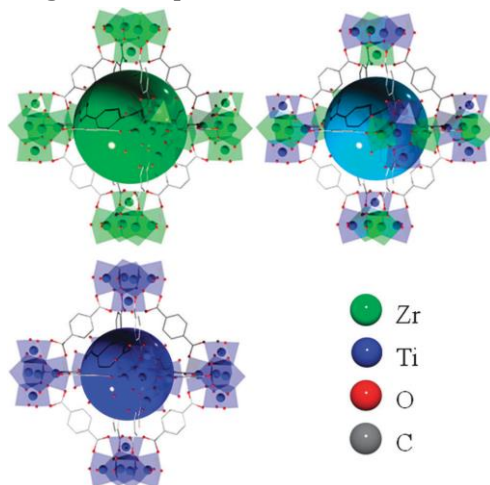


Fig. 2 UiO-66 can produce heterometallic MOFs through postsynthetic exchange with Ti(IV)[31]

Xiao, Li, and coworkers successfully synthesized magnesium-doped bimetallic MIL-101 (Cr, Mg) which shows increased CO₂ adsorption capacity. MIL-101(Cr, Mg) had a CO₂ adsorption rate of 3.28 mmol g⁻¹ at 298 K and 1 bar, which was a 40 percent increase over MIL-101 (Cr). The doping of Mg in MIL-101 (Cr) led to a larger surface area and stronger CO₂ adsorptive sites. As a result, the MIL-101(Cr, Mg) capacity for CO₂ adsorption increased [32].

Feng et al[33]. reported a family of bimetallic MOFs based on heterometal-modified (CPM-200 series), CPM = crystalline porous materials) combining trivalent (In³⁺, Ga³⁺, Fe³⁺, V³⁺, Sc³⁺) and divalent cations (Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺), fig.4. The CO₂ uptake and CO₂/N₂ selectivity can be fine-tuned using this M²⁺/M³⁺ heterometallic composition. The Mg²⁺ CMP-200 family produced a strong CO₂ uptake in the range of Fe³⁺/Mg²⁺ > In³⁺/Mg²⁺ > V³⁺/Mg²⁺ > Ga³⁺/Mg²⁺ > Sc³⁺/Mg²⁺. At 273 K and 1 bar, the CO₂ adsorption of the CMP-200(Fe³⁺/Mg²⁺) was 9.27 mmol g⁻¹. Moreover, the heat of CO₂ adsorption is the highest in case of CMP-200(V³⁺/Mg²⁺) at 79.6 kJ /mol. The cation charge/radius ratio and the isosteric heat had a significant impact on the CO₂ separation performance of mixed-metal systems. This correlation can be used to develop new materials for adsorption-based separation of CO₂. The Ti-UiO-66 mixed matrix membrane was investigated for CO₂/N₂ separation. When compared to the original UiO-66 matrix membranes, the combined Ti-UiO-66 membranes revealed a 153 percent increase in CO₂ permeability. This is because CO₂ interacts more strongly with Ti⁴⁺-nodes, and Ti⁴⁺ exchanged UiO-66 interacts with the membrane polymer (PIM-1) considerably better.

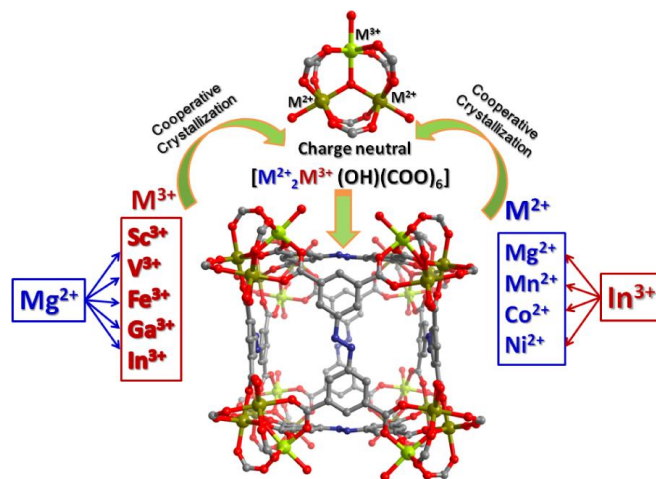


Fig. 3 Combinations of M^{2+} and M^{3+} for CPM-200s[33]

2- Based on the functionalization of linker

The effective CO_2 capture ability of MOFs can be improved by altering the structure with designed pore, and porosity of the MOF.

The effect of ligand functionalization on MOF affinity for CO_2 adsorption and separation is significant. This method is one of the best and efficient processes for achieving high CO_2 storage properties due to the ease of the modification process and the diversity of functional groups[5].

Specific framework qualities can be obtained by carefully selecting the linker based on geometry, length, and functionality[34]. The adsorption of CO_2 by MOFs is related to the number of polar groups on the linker. The introduction of polar groups, such as $-Cl$, $-OH$, and $-COOH$ containing functional groups on MOFs with Lewis basic sites could enhance the adsorption capacity of CO_2 [35]. A higher capacity for CO_2 and/or preferred CO_2 uptake over other guest's molecules including N_2 , CH_4 , and H_2O attributed to the interacts with these sites. In this section, we have evaluated the impact of most relevant functional groups in MOFs on excellent adsorption capacity CO_2 adsorption capacity with high selectivity.

Amino group

Amine is a simple structure that capable of forming hydrogen bonds. The nitrogen in amine has lone pair electrons, which can be donated to other hydrogen bonds, and the hydrogen atoms can accept hydrogen bonds. Functional MOFs can be designed by introducing functional groups with simple and multiple chemistry of amine incorporation. The chemistry of this guest gas molecule such as CO_2 act as a Lewis acidic and quadrupole, which gives it high affinity for interacting with $CO_2(C) \dots (N)$ amine and $CO_2(O) \dots (H)$ amine molecule[36].

Amine-substituted functionalized MOF linkers, first described by Arstrad et al. (2008)[37], is a simple approach to enhance CO_2 adsorption capacity. Later, several works have been published.

Xian et al[38]. reported the Functionalization of PEI -based ZIF-8 CO_2 adsorbent, fig.5. The study found the PEI functionalized ZIF-8 CO_2 working capacity were up to 1.61 mmol/g which is 27 times higher than that of ZIF-8. More importantly, it was observed that in the hydrous condition, the CO_2 capacity was increased to 1.99 mmolg-1with increase a 23.6 percent over

the CO₂ capture amount under dry conditions. CO₂ adsorption selectivity and capacity at low pressure have shown to be enhanced by alkyldiamines functionalization on the unsaturated metal sites of M₂(dobpdc), (dobpdc⁴⁻ = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate).

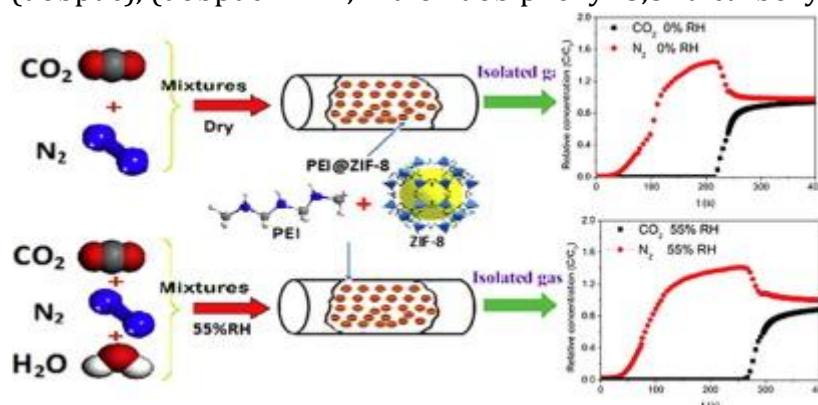


Fig. 4 PEI@ZIF-8 for CO₂/N₂ separation in dry condition and in presence of water vapor[38]

Ge et al. combined microwave and ultrasound irradiation methods to prepare 2-aminoterephthalic acid modified MIL-53(Al). the NH₂-MIL-53(Al) produced quickly under the synergistic effect of microwave and ultrasound irradiation. The amine functionalized MIL-53(Al) show excellent performance of carbon dioxide capture capacity of 33.86 cm³ g⁻¹. Furthermore, the prepared adsorbent exhibits good carbon dioxide adsorption regenerability and stability. Jo et al observed that when alkylamine ligands such as diamines [ethylenediamine (en), 1-methylethylenediamine (men), and 1,1-dimethylethylenediamine (den)] are grafted onto the coordinatively unsaturated metal centers of Mg(dobpdc)₂, the framework's affinity for CO₂ is significantly improved[39]. Ferey et al published the first alkyl amine-functionalized MOF, ethylenediamine -incorporated MIL-101(Cr), however they did not discuss its CO₂ adsorption functionality[40]. Flaig et al[41] study reported that IRMOF-74-III-CH₂NH₂ has the maximum CO₂ uptake capacity in the series (3.2 mmol g⁻¹ at 800 Torr) due to the linker-based amine functional groups, fig.6. The primary alkylamine can be covalently tethered to the linkers of IRMOF-74-III results (IRMOF-74-III-CH₂NH₂) that chemically bond CO₂ in contrast to the aromatic amine. Ammonium carbamate (RNHCOO + H₃NR) and carbamic acid (RNHCOOH) framework are the predominant chemisorption product, producing IRMOF-74-III-(CH₂NH₂)₂ according to solid-state crosspolarization magic angle spinning (CP-MAS) ¹³C NMR spectra. Furthermore, it was demonstrated that after grafting diamines onto the unsaturated metal sites of M₂(dobpdc) framework (M = Mg, Mn, Fe, Co, Ni, Zn; dobpdc⁴⁻ = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate), the resulting materials exhibited great potential for CO₂ capture.

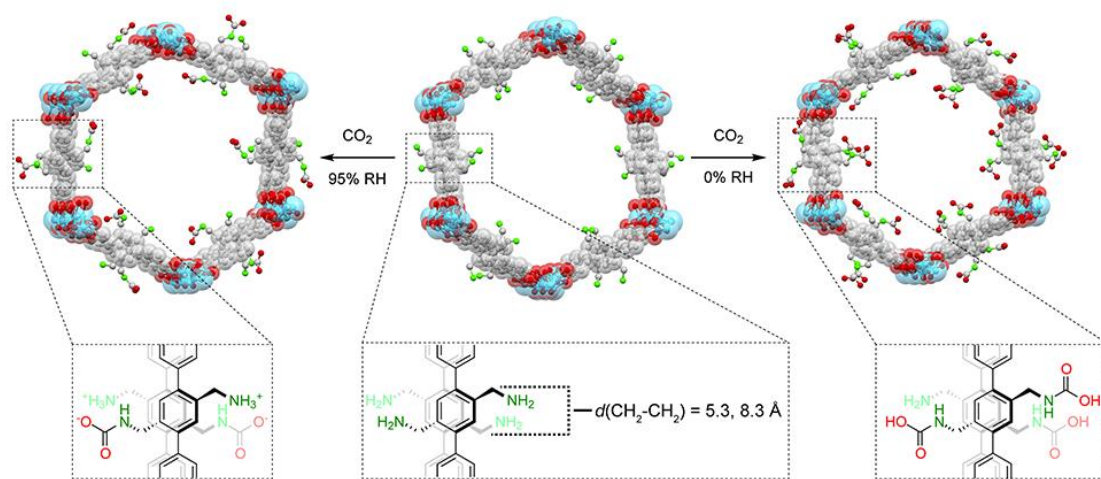


Fig. 5 CO₂ adsorption in IRMOF-74-III-(CH₂NH₂)₂ under dry loading conditions and both 95% RH38[41].

Polyethylenimine (PEI) has been reported to be successful in corporation into MOFs to achieve high CO₂ adsorption capacity because the chain ends possess primary amine sites that can react with CO₂ to produce carbamates, such as PEI/MIL-101, PEI/MIL-101-NH₂, PEI/HKUST and PEI/UiO-66 composites[42]. Vismara et al.[43] functionalized Micro-mesoporous amino-decorated BPZ-based MOFs, M(BPZNH₂) (M = Zn, Ni, and Cu), with 3-amino-4,4'-bipyrazole and the uptake capacity for CO₂ is 3.07 mmol g⁻¹ (13.5 wt. percent CO₂). Moreover, the CO₂/N₂ selectivity is 17.

A new Amino-functionalized Cu (amino-Cu-MOF) using 2-aminoterephthalic as an organic linker was synthesized by Khan et al[44]. According to their study, the MOF exhibits a higher CO₂ capture rate of 5.85 mmol g⁻¹ at 25 °C as compared to Cu-BDC MOF. The results show that the amine-functional group are likely to play a significant role in CO₂ uptake in MOFs, and these outstanding properties make it promising candidates for the storage and separation of CO₂.

Amide group

There are two accessible gas binding sites for the amide group. The amine (NH...gas). and the carbonyl (C=O...gas) are related. The carbonyl group is the amide guest binding site, according to theoretical calculations on amide MOFs[36]. There are few reports about directly probing gas-amide MOFs binding sites. Benson et al[45]. combined neutron powder diffraction (NPD) and inelastic neutron spectroscopy (INS). At 20 bar and 298 K, MFM-136, an amide (MOF), showed a strong CO₂ absorption of 12.6 mmol g⁻¹. Safarifard et al[46]. created new three-fold interpenetrated MOFs (TMU-22, -23, and -24) that were functionalized with various amide groups, fig.7. Kinetic study and breakthrough experiments show CO₂/N₂ selectivity of CO₂ over N₂ in TMU-24 was significantly higher than in TMU-22 and -23. The amide groups in this framework were more interpenetrated into the pores than the amide groups in the other isorecticular MOFs. This led to a strong CO₂ selective adsorption due to the amide functional groups are more easily accessible in TMU-24.

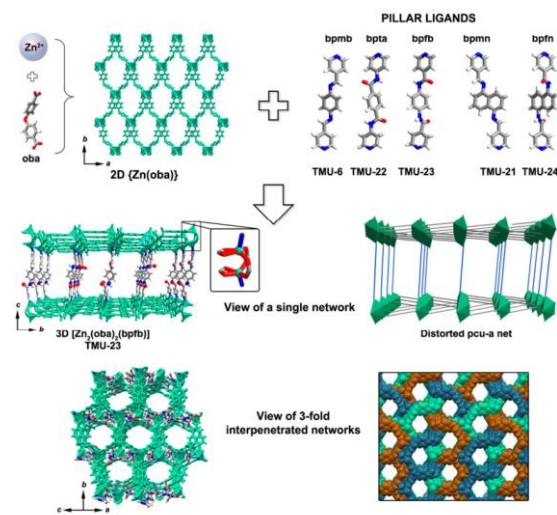


Fig. 6 3D-interpenetrated porous pcu-MOFs created by the interaction of Zn(II) ions with oba linkers and dipyridyl-based ligands[46].

[$\text{Sc}_3(\mu_3\text{-O})(\text{L})1.5(\text{H}_2\text{O})_3\text{Cl}]_n$ where H_4L = 5-(3,5-dicarboxybenzamido)isophthalic acid] was created by Chen et al[47]. As a novel amide-functionalized metalorganic framework (AFMOF) with the combined property of highly selective CO_2 adsorption and good thermal and chemical stability. According to simulations, both the amide-decorated group and the open metal site cooperate as CO_2 binding sites, which might help explain its extremely selective CO_2 absorption. Moreau et al[48]. reported CO_2 and C_2H_2 uptake in MFM-188, within a tetra-amide octacarboxylate functionalized MOF. Due to its framework structure and pore shape, MFM-188a has a suitable high surface area (BET) and strong density of binding sites, as well as a record high CO_2 uptake of 120 cm^3/g (23.7 wt%) at 298 K and 1 bar.

Halide group

The design, synthesis and application of halogenated organic ligands into MOFs are introduced. The research on the halogenation of organic ligands provides a new approach to improve the gas storage and separation properties of MOFs. The polarity, stability and hydrophobicity of MOFs can be tuned by modifying the organic ligands. TKL-doped mixed matrix membranes (MMMs), Ni(II) anions with 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (tpt) and o-phthalic acid (OPA) as co-ligand were prepared to examine the efficiency of these materials for separation of CO_2 [49].

An important factor in the stability of the framework structures of TKL MOFs with 3-F decorated pores is believed that due to the additional weak bonds of ambient atoms inside the framework to the inserted fluorine. The fluorine-functionalized TKL MOFs showed great CO_2 selectivity over CH_4 and N_2 . LIFM-26, a porous perchlorinated linear dicarboxylate to link trigonal prismatic $\text{Fe}_3(\mu_3\text{-O})$ units through $\text{Fe}_3\text{O}(\text{H}_2\text{O})_3$ cluster and 2,3,5,6-tetrachloride terephthalic acid (H_2TCDC) with 4 Cl atoms per ligand, fig.8, has been synthesized and studied in three dimensions[50].

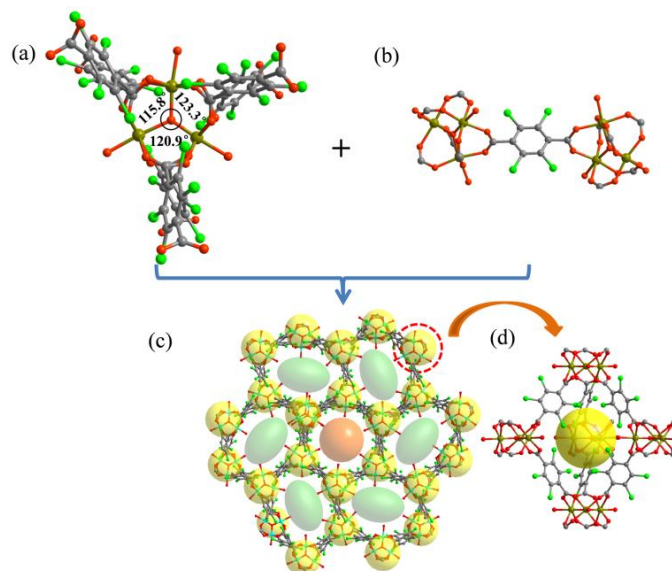


Fig. 7 (a) 3D Fe₃O cluster; (b) TCDC ligand; (c) two different types of channels along the c axis; (d) The framework consists of five Fe₃O clusters and six TCDC ligands[50].

It has functional polar groups as well as open metal sites, the open Fe sites were created by removing solvent molecules, giving it dual functionality. It was significantly more selective for CO₂ vs N₂.

The LIFM-26 has a high Carbon dioxide uptake of 3.3 mmol/g and a high CO₂ at 1 bar and 298 K due to the polar Cl groups and OMSs, which interacted strongly with the guest CO₂.

Other functional groups

Modifying the appropriate functional groups on a adsorbent's surface can improve CO₂ adsorption. Hydroxyl is a functional group that has great potential for interactions with various guest molecules. These interactions are attributed to a hydroxide electron donor with high polarity. These common features of hydroxide allow interactions with other guest molecules such as hydrogen bond donors, Lewis acidic molecules, and partially positive atoms such as CO₂. The MOF hydroxylic guest consists of two interactive oxygen and hydrogen atoms, which represent the ability of hydroxyl function to the design and application of hydroxyl functionalized MOFs for a variety of purposes. Qian et al.[51] investigated the presence of hydroxy host-guest interactions increased CO₂ capture. Adsorption sites in hydroxo (μ_2 -OH) functionalized MOFs [M₂(OH)₂(BPTC)] (M = In, Ga, and Al) through a moderate to weak H-bond. Yin et al.[52] reported that a bonding pair of electrons between oxygen atoms of CO₂ and hydrogen atoms of OH is the main interaction of CO₂ with benzotriazole-based microporous aerogel (HOPBTA), fig.9.

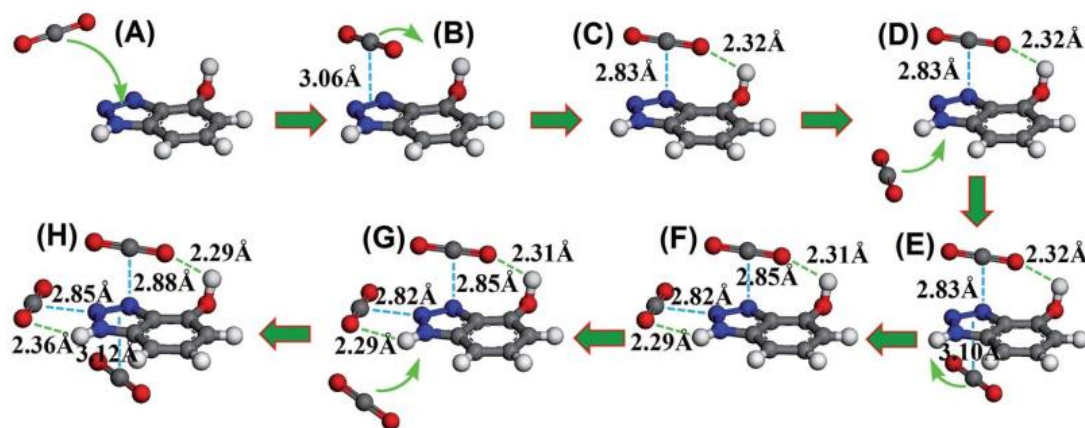


Fig. 8 DFT results of CO₂ capture by an adjacent hydroxyl group[52].

Cd-based coordination polymers containing phenolic hydroxyl groups as hydrogen-bonding donors were described by Zheng et al.[53]. Two Cd(II) MOFs containing hydroxyl groups, have CO₂ uptakes of more than 20%, suggesting that phenolic hydroxyl-functionalized groups are more favorable for CO₂ adsorption and are also utilized in metal ion detection. Lui et al.[54] found that the breathing ability of MIL-53 was influenced by the hydroxyl groups. The CO₂ adsorption capacities of Al-MIL-53-OH₂₅ and Al-MIL-53-OH₅₀ were more than that of Al-MIL-53 under the same conditions.

Mixed ligand

The mixed organic ligands are used for the synthesis of MOFs with new functionalities, including the synthesis of MOFs with anisotropic structures. It has great choice for a variety of applications and as an alternative to the traditional ligands, such as inorganic salts. It is based on using a tiny polydentate ligand to form Layered Frameworks with ditopic linkers. The materials' frameworks can be categorized into the following: layer-like linkers, cluster-like linkers, and rod-like linkers. Polycarboxylates and polypyridines, as well as other anionic linkers such as azolates, are commonly used to construct mixed ligand MOFs[55]. Several researches have been published on the grafting of mixed ligands frameworks using polar functional groups such as fluorine, amine, amide, and azo/azine.

Using a solvothermal synthesis method, Liu et al[56]. effectively decorated a cobalt-based MOF with benzenetricarboxylic and triazole-based ligands. The products absorbed a considerable amount of CO₂ and had a significant selectivity over N₂. At 1 bar and 295 K, the absorption of CO₂ is 77.3 cm³ g⁻¹. This is due to the presence of a number of functional groups on the pore surfaces of the framework, including amino groups, unsaturated metal sites, and -C=O/-COOH sites. Halder et al. reported mofs with mixed ligands[57]-[58]. One of these studies he described three MOFs with different crystal structures based on carboxylic acid donors and pyridyl bridging ligands, which are widely used as co-ligands. The dehydrated forms selectively adsorb CO₂ over N₂ and have a progressive water absorption pattern[57]. Vismara et al. reported mixed ligand systems in ZnBPZ-X, (BPZ= bipyrazolate). Various functional groups have been used to determine multivariate MOFs. The unique characteristics of these MOFs increased gas adsorption capability and CO₂/N₂ selectivity. The authors stated that linker combinations can enhance adsorption capacity when compared to the single ligand Zn(BPZ) system[59]. Recent study reported enhanced CO₂ adsorption on a mixed ligand mofs,

$[\text{Zn}_2(\text{H}_2\text{O})(\text{nic})(\text{pyrz})]\text{nH}_2\text{O}$, fig.10, where H_3pyrz and Hnic are respectively pyrazole-3,5-dicarboxylic acid and isonicotinic acid[60].

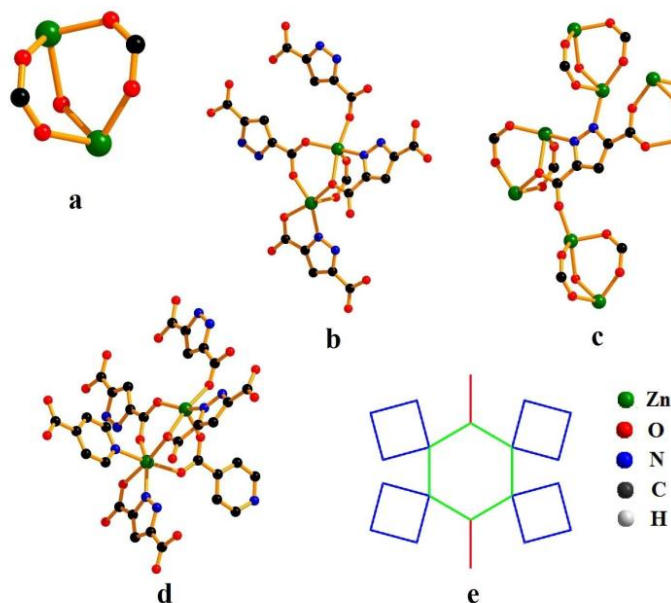


Fig. 9 Connected linker in $[\text{Zn}_2(\text{H}_2\text{O})(\text{nic})(\text{pyrz})]\text{n}\cdot\text{nH}_2\text{O}$ [60].

The dehydrated framework revealed a carbon-dioxide absorption of 2.2 and 5.7 wt% at 0.15 bar and 12.2 wt% at 298 K. At low partial pressures, this is comparable to H_2 , N_2 , and CH_4 . The selectivity of CO_2 with regard to CH_4 was determined to be 22.4 when cooled to 273 K.

Conclusions

CCS is the process of capturing and compressing CO_2 from combustion sources, and then storing it away from the atmosphere, typically in deep, unmineable reservoirs in the Earth. Adsorbents are materials used to capture CO_2 from gas streams by physical or chemical adsorption by binding CO_2 molecules to the surface of the adsorbent. The development of efficient adsorbents is essential to enable the implementation of CCS technologies. MOFs have an advantage over other materials because they can easily be modified with changing environmental conditions. They can also adsorb carbon dioxide with a high surface area and adjustable pore characteristics, which take a new direction for CO_2 capture. It may be possible to fine-tune of metal clusters and/or organic ligands of the metal-organic framework (MOF) assembly process to produce novel and more specific MOFs for a variety of applications. This control over the assembly process could lead to the production of MOFs with tailored electronic, spectroscopic, photonic, and catalytic properties. This control can be achieved by tuning the metal concentration in a mixed-metal MOF, improving the stability of the material, or rendering it more hydrophobic. The major groupings (amine, amid, and hydroxyl) are evident in the adsorption process. The high performance of the amine, amide and hydroxyl functions in CO_2 separation was observed in MOFs with CO_2 vacancies. These functions showed an improvement over the competitive reaction in terms of selectivity, purity and storage. Through their Lewis basicity, polarity, and hydrogen bonding. In this way, a fingerprint of the desired mixed metal MOFs and functional group can be created which will help guide the selection of the appropriate MOF.

Author declaration

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الأطر الفلزية العضوية لامتزاز غاز CO₂ باستخدام مزيج فلز ومجاميع ليكاند وظيفية

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الخلاصة:

أصبحت تأثيرات غازات الدفيئة، مثل ثاني أكسيد الكربون، أكثر وضوحاً، من خلال التغيرات المناخية القاسية إلى ارتفاع مستوى سطح البحر العالمي. أصبح الاحتباس الحراري الناتج عن ذلك قضية بيئية تثير قلقاً كبيراً في السنوات الأخيرة. تمت دراسة إمكانية احتجاز غاز ثاني أكسيد الكربون من خلال الأطر الفلزية العضوية على نطاق واسع ويتم استكشافها حالياً كطريقة لتقليل انبعاثات غازات الاحتباس الحراري. الخصائص الهيكلية والإلكترونية القوية لهذه الأطر تجعلها مرشحة ممتازة لالتقاط ثاني أكسيد الكربون بسبب مساميته العالية وتكوينها القابل للضبط والاستقرار الكيميائي الجيد. تعد الأطر العضوية المعدنية الوظيفية مهمة لأنها تسمح بتطوير مواد الأطر العضوية المعدنية بخصائص يمكن ضبطها للعديد من التطبيقات المختلفة. العديد من هذه الوظائف هي امتصاص الغاز، والتحفيز، والفصل. اعتماداً على تكوين الروابط والعقد، يمكن إدخال مجموعات وظيفية مختلفة في الشبكة من خلال الروابط العضوية والعقد المعدنية، مما ينتج عنه الأطر العضوية المعدنية ذات الوظائف المختلفة. تتكون الأطر العضوية المعدنية المختلطة من عدة معادن مختلفة. يمنح تنوع المعادن في الأطر العضوية المعدنية المختلطة الأطر العضوية العديد من الخيارات لتكييف خصائصها. لا تكون الأطر العضوية المعدنية الناتجة ثنائية المعدن أكثر استقراراً من الناحية الحرارية والكيميائية فحسب، بل يمكنها أيضاً امتصاص المزيد من الغازات. الهدف الآخر من هذه الدراسة هو ملاحظة تأثير المجموعات الوظيفية العضوية على امتصاص ثاني أكسيد الكربون في الأطر العضوية.