Trace Carbon Dioxide Capture by Metal−Organic Frameworks

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Abstract: Climate deterioration is closely related to the CO_2 concentration in atmosphere, which is considered one of the major environmental challenges we are facing today. It is urgent to take immediate actions to prevent further climate change. In comparison with post-combustion CO_2 capture technologies from flue gas, trace CO_2 capture directly from air is still a challenge but very important for both CO_2 control in atmosphere and air condition control in confined space. This review highlights recent research advances in the use of metal-organic frameworks (MOFs) for trace CO_2 capture, with the emphasis on employing amine functionalized MOFs and ultra-microporous MOFs. Herein, the reported strategies to enhance CO_2 adsorption capacity and selectivity by MOFs are categorized into three main directions, including the developments of MOFs with open metal sites, ultra-microporous MOFs, and amine functionalized MOFs. The mechanisms combined with trace CO_2 capture performance by these MOFs are discussed in detail, offering some promising adsorption solutions for future practical applications of MOF materials. In addition, the performance for CO_2 capture under humid conditions and the regenerability of these MOF adsorbents are revealed. In order to address major issues of capacity, selectivity and stability especially under humid conditions, precise construction and engineering of MOFs to achieve the optimized porous materials are needed.
Keywords: adsorption mechanism, amine grafting, CO_2 adsorption, direct capture, metal-organic frameworks

The carbon mass fraction is only 0.08%, and its richness ranks the 14th, far lower than oxygen, silicon, aluminum, iron and other elements on the earth. On the other hand, carbon element can become the main carrier of solar energy, and the skeleton element of various organisms on the earth. Therefore, carbon cycle is important for life. As a significant component of the carbon cycle, CO_2 plays an essential role. CO_2 is a movable carbon medium that continuously exchanges between different systems such as lithosphere, fossil fuels, hydrosphere, biosphere and atmosphere. The increase of human population and activities has resulted in over emission of CO_2 into atmosphere. Such a significant increase of CO_2 exhausted beyond the moment capacity of the earth breaks the balance of each earth systems, causing a series of environment and climate issues.[1]

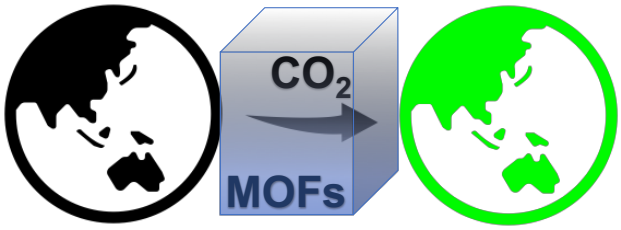

Figure 1. MOFs employed for CO_2 capture toward a sustainable future.

Currently, the level of CO_2 in the atmosphere hits a new record (*i.e.*, 406 ppm).[2] That is the highest point we have for the last 800,000 years with increasing rate of 2 ppm/year. Atmospheric CO_2 concentration is predicted to reach 500 ppm by 2050. There is a feedback effect between CO_2 and global warming.[3] Increasing CO_2 concentration leads to global warming, while the global warming results in the capacity decrease of seawater for CO_2 sorption, accelerating more CO_2 releasing into atmosphere. Global warming resulted from greenhouse effect of CO_2 is a direct reason in a series of serious problems such as sea level elevation, human health, and food safety. The CO_2 capture was proposed by the Intergovernmental Panel on Climate Change as an important technology for restraining further growth of atmospheric CO_2 concentration.

Conventional CO_2 capture commonly addresses the CO_2 emission from industrial sources, such as cement plants, power stations, iron/steel industry installations, and oil refineries. Based on different processes, the CO_2 capture could be conducted by three main technologies, *i.e.*, liquid amine sorption,[4-8] membrane separation,[9,10] and adsorption.[11-13] As far, large-scale post combustion CO_2 separation has been mainly based on liquid amine absorption technique, in despite of amine loss during the operation, corrosive properties of liquid amine, energy consumption during the regeneration process, and large energy penalty resulted from high calorific heat of water. In addition, relatively low concentration of CO_2 in air is a challenge for CO_2 capture.[14] The low concentration of CO_2 not only results in low diffusion rate due to lack of drive forces determined by partial pressure of CO_2, but also causes low CO_2 uptake on account of low chemical potential of gas phase. Thus, direct CO_2 capture from the air, a demonstrated CO_2 removal approach, involving the use of artificial materials to capture CO_2 from ambient air through chemical bonding attracts much attention.[15-17] Amine grafted solid adsorbents[7,18,19] were employed as one of most promising candidates for trace CO_2 capture or CO_2 capture directly from air. CO_2 capture by solid adsorbents with porous structure and adsorptive site having high affinity for CO_2 has been extensively investigated, including materials development, mechanism study, and performance test.

Amine appended solid adsorbents are facilely used in trace CO_2 capture with advantages of easy package and storage, low leakage risk, weak corrosion, good diffusion property, high capture efficiency, high stability, and low calorific heat.[11,12] Generally, there are two ways to enhance the CO_2 capture capacity. One is to improve the affinity between adsorptive site and CO_2 molecule, which always involves amine grafting and component design. The other way is to construct special geometric channels to trap CO_2 molecule, including the pore size adjustment and active site distribution. Some conventional porous materials such as silica gels present amorphous property and do not possess continuously uniform porous structure, showing unfavorable diffusion performance. Although Si-based mesoporous materials, including SBA-15,[20,21] MCM-41,[22,23] and KIT-6,[24,25] own uniform meso-sized channels, the distribution of amine

groups on the surface of such silica materials cannot be precisely predicted and controlled. Therefore, the mechanisms of CO_2 adsorption on amine appended porous materials could be facilely investigated using metal-organic frameworks (MOFs) as the models.

MOFs are a class of crystalline materials and can be constructed by various metal ions/clusters and organic ligands with functional groups, showing high surface area, uniform porous structure, adjustable channel, and orderly distributed active sites.[26,27] On account of these advantages, a lot of MOFs have been designed for different applications, such as gas storage and separation,[28] catalysis,[29,30] chemical sensor,[31] and biomedicine.[32] Because of observable structures of MOFs, most physical processes and chemical reactions occurred on MOFs could be accessed by characterization methods including spectrum technology, X-ray crystallography, microscopic imaging technology, and molecular dynamic simulations. MOF materials have been specially developed and employed in CO_2 capture (Figure 1).[33-40] Some of them exhibited high capacity at relatively lower CO_2 partial pressure and lower adsorptive heat when compared with conventional porous materials such as molecule sieves and amine grafted porous silica.[41,42] Although some studies about CO_2 capture by MOFs have been well summarized and reviewed,[12,43-46] discussing trace CO_2 capture of MOFs has not been well reported so far. Generally, the materials designed or selected for trace CO_2 capture could be classified into two groups. One is microporous MOFs with special geometric porous structures to achieve trace CO_2 capture. The other one is amine grafted MOFs having enhanced capability of CO_2 capture by anchoring the amine group on the skeleton of MOFs. Both strategies have been proven promising for trace CO_2 capture. In addition, some new mechanisms for trace CO_2 adsorption on MOFs have been proposed to enrich the adsorption knowledge. Therefore, it is necessary to systemically summarize recent exciting experiment results and conclusions combined with comprehensive discussions from the materials design to the adsorption mechanism. In this review, we mainly discuss the strategies proposed for trace CO_2 capture, as well as intrinsic relationship between MOF structures, functional groups, and performance on CO_2 capture, aiming at not only providing a summary of recent achievements in trace CO_2 capture *via* MOF materials and but also inspiring new ideas to further address the challenge of trace CO_2 capture.

Strategies for trace CO_2 capture

For trace CO_2 capture directly from air or confined space, low CO_2 partial pressure should be considered as the main factor strongly related to the gas diffusion and uptake corresponding to the adsorption kinetics and thermodynamics. From statistical thermodynamics, once CO_2 molecule is adsorbed on adsorbents, the entropy of CO_2 is reduced, because that partial freedom (such as molecular rotation) of adsorbed CO_2 is restricted when compared with free molecule. In order to proceed the adsorption, the enthalpy should be less than zero to ensure the Gibbs free energy of whole adsorption process is less than zero. Obviously, lower Gibbs free energy is beneficial to the CO_2 adsorption especially in the case of low CO_2 partial pressure. Generally, the enthalpy value of physical adsorption is not high enough for adequate CO_2 adsorption under low CO_2 partial pressure. The CO_2 uptake based on physical adsorption is linearly related with pressure at a considerably low pressure by following the Henry laws, resulting in an inadequate CO_2 adsorption on the adsorbents and low capture efficiency. Therefore, enhancing CO_2 binding energy on adsorbents *via* employing functional groups or building special pore structures with well distributed active sites on adsorbents should be explored. Three strategies have been proposed to enhance CO_2 binding energy on MOFs, including the developments of MOFs with open metal sites, ultra mircoporous MOFs, and amine functionalized MOFs.

Mechanism of CO_2 capture by MOFs

MOFs with open metal sites

CO_2 is a nonpolar linear molecule in which carbon atom adopts *sp* hybridization combined with oxygen atoms. Electrons from *p* orbital of C and O atoms form strong $\pi_{3\text{-}4}$ dislocated bonds. The remained electrons from *p* orbital of O atoms contribute to anti-bond orbital of CO_2 molecule. Here, O atoms present electronegativity and C atom shows electropositivity. Therefore, functional groups with special adsorptive sites that can accept electrons or donate electrons would have strong affinity to CO_2. MOFs constructed by organic ligands and metal ions through coordinative bonds could exhibit large surface area and high porosity. Some of them owning unsaturated coordinative metal sites that can accept electrons transferred from CO_2 were employed for CO_2 capture. However, most of them did not perform outstanding capacity under low CO_2 partial pressure (400 ppm) in comparison with some conventional adsorbents.

Cu-BTC (HKUST-1)[47] constructed by dinuclear paddlewheel copper(II) cluster and 1,3,5-tri(1H-1,2,3-triazol-4-yl)benzene showed CO_2 capture capacity only about 0.05 mmol/g at 400 Pa, although this MOF has unsaturated coordinative copper metals. The calculated isosteric heat of CO_2 on HKUST-1 is about 25 kJ/mol, revealing the main reason for such a low CO_2 capture capacity under low CO_2 partial pressure. The similar results were also found from MIL-101-Cr,[48] MIL-53(Al),[49] and MIL-100(Al).[50] The Mg-MOF-74 constructed by 2,5-dihydroxyterephthalic acid and MgO cluster with BET surface area about 1600 m^2/g exhibited a high CO_2 adsorption capacity of 0.38 g/g when CO_2 pressure was 1 atm, which is one of the best capacities reported in the MOF family. However, adsorptive isothermal curve results showed that the CO_2 capture capacity of Mg-MOF-74 was just similar to other physisorbents such as zeolite 13X under air conditions. The isosteric heat (47 kJ/mol) of CO_2 on Mg-MOF-74 indicated that the interaction between open metal site Mg and CO_2 molecule is not high enough for CO_2 capture under a low CO_2 partial pressure (400 ppm).[51] To enhance the CO_2 capture capacity by MOFs with open metal sites, the screening of metal species and coordinative environment is needed. The metal ions with strong basic property such as Mg, Ca, Li, Mn, Zn, and Cu are promising for building MOFs toward trace CO_2 capture. As for MOFs without unsaturated metal sites, they are generally inadequate to achieve trace CO_2 capture due to lack of strong adsorptive sites for CO_2. It is worth noting that Cu-BTC and Mg-MOF-74 could easily degrade in the presence of moisture and humidity, making their practical implementation difficult.

MOFs with ultra mircoporous structures

Some of MOFs such as SIFSiX-n-M own ultra micropores, of which the pore size can be accurately adjusted by exchanging organic ligands and metal ions in the framework. As shown in Figure 2a,b, SiFSiX-3-M was

constructed by $MSiF_6$ (M = Cu, Ni, and Zn) inorganic species and pyrazine ligand.[41] SIFSIX-3-Cu presents CO_2 capture capacity of 1.24 mmol/g at 400 ppm and 298 K resulted from its tailored one dimension channel and uniform distribution of adsorptive sites (Figure 2c). The isosteric heat of SIFSIX-3-Cu reaches about 54 kJ/mol (Figure 2d) with steep adsorption isotherm at relatively low pressure, which is much higher than that of Mg-MOF-74. When using the NbOF cluster, the obtained NbOFFIVE-1-Ni shows higher CO_2 capture capacity of 1.3 mmol/g than SiFSIX-3-Cu, in which CO_2 molecules could form a one dimension chain under strong binding interactions between electronegative F^- ion and electropositive carbon atom of CO_2.[52]

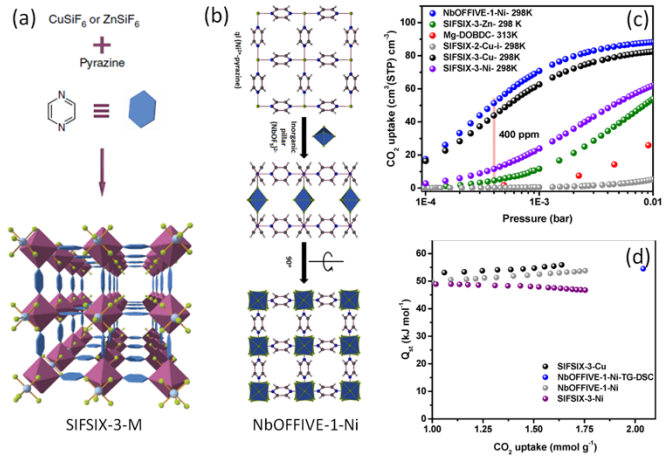

Figure 2. Porous structures of (a) SIFSIX-3-M and (b) NbOFFIVE-1-Ni. (c) CO_2 sorption isotherm curves at 298 K and (d) isosteric heat of CO_2 based on these MOFs. Reproduced with permission from ref 41,52. Copyright 2015 Macmillan Publishers Ltd and 2016 American Chemical Society.

Evidently, high capture capacities of CO_2 on the MOFs could be assigned to the small channel size (0.32 nm), which is even smaller than the kinetic diameter of CO_2 molecule (0.33 nm). Therefore, CO_2 molecule located in the channel has its special configuration (Figure 3), resulted from slow gas diffusion. When these kinds of microporous MOFs are applied in air conditioning, water molecule prefers to occupy the channel and it is hard to disperse, arising a regeneration issue. Further work on how to tune the pore properties to prevent water competition and diffusion should be considered. In addition, developing novel MOFs with higher capture capacity than NbOFFIVE-1-Ni by keeping the key structural features would be promising.

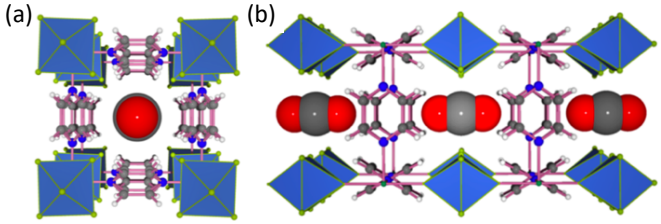

Figure 3. Configuration of CO_2 molecule located inside NbOFFIVE-1-Ni channel along (a) [001] and (b) [010]. Reproduced with permission from ref 52. Copyright 2016 American Chemical Society.

Amine functionalized MOFs

MOFs with functional groups that can donate electrons are considered an alternative approach to enhance CO_2 capture capacity. High CO_2 capture capacities of aforementioned SiFSIX-3-Cu and NiOFFive-1-Ni are attributed not only to the microchannels, but also to the proper distribution of F^- ions. Electrons on F^- ions having strong affinity to positive C atom of CO_2 lead to the enhancement of the adsorptive interaction. Nitrogen as another type of electronegative atom is usually employed to construct active sites for CO_2 capture. N atom in amine group owning one pair electrons in its outer orbital can present basic property. Initial inspiration of using amine to modify MOFs was derived from integrating amine on mesoporous silica materials.

There are two strategies for tethering amine unit on MOFs. One is to anchor amine on the open metal sites *via* strong binding interaction between positive N atom and open metal cation with unoccupied orbital. The other way is to link amine group on organic ligands. To achieve amine introduction on MOFs, one of the most important requirements is the stability of MOFs. Only a few types of MOFs can bear the corrosion of amine. An amine modified MOF for CO_2 capture was reported.[53,54] In this case, ethylenediamine (en) was incorporated into Cu-BTTri (H_3BTTri = 1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene). At low pressure, the obtained Cu-BTTri-en adsorbs a great amount of CO_2 (1.6 wt %, 0.366 mmol/g) due to strong interaction between CO_2 and basic amine unit at low pressure, which is much higher than that of original Cu-BTTri (0.92 wt %, 0.277 mmol/g). Although the CO_2 uptake of Cu-BTTri-en is lower than that of Mg-MOF-74 or other microporous MOFs, the obvious increase of CO_2 uptake resulted from amine incorporation proves the feasibility of this strategy. The incorporation of N,N'-dimethylethylenediamine (mmen) into Cu-BTTri drastically improves the CO_2 adsorption amount, too. At 25 ^oC under a mixture of 0.15 bar CO_2/0.75 bar N_2, the obtained Cu-BTTri-mmen adsorbs CO_2 of 2.38 mmol/g (9.5 wt%) with a CO_2/N_2 selectivity of 327 estimated by the ideal adsorbed solution theory (IAST). The isosteric heat of CO_2 adsorption on Cu-BTTri-mmen was calculated to be 96 kJ/mol at zero coverage, indicating the existence of strong interaction between CO_2 and amine incorporated in Cu-BTTri. On the other hand, the enhancement of CO_2 capture capacity only attributed to the interaction between N of diamine and CO_2 (Figure 4a) is incomplete. The configuration of CO_2 molecule upon the adsorption on amine grafted Cu-BTTri and the effect of proton H on secondary amine would need further investigation.

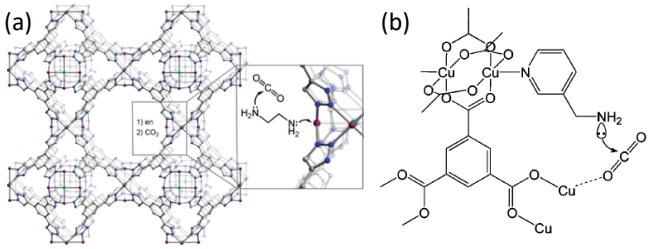

Figure 4. Schematic adsorption mechanism of CO_2 on (a) Cu-BTTri-en and (b) Cu-BTC-3-pio. Reproduced with permission from ref 53,55. Copyright 2009 American Chemical Society and 2012 Royal Society of Chemistry.

Shortly after, the effect of amine stereochemistry on CO_2 capture based on Cu-BTC was investigated by Navarro *et al*.[55] Ethylenediamine, 3-picolylamine and 4-picolylamine were tethered on Cu-BTC to reveal the stereochemistry effect on CO_2 adsorption. According to CO_2 sorption isotherm curves, it was obviously found that Cu-BTC modified with 3-pio

(Cu-BTC-3-pio) performed the best on the CO_2 capture. The reason could be attributed to the cooperative effect between basic amine and CO_2 molecule. In the pore of Cu-BTC-3-pio, the N atom from amine binds with the C atom of CO_2 *via* strong Coulomb force, and the O atoms of CO_2 would bind with unsaturated copper site (Figure 4b). Therefore, Cu-BTC-3-pio exhibits higher isosteric heat than that of bare Cu-BTC and Cu-BTC-4-pio. Apparently, the CO_2 uptake of amine grafted Cu-BTC is not high enough due to the small pore size especially after incorporating the amine unit. The small pore was filled by amine unit, leading to an obvious decrease of CO_2 uptake in comparison with bare Cu-BTC at relatively high CO_2 partial pressure. Hence, some mesoporous MOFs were employed for the amine modification.

MIL-100(Cr) consists of two types of meso cages built by chromium(III) carboxylate octahedra through sharing a common oxygen atom and linking together by trimesate rigid ligands. When MIL-100(Cr) was grafted with en and mmen *via* binding with open metal site Cr(III), the expected enhancement of CO_2 capture capacity was observed in comparison with bare MIL-100(Cr).[56] The isosteric heat of CO_2 adsorption of MIL-100(Cr)-en is about 80 kJ/mol near zero coverage, which is about 3 times higher than that of bare MIL-100(Cr). Such a high binding energy for CO_2 in amine-functionalized MIL-100 is attributed to the chemisorption mechanism. On the other hand, the estimated binding energy of direct interaction between the N atom of amine and CO_2 cannot reach such high value. The chemisorption mechanism should be further investigated.

Other amines were also used to enhance CO_2 capture capacity on MIL-101(Cr). The MIL-101(Cr)-TREN (TREN = tris(2-aminoethyl)amine)[57] presented good CO_2 capture capacity because of its high TREN loading. However, an obvious amine loss was found during the multicycle temperature swing adsorption tests. For comparison, MIL-101(Cr)-PEI-800 (PEI-800 = poly(ethylene imine)) showed better cycling capability. The amine efficiency (mol CO_2/mol amine) as a function of the amine loading was employed as the measure to investigate these adsorbent materials. The amine efficiency of MIL-101(Cr)-PEI-800 exhibited high dependence on the loading of amine. A sharp increase of amine efficiency occurred at a mole ratio of 0.8 mmol PEI/g MOF. When the mole ratio of PEI/MOF is less than 0.8, the amine efficiency is much lower. In this case, the amine molecules were uniformly distributed in MIL-101(Cr) cage. The distance between two NH_2 groups is too long to achieve cooperative interaction on CO_2. Most of NH_2 groups do not participate in the CO_2 chemisorption, leading to low amine efficiency. When the PEI/MOF mole ratio is higher than 0.8, the NH_2 groups can approach to each other. The proton H of NH_2 groups could transfer from one NH_2 to another to form R-NH^{3+} that binds strongly with CO_2 *via* Coulomb force. Because PEI-800 amine is a kind of flexible polyamine, the CO_2 configuration upon the adsorption is hard to predict. The chemisorption mechanism is similar to the case grafting on porous silica materials. Hence, achieving regular structures of amine functionalized MOFs is necessary for the investigation of CO_2 adsorptive mechanism.

In comparison with MIL-101 and Cu-BTC, investigations were more focused on MOF-74 series materials because of their simple structures. In MOF-74, the open metal site can accept electrons from one of N atoms in diamine to form a stable complex. The other N atom in diamine can be used for interacting with CO_2. Ethylenediamine (ED) was employed as a grafting amine to functionalize Mg_2(dobdc), where each open coordination site in the unit cell of Mg_2(dobdc) could bind up to 1 ED molecule.[34] After the functionalization, the surface area decreased from 1094 to 469 m^2/g. However, Mg_2(dobdc)-ED showed relatively high CO_2 capture capacity of 1.51 mmol/g when simulated CO_2 concentration was 400 ppm, much higher than that of bare Mg-MOF-74.

Similarly, MOF-74 having the channel with the pore size of 8.4 Å was functionalized with mmen to afford Mg_2(dobpdc)-mmen (H_4dobpdc = 4,4'-dihydroxy-(1,1'-biphenyl)-3,3'-dicarboxylic acid), reported by Chong and co-workers.[58] Mg_2(dobpdc)-mmen showed an excellent CO_2 adsorption capacity at low pressures, *i.e.*, 2.0 mmol/g (8.1 wt %) at 0.39 mbar and 25 °C (the condition for the removal of CO_2 from air), and 3.14 mmol/g (12.1 wt %) at 0.15 bar and 40 °C (the condition for the CO_2 capture from post-combustion flue gas). In comparison with previous reports, this work provided abundant thermodynamic experimental results, and the enhancement of CO_2 capture capacity at low pressures was still ascribed to the interaction between the electron pair from N atom of diamine and electropositive C atom of CO_2. The calculated isosteric heats quickly reached and maintained at a value of −71 kJ/mol, likely corresponding to the chemisorption of CO_2 onto the free amine of mmen.

Tetraethylenepentamine (TEPA) was also tethered on Mg_2(dobdc) for CO_2 capture from flue gas.[59] The obtained Mg(dobdc)-TEPA adsorbs more CO_2 (6.06 mmol/g) at 60 °C than that (2.67 mmol/g) of parent Mg(dobdc) when CO_2 concentration is vol. 15%. More interestingly, the moisture was found to promote the CO_2 adsorption performance of the adsorbent. The CO_2 adsorptive capacity can reach as high as 8.31 mmol/g in moisture condition. The increase of the CO_2 adsorption capacity with moist gas mixture could be assigned to the formation of the bicarbonate unit. When moisture is added to the flue gas, carbamic acid would react with H_2O and CO_2 to form the bicarbonate unit as shown in the following reaction (1). The amine group itself could also directly react with H_2O and CO_2 to form the bicarbonate species shown in reactions (2) and (3).[8]

$$CO_2 + R_2NCOO^- + 2H_2O \Longleftrightarrow R_2NH_2^+ + 2HCO_3^- \quad (1)$$

$$CO_2 + RNH_2 + H_2O \Longleftrightarrow RNH_3^+ + HCO_3^- \quad (2)$$

$$CO_2 + R_2NH + H_2O \Longleftrightarrow R_2NH_2^+ + HCO_3^- \quad (3)$$

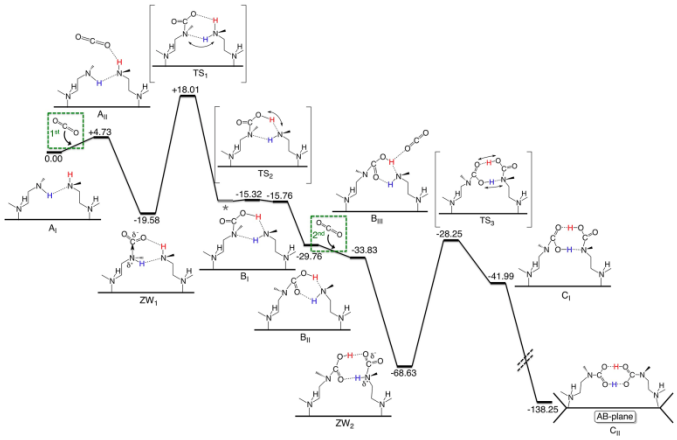

Figure 5. Plausible pathway of stepwise CO_2 adsorption on Mg_2(dobdc)-mmen. Reproduced with permission from ref 60. Copyright 2013 American Chemical Society.

Actually, CO_2 adsorption mechanism on amine grafted MOFs is not as simple as it looks like. The enhancement of CO_2 capture capacity is not solely attributed to the interaction between negative N atom in amine and positive carbon atom in CO_2. In 2013, Long *et al.* proposed one plausible mechanism for the CO_2 adsorption on mmen grafted Mg_2(dobdc) (Mg_2(dobdc)-mmen) *via* density functional theory (DFT) studies.[60] The pathway shown in Figure 5 proposed that the CO_2 adsorption process on Mg_2(dobdc)-mmen is accompanied with a series of N−C bond formation steps, including the N-H bond cleavage and the formation of hydrogen-bonded adducts. These hydrogen bonds play an important role in avoiding the formation of some side intermediates and products. As illustrated in Figure 5, the initial lowest-energy state (A_I) contains two amines bound on neighboring Mg^{2+} cation. One proton H on amine can form hydrogen bond with the N atom of the neighboring amine group. When CO_2 molecule is approaching, one O atom of CO_2 would interact with H atom of amine to form weak initial N-H hydrogen bond. After rotating the amine group and CO_2 molecule, the H-N hydrogen bond is completely broken and substituted by N-C bond formed *via* negative N atom on amine and electropositive C atom of CO_2. In this state, the N atom of amine binds with one C atom, which is facile to donate its proton H to the neighboring N atom of amine to form carbamic unit. Meanwhile, the other N atom of amine accepts this proton H to form R-NH_3^+. Under the Coulomb force, R-NH_3^+ would approach N-CO_2^+ to form new N-H and O-H hydrogen bonds with a low energy state (B_I). The addition of second CO_2 molecule forming a hydrogen bond with the carbamic acid−amine adduct (B_{II} to B_{III} in Figure 5) readily yields second zwitterionic species, again stabilized by dual hydrogen bonds. Subsequent proton exchange followed by the product reorganization gives the formation of bis(carbamic acid), stabilized by two hydrogen bonds in the final structure. Based on the proposed mechanism, the adsorption energy of −138.25 kJ per 2 moles of CO_2 corresponding to an average adsorption energy of −69.13 kJ/mol is in good agreement with the experimental Q_{st} value of −71 kJ/mol.

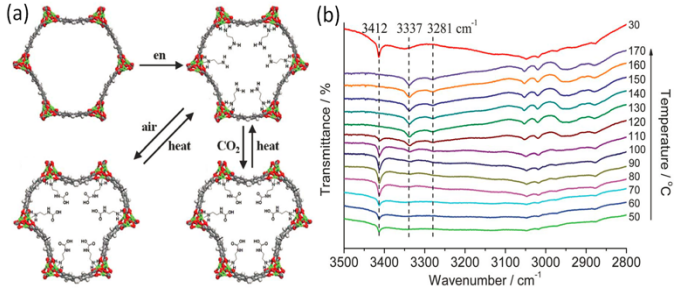

Figure 6. (a) CO_2 adsorption mechanism on Mg_2(dobpdc)-en and (b) *in situ* FTIR spectra of Mg_2(dobpdc)-en in the presence of CO_2 with variable temperatures. Reproduced with permission from ref 61. Copyright 2014 Royal Society of Chemistry.

In the same year, Hong *et al.*[61] proposed another plausible mechanism based on the CO_2 adsorption on Mg_2(dobpdc)-en. Mg_2(dobpdc) has wider channel than Mg-MOF-74. The enlarged distance between neighboring open Mg cations results in thoroughly different CO_2 adsorption mechanism. The specific interaction between the partial positive carbon of CO_2 and the amine group of en allows for the generation of either carbomate or carbamic acid species (Figure 6). In the case of the carbamate formation, two primary amine groups work together to generate an ionic pair of R–$NHCO_2^-$ and R–NH_3^+, and then afford a half capacity of CO_2 relative to the number of free amines. On the other hand, the formation of carbamic acid requires an equivalent number of CO_2 and amine groups to give R–NHCOOH species. Because of the long distance of two neighboring amine groups, the formed neighboring carbamic groups do not have interactions with each other, similar to that on Mg_2(dobdc)-mmen. The calculated enthalpy (Q_{st}) slowly increases and then remains constant in the range of 49–51 kJ/mol, which is consistent with the formation enthalpy of carbamic acid obtained by DFT calculations. Furthermore, the studies on the FTIR spectra clearly support that the carbamic acid group is formed upon the CO_2 adsorption. With the temperature increase, the characteristic O–H peak at 3412 cm^{-1} disappears, while the N–H stretching at 3337 and 3281 cm^{-1} start to emerge, indicating that the CO_2 desorption of Mg_2(dobpdc)-en occurs.

In 2014, Long[42] and Hong[62] *et al.* almost simultaneously proposed a new mechanism of cooperative insertion of CO_2 on mmen grafted Mg_2(dobpdc) and Mg_2(dobpdc)-dmen (dmen = N,N-dimethylethylenediamine) based on a series of experiments, respectively. The amine was assumed to be grafted to the open metal center with only its terminal available to capture CO_2. After the addition of CO_2 in Mg_2(dobpdc)-mmen, CO_2 first attacks N atom of amine. After transferring one proton H of amine to the neighboring amine N atom, carbamic species forms. In this model, CO_2 coordinates to the metal-bound nitrogen, and has favorable interactions with the neighboring amine. Comparing with the N atom of amine binding with Mg cation, the O atom of formed carbamic unit prefers to bind with Mg based on the DFT calculation. Upon simultaneous cleavage of the Mg-N bond and formation of the Mg-O bond, a highly ordered chain formed is referred to as the chain model (Figure 7).

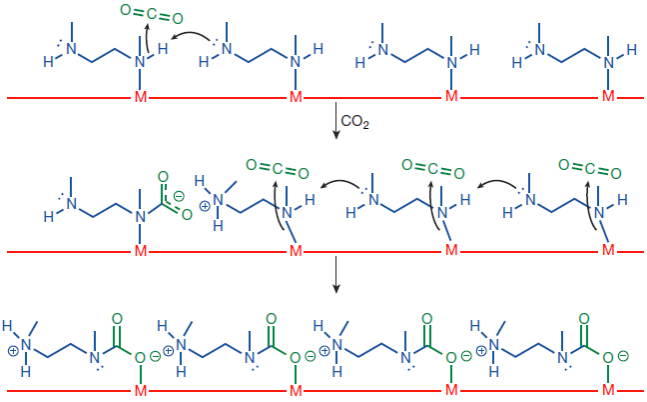

Figure 7. Mechanism of CO_2 adsorption on Mg_2(dopbdc)-mmen. Reproduced with permission from ref 42. Copyright 2015 Macmillan Publishers Ltd.

The observation on the conversion of Mg-N bond by Mg-O bond in this process is the key evidence to support the hypothesis. In order to verify the mechanism, a series of isostructural compounds, *i.e.*, M_2(dobpdc)-mmen (M = Co, Ni, Mg, Mn, Fe, and Zn) were prepared, and their CO_2 adsorption isotherms were measured.[42] Apparently, all of the MOFs showed sharp isothermal steps that shifted to higher pressure with the increase of temperature. Based on thermodynamic theory analysis, the sharp increase of isotherm curves should correspond to some phase changes. FTIR data showed a broad

peak centered at 2200 cm^{-1}, assigning to a combination band from the ammonium cation, and multiple peaks in the range of 1700–1630 cm^{-1}, corresponding to the C-O stretching of the amide group and asymmetric deformation of the ammonium cation. These peaks simultaneously disappeared and the N–H stretching peak at 3397 cm^{-1} vanished, suggesting the formation of the carbamate species during the CO_2 adsorption. Upon the exposure of Mg_2(dobpdc)-mmen to CO_2, ^{15}N chemical shifts of solid state NMR spectrum observed at 31 and 72 ppm were for ammonium and carbamate species, respectively. Only a single ^{15}N resonance was observed for Mg_2(dobpdc)-mmen in the absence of CO_2. These observations indicate that the coordinated and uncoordinated ends of the mmen molecule were capable of interconversion. From the X-ray absorption near edge structure (NEXAFS) spectra, the new pre-edge peak at 402.3 eV solely from the carbamate nitrogen was clear indication of the carbamate insertion into the metal–nitrogen bond.

Hong and co-workers performed the time-dependent *in situ* FTIR spectroscopy to test the CO_2 capability under humid conditions upon simultaneous exposure to 100% relative humidity (RH) simulated flue gas (15% CO_2). Remarkably, the band (3397 cm^{-1}) of N–H stretching appears under humid CO_2 flowing conditions. After purging with pure N_2 for 1 min, the characteristic peak of 3397 cm^{-1} still survives, while the free CO_2 peak at 2355 cm^{-1} disappears. This observation indicates that CO_2 is preferably adsorbed onto the grafted amine group even under humid conditions. More interestingly, the CO_2 capture capacity in humid CO_2 is greater than that in dry CO_2. Generally, the water occupancy may reduce the CO_2 capture capacity in the pores because of the competition adsorption. Long *et al.*[63] studied multicomponent (CO_2, N_2, and H_2O) adsorption on 15 materials including MOFs, zeolites, silica materials, and activated carbon. The interesting results observed on amine-appended materials indicate that the CO_2 uptake measured from a mixture gas exceeds that from pure CO_2. In contrast, for the materials without amine unit, water competition led to a dramatic decrease of CO_2 uptake. The reason is attributed to that CO_2 and H_2O do not compete for the same binding site. We proposed another reasonable mechanism for the CO_2 adsorption on amine grafted MOFs in humid conditions. In the presence of amine group in MOFs, it can be deduced that water molecule would react with amine by transferring one H proton from O of water to N of amine to form HO-NH_2-R hydrogen bond. Upon the CO_2 adsorption, the electrons of O atom from HO-NH_2-R would attack positive C atom of CO_2 to form HCO_3^- species that is stabilized by nearby R-NH_2^+ *via* strong Coulomb force. This is just one of hypotheses when the CO_2 adsorption on amine grafted Mg_2(dobpdc) occurs in the presence of water. More studies should be conducted to fully understand the mechanism.

To achieve cooperative insertion of CO_2, a homogeneous surface with appropriately positioned adsorption sites within the pores of MOFs is necessary. Only a very limited number of MOF materials could be used to mimic the adsorption behavior. In contrast to the pore expanded derivatives of M_2(dobdc), the amine functionalization of Mg_2(dobdc) did not lead to stepped adsorption isotherms. Based on the investigation of nine diamine-appended Mg_2(dobpdc), it was found that slight modifications to the diamine structure could change the threshold pressure for cooperative CO_2 adsorption resulted from reversible insertion of CO_2 into metal-amine bonds.[64] The proposed mechanism is that, (1) steric hindrance on the metal-bound amine results in the reduction of step pressures by destabilizing the diamine-bound phase, (2) by adding substituents on the terminal amine, the step pressure increases on account of weaker ion-pairing interactions within ammonium carbamate chain formed upon the CO_2 insertion, and (3) specific ion-pairing and hydrogen-bonding interactions stabilize the CO_2-inserted phase and consequently decrease the step pressure for cooperative CO_2 adsorption.

Facile functionalization with various groups on MOFs is one of important merits. Stable MOFs with amine group tethered on organic ligands have attracted much attention, which include MOF-46 constructed by 1,4-benzenedicarboxylate (NH_2BDC) linker and Zn ion,[46] IR-MOF-3 constructed by Zn_4O secondary building unit and NH_2BDC rod,[65] UiO-66-NH_2,[66,67] MIL-100-NH_2,[56] MIL-101-NH_2,[68] and MIL-53-NH_3.[69] To achieve amine grafted MOFs, another strategy was to construct MOFs with amine group on organic ligands.[40,56,68-71] By using the click reaction, (3,24)-connected rht-MOF (NTU-105-NH_2) constructed by dendritic amine-functionalized hexacarboxylate ligand containing triazole unit was synthesized. NTU-105-NH_2 exhibited the CO_2 capture capacity of 167 $cm^3\ g^{-1}$ (32.8 wt %) at 1 atm, which is comparable to NUT-105 without the NH_2 group on the ligand. Considering lower surface area in comparison with NTU-105, the similar CO_2 uptake should be attributed to the NH_2 group on the ligand.[33]

The basic property of the NH_2 group on aromatic fragment is not as obvious as it on alkane, due to the dispersion of N electrons on aromatic fragment by the conjugation effect. Thus, the amine modification on organic ligands of MOFs did not show significant improvement when comparing with amine grafting on open metal sites. On the other hand, the NH_2 binding with ligands is more stable than its binding with metal. NH_2-MIL-53(Al) presented an excellent adsorption capacity for CO_2.[69] The CO_2 capture capacity is up to 33.86 $cm^3\ g^{-1}$ at 25 ^oC at low pressures, suggesting the chemisorption between CO_2 and amine groups. Under humid conditions, however, the CO_2 uptake drops off obviously due to the competition adsorption of water. The NH_2 conjugation in organic ligands has a strong effect on water adsorption, resulting in dramatic decrease of CO_2 capture capacity under humid conditions. When RH reaches 30%, the CO_2 uptake almost reduces to 0.5 wt %. Hence, how to avoid the water adsorption on these kinds of MOFs is still a challenge for further investigations.

Zhou *et al*. developed a new method based on Brønsted acid–base reaction to tether tris(2-aminoethyl)amine (TAEA) onto Cr-MIL-101-SO_3H for the CO_2 capture.[72] Cr-MIL-101-SO_3H-TAEA presents cyclic CO_2 uptake of 2.28 mmol g^{-1} at 150 mbar and 40 ^oC, and 1.12 mmol g^{-1} at 0.4 mbar and 20 ºC. There is no doubt that the adsorbent has high CO_2 capture capacity on account of the incorporated amine. However, no direct evidence supports that amine binds with the HSO_3 group rather than open metal Cr.

The ligand of IRMOF-74-III was covalently functionalized by two primary alkylamine units, leading to a material capable of adsorbing CO_2 at low pressures under the chemisorption mechanism.[73] The covalent bond being formed upon the CO_2 chemisorption was evaluated by solid state ^{13}C and ^{15}N NMR spectra. The results reveal the formation of carbamic species upon the CO_2 adsorption (Figure 8). When CO_2 is loaded into dry adsorbent, H atoms from the NH_2 group transfer to the O atom of CO_2 to from H-O-C-O species,

and CO_2 molecule bends to make the C atom of CO_2 closer to the N atom of the NH_2 group. Under the water vapor, the species observed here is ammonium carbamate. Corresponding shift of ^{15}N NMR spectra from carbamic acid to ammonium carbamate occurs as a function of the amount of water vapor added.

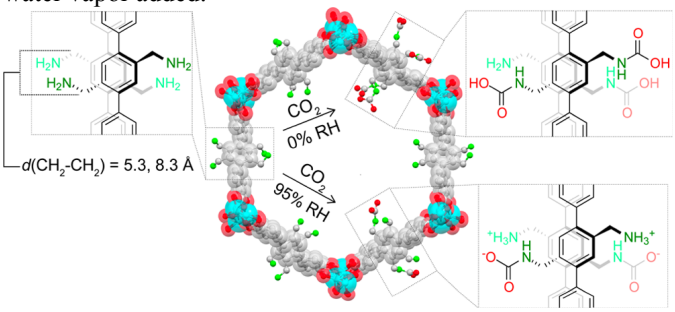

Figure 8. Structure of IRMOF-74-III-$(CH_2NH_2)_2$ viewed from c-axis, showing three possible pore environments before and after CO_2 adsorption under dry or humid conditions (RH 95%). H atoms are omitted. Color: carbon, gray; oxygen, red; nitrogen, green; and Mg, blue. Reproduced with permission from ref 73. Copyright 2017 American Chemistry Society.

Application of functionalized MOFs for trace CO_2 capture

Grafting amine to the pores of MOFs could enhance the affinity for CO_2, and the obtained materials could be applied in various CO_2 separation systems[36,37,39,67,74,75] including the pressure swing adsorption (PSA), temperature swing adsorption (TSA),[76] and membrane separation technologies.[77] As for PSA and TSA, important parameters including the working capacity, selectivity and regeneration cost can be obtained from dynamic experiments (breakthrough experiments) or calculated from single component thermodynamic experiments to assess the performance of adsorbents. It was noted that the selectivity obtained from the breakthrough experiments and calculated from single component isotherms would be significantly different. The breakthrough experiments are carried out under the conditions similar to real industrial process, hence the selectivity and capacity obtained have meaningful reference value. The selectivity can also be calculated based on the isotherm curve to predict the value under various ranges of conditions. In literature, the IAST is the most accurate method to predict the adsorption selectivity from gas mixture based on single component adsorption isotherms, because the competition adsorption of gas mixture is considered. The working capacity is another factor to assess the performance of adsorbents. High working capacity brings advantages of low usage amount of adsorbents, low occupancy, and long serving time. The working capacity can be estimated from isotherm curves or directly obtained from breakthrough experiments and thermogravimetric analysis.

The regeneration is also an important factor of adsorbents employed in PSA and TSA. The isosteric heat (Q_{st}) of gas on adsorbents can serve as criteria to assess the regeneration. Generally, the isosteric heat can be calculated based on single component isotherm curves at different temperatures according to the Clapeyron equation. The Q_{st} at each adsorption point is calculated based on the slope of the plot ln$P$ as a function of (1/T).

$$LnP = -\frac{Q}{RT} + C \quad (4)$$

in which, P is pressure corresponding to the same CO_2 uptake under different temperatures, R is universal gas constant, T is temperature, and C is a constant. The isosteric heat of adsorption could also be assessed by fitting the temperature-dependent isotherms to a virial-type expression:

$$LnP = LnN\frac{1}{T}\hat{A}_{i=0}^{m} a_i N^i + \hat{A}_{i=0}^{n} b_i N^i \quad (5)$$

where a_i and b_i are virial coefficients, as well as m and n are the numbers of virial coefficients required for adequate fitting of the isotherms. Then, the isosteric heat of adsorption can be calculated using the following expression:

$$Q_{st} = \hat{A}_{i=0}^{m} a_i N^i \quad (6)$$

The isosteric heat of adsorption using virial-type expression can give a Q_{st} value at zero coverage.

Table 1. Selected MOFs with high capacity for trace CO_2 capture.

MOFs	BET surface area (m^2/g)	T (^{o}C)	CO_2 (ppm)	Capacity (mmol/g)	Q_{st} (kJ/mol)	Selectivity	Ref
SIFSIX-3-Cu	-	25	400	1.24	54	10500(CO_2/N_2)	41
SIFSIX-3-Zn	250	25	400	0.13	45	7259(CO_2/N_2)	41,77
SIFSIX-3-Ni	368	25	400	0.18	51	-	41,77
SIFSIX-2-Cu-i	503	25	400	0.068	32	-	41,78
HKUST	1,900	25	400	0.05	34	-	51
Mg-MOF-74	1,000	25	400	0.088	47	-	41,51
Mg-MOF-74-mmen	70	25	400	2.05	74	49000 (CO_2/N_2), 27000 (CO_2/O_2)	58
Mg-MOF-74-en	469	25	400	1.51	-	-	34
Mg_2(dobpdc)	1,253	25	390	0.13	44	-	58
Mg_2(dobpdc)-mmen	70	25	390	2	71	-	58
Mg_2(dobpdc)-mmen	-	25	400	3	74	-	42
Mg_2(dobpdc)-en	1,253	25	390	2.83	50	-	61
Mg_2(dobpdc)-dmen	675	40	100,000	2.6	75	554 (CO_2/N_2)	62
Mg_2(dobdc)-TEPA	132	25	150,000	6.06	-	-	59

MIL-101(Cr)-TEPA	1,553	25	150,000	1.25	43	70 (CO_2/CO)	35
MIL-101(Cr)-TREN	-	25	400	0.35	-	-	57
MIL-101(Cr)-PEI-300	33.5	25	150,000	4.1	-	Over 1000 (CO_2/N_2)	79
MIL-100(Cr)-en	484	25	150,000	2.1	80	-	57
MIL-100 (Cr)-mmen	893	25	150,000	1.4	80	-	57
Cr-MIL-101-SO_3H-TETA	-	20	400	1.12	87	-	72
CuBTTri	1,700	25	150,000	0.27	24	10 (CO_2/N_2)	54
CuBTTri-pip	380	25	150,000	0.75	96	130 (CO_2/N_2)	37
CuBTTri-en	345	25	600,000	0.36	90	13 (CO_2/N_2)	53
CuBTTri-mmen	870	25	150,000	2.38	96	327 (CO_2/N_2)	54

Various N-rich MOFs and amine grafted MOFs have been reported in the separation of CO_2 from gas mixtures (Table 1). Most of amine grafted MOFs[36,67] exhibited obviously increased CO_2 capture capacity and selectivity when comparing with original unmodified MOFs. For example, TEPA was successfully grafted on the coordinative unsaturated Cr(III) sites of MIL-101 and the obtained materials were thermally stable at 50 °C.[35] The grafted MIL-101-TEPA prevents high CO adsorption amount without decreasing the CO_2 adsorption capacity at relatively low pressures, resulting in an outstanding CO_2/CO selectivity. By comparing bare MIL-101 and MIL-101-TEPA, the CO_2/CO selectivity based on IAST was obviously improved from 1.77 to 70.2 under total pressure of 40 kPa at 298 K. For the evaluation of the cyclic performance, the MIL-101-TEPA adsorbent was generated at 373 K under high vacuum for 1 h, and its CO_2 adsorption capacity was nearly constant after five cycles.

When using en grafted Cu-BTTri as the adsorbent for CO_2/N_2 separation,[51] due to selective effect of amine group to CO_2 and a reduction of N_2 uptake on Cu-BTTri-en, the CO_2/N_2 selectivity slightly improves from 10 to 13 at 0.1 bar and 21 to 25 at 1 bar. As for CuBTTri-mmen, a great improvement of selectivity based on IAST for a mixture of 0.15 bar CO_2 and 0.75 bar N_2 was calculated to be 327 at 25 °C. Utilizing a thermogravimetric analyzer, the mass of Cu-BTTri-mmen increased by nearly 7% upon the introduction of the gas mixture, due to strong adsorption of CO_2. After 72 cycles with purging by N_2 at 60 °C, the sample still kept high CO_2 capture capacity. In comparison with CuBTTri-en, CuBTTri-mmen showed outstanding CO_2 capture capacity and selectivity.

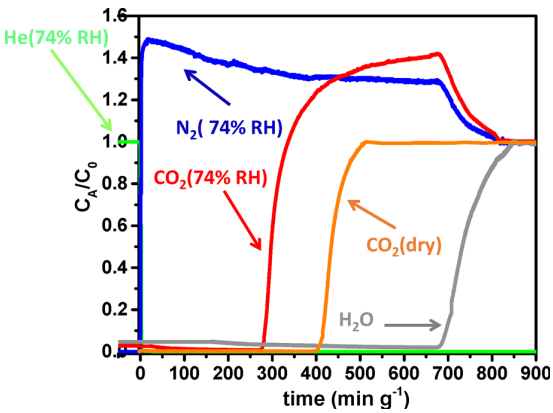

Figure 9. Breakthrough tests for NbOFFIVE-1-Ni carried out at 1 bar and 25 °C under both dry and humid conditions with the mixed gas of CO_2/N_2 (1%/99%). Reproduced with permission from ref 52. Copyright 2016 American Chemistry Society.

The performance of Mg_2(dobpdc)-mmen[58] and Mg_2(dobpdc)-en as regenerable adsorbents for CO_2 capture from air was estimated by utilizing thermogravimetric analysis (TGA). The CO_2 capture capacity of the former reaches about 4.6% in simulated air containing 390 ppm CO_2 and 21% O_2 balanced with N_2 flow at 25 °C, and about 9.9% in simulated flue gas containing 15% CO_2 balanced with N_2 flow at 40 °C for 50 cycles. The CO_2 capture capacity of the later could reach 10% in 20 cycles at 40 °C in simulated air containing 0.39 mbar CO_2. When Mg_2(dobpdc)-en was exposed in RH 100% simulated flue gas at 21 °C, a capacity loss of 5% was observed after 5 cycles, indicating a good stability of the adsorbent. In comparison with dry conditions, an enhancement of 7 min of CO_2 breakthrough time was observed in humid conditions.[59] Dynamic cycling experiments of gas adsorption/desorption demonstrate that Mg_2(dobdc)-mmen can be regenerated upon repeated exposures to simulated air and flue gas mixtures, where the cycling capacity still kept at 1.05 mmol/g (4.4 wt %) after continuously exposed to flowing 390 ppm CO_2 in air at 25 °C for 1h and 2.52 mmol/g (9.9 wt %) after 15 min of exposure to flowing 15% CO_2 in N_2 at 40 °C.

The breakthrough test for NbOFFIVE-1-Ni (Figure 9) showed a high CO_2 capture capacity of 8.2% in dry CO_2, while dropping off to 5.6% when the humidity was 74%.[52] The water capture capacity under the same conditions at about 13.8 indicates simultaneous adsorption of CO_2 and water. The reason that the water adsorption did not hinder CO_2 adsorption may be attributed to the formation of carbonate unit in the micropore of the MOF. Although some MOFs or amine functionalized MOFs exhibited good performance for trace CO_2 capture, more MOF examples are required to investigate robust structure-property relationship toward trace CO_2 capture.

Conclusion

CO_2 capture under low partial pressure and humid condition is very challenging. MOF based materials with advantages of high surface area, tunable channel and controllable surface chemical property are promising adsorbents for CO_2 capture. Research progress in trace CO_2 capture by MOFs has been reviewed and systematically summarized, including strategies for the materials development, mechanism investigation, and performance on trace CO_2 capture. Low CO_2 partial pressure brings a great difficulty for most of MOF adsorbents, especially under humid conditions with the competition of water sorption. In order to enhance the CO_2 capture capacity, the interaction strength between CO_2 and MOFs should be improved by introducing unsaturated metal centers, optimizing the geometry of pore structures, and

functionalizing electron donating or accepting groups such as amine.

To have open metal sites for enhancing CO_2 infinity, MOFs should have strong binding energy with CO_2 *via* the coordinative interaction between electrons of CO_2 and unoccupied orbital of metal sites. The metal cations with lower orbital energy are promising to build high intensity potential field for CO_2 trapping. Mircoporous MOFs with special geometric channels is another strategy for trace CO_2 capture. The key point for this strategy is how to design reasonable structures and how to synthesize the expected MOFs. Nevertheless, research for further improving CO_2 capture capacity and selectivity, especially under moist conditions, is still necessary. Although some amine functionalized MOFs have been reported for their outstanding performance of trace CO_2 capture, developing amine functionalized MOFs is still in its early stage. Exploring the mechanisms of CO_2 adsorption on these unique MOFs under practical conditions is also needed. A large amount of dynamic breakthrough test data should be collected to build the relationship among the materials structure, surface chemical property, and CO_2 capture efficacy. In addition, two important issues to be addressed when employing MOFs into practical applications of CO_2 capture are how to synthesize MOFs in large scale with reasonable cost and how to stabilize the capacity and structure of MOFs or functionalized MOFs toward water vapor, heat regeneration, and acid gases. In summary, although the route for trace CO_2 capture by MOFs is full of challenge, it is worthy of devoting our best research efforts to achieve the target.

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References

1. Boden, T. A.; Marland, G.; Andres, R. J. Global, Regional, and National Fossil-Fuel CO_2 Emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, 2017. DOI 10.3334/CDIAC/00001_V2017.
2. Nield, D. CO_2 Levels Have Reached a Scary New Milestone, But You're Gonna Ignore It Anyway, Aren't You? *ScienceAlert* 2018.
3. Hansen, J.; Ruedy, R.; Sato, M.; Lo, K. Global Surface Temperature Change. *Rev. Geophys.* **2010**, *48*, RG4004, DOI 10.1029/2010RG000345.
4. Yang, J.; Yu, X.; Yan, J.; Tu, S.-T., CO_2 Capture Using Amine Solution Mixed with Ionic Liquid. *Ind. Eng. Chem. Res.* **2014**, *53*, 2790-2799, DOI 10.1021/ie4040658.
5. Dutcher, B.; Fan, M.; Russell, A. G. Amine-Based CO_2 Capture Technology Development from the Beginning of 2013—A Review. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2137-2148, DOI 10.1021/am507465f.
6. Rochelle, G. T. Amine Scrubbing for CO_2 Capture. *Science* **2009**, *325*, 1652-1654, DOI 10.1126/science.1176731.
7. Ünveren, E. E.; Monkul, B. Ö.; Sarıoğlan, Ş.; Karademir, N.; Alper, E. Solid Amine Sorbents for CO_2 Capture by Chemical Adsorption: A Review. *Petroleum* **2017**, *3*, 37-50, DOI 10.1016/j.petlm.2016.11.001.
8. Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO_2 from Ambient Air. *Chem. Rev.* **2016**, *116*, 11840-11876, DOI 10.1021/acs.chemrev.6b00173.
9. Pera-Titus, M. Porous Inorganic Membranes for CO_2 Capture: Present and Prospects. *Chem. Rev.* **2014**, *114*, 1413-1492, DOI 10.1021/cr400237k.
10. Fu, Y.; Jiang, Y.-B.; Dunphy, D.; Xiong, H.; Coker, E.; Chou, S. S.; Zhang, H.; Vanegas, J. M.; Croissant, J. G.; Cecchi, J. L.; Rempe, S. B.; Brinker, C. J. Ultra-Thin Enzymatic Liquid Membrane for CO_2 Separation and Capture. *Nat. Commun.* **2018**, *9*, 990, DOI 10.1038/s41467-018-03285-x.
11. Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 724-781, DOI 10.1021/cr2003272.
12. Trickett, C. A.; Helal, A.; Al-Maythalony, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The Chemistry of Metal–Organic Frameworks for CO_2 Capture, Regeneration and Conversion. *Nat. Rev. Mater.* **2017**, *2*, 17045, DOI 10.1038/natrevmats.2017.45.
13. Lin, Y.; Kong, C.; Zhang, Q.; Chen, L. Metal-Organic Frameworks for Carbon Dioxide Capture and Methane Storage. *Adv. Energy Mater.* **2017**, *7*, 1601296, DOI 10.1002/aenm.201601296.
14. Negative Emissions Technologies and Reliable Sequestration: A Research Agenda. The National Academies Press: Washington D. C., 2018, DOI 10.17226/25259.
15. Direct Air Capture of CO_2 with Chemicals: A Technology Assessment for the APS Panel on Public Affairs. American Physical Society: College Park, Maryland, 2011.
16. Wilcox, J.; Psarras, P. C.; Liguori, S. Assessment of Reasonable Opportunities for Direct Air Capture. *Environ. Res. Lett.* **2017**, *12*, 065001, DOI 10.1088/1748-9326/aa6de5.
17. Keith, D. W.; Holmes, G.; St. Angelo, D.; Heidel, K. A Process for Capturing CO_2 from the Atmosphere. *Joule* **2018**, *2*, 1573-1594, DOI 10.1016/j.joule.2018.05.006.
18. Ebner, A. D.; Gray, M. L.; Chisholm, N. G.; Black, Q. T.; Mumford, D. D.; Nicholson, M. A.; Ritter, J. A. Suitability of a Solid Amine Sorbent for CO_2 Capture by Pressure Swing Adsorption. *Ind. Eng. Chem. Res.* **2011**, *50*, 5634-5641, DOI 10.1021/ie2000709.
19. Lee, S.; Filburn, T. P.; Gray, M.; Park, J.-W.; Song, H.-J. Screening Test of Solid Amine Sorbents for CO_2 Capture. *Ind. Eng. Chem. Res.* **2008**, *47*, 7419-7423, DOI 10.1021/ie8006984.
20. Ullah, R.; Atilhan, M.; Aparicio, S.; Canlier, A.; Yavuz, C. T. Insights of CO_2 Adsorption Performance of Amine Impregnated Mesoporous Silica (SBA-15) at Wide Range Pressure and Temperature Conditions. *Int. J. Greenh. Gas Con.* **2015**, *43*, 22-32, DOI 10.1016/j.ijggc.2015.09.013.
21. Sanz-Pérez, E. S.; Olivares-Marín, M.; Arencibia, A.; Sanz, R.; Calleja, G.; Maroto-Valer, M. M. CO_2 Adsorption Performance of Amino-Functionalized SBA-15 under Post-Combustion Conditions. *Int. J. Greenh. Gas Con.* **2013**, *17*, 366-375, DOI 10.1016/j.ijggc.2013.05.011.
22. Gholami, M.; Talaie, M. R.; Aghamiri, S. F. CO_2 Adsorption on Amine Functionalized MCM-41: Effect of Bi-Modal Porous Structure. *J. Taiwan Inst. Chem. Eng.* **2016**, *59*, 205-209, DOI 10.1016/j.jtice.2015.07.021.
23. Klinthong, W.; Chao, K.-J.; Tan, C.-S. CO_2 Capture by As-Synthesized Amine-Functionalized MCM-41 Prepared through Direct Synthesis under Basic Condition. *Ind. Eng. Chem. Res.* **2013**, *52*, 9834-9842, DOI 10.1021/ie400865n.
24. Lin, Z.; Wei, J.; Geng, L.; Mei, D.; Liao, L. Adsorption of Carbon Dioxide by a Novel Amine Impregnated ZSM-5/KIT-6 Composite. *RSC Adv.* **2017**, *7*, 54422-54430, DOI 10.1039/C7RA11235A.
25. Kishor, R.; Ghoshal, A. K. Amine-Modified Mesoporous Silica for CO_2 Adsorption: The Role of Structural Parameters. *Ind. Eng. Chem. Res.* **2017**, *56*, 6078-6087, DOI 10.1021/acs.iecr.7b00890.
26. Kitagawa, S.; Kitaura, R.; Noro, S.-i. Functional Porous Coordination Polymers. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334-2375, DOI 10.1002/anie.200300610.
27. Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and the Design of New Materials. *Nature* **2003**, *423*, 705-714, DOI 10.1038/nature01650.
28. Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. Selective Gas Adsorption and Separation in Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**,

38, 1477-1504, DOI 10.1039/B802426J.
29. Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal–Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450-1459, DOI 10.1039/B807080F.
30. Liao, P.-Q.; Shen, J.-Q.; Zhang, J.-P. Metal–Organic Frameworks for Electrocatalysis. *Coord. Chem. Rev.* **2018**, *373*, 22-48, DOI 10.1016/j.ccr.2017.09.001.
31. Yi, F.-Y.; Chen, D.; Wu, M.-K.; Han, L.; Jiang, H.-L. Chemical Sensors Based on Metal–Organic Frameworks. *ChemPlusChem* **2016**, *81*, 675-690, DOI 10.1002/cplu.201600137.
32. Giménez-Marqués, M.; Hidalgo, T.; Serre, C.; Horcajada, P. Nanostructured Metal–Organic Frameworks and Their Bio-Related Applications. *Coord. Chem. Rev.* **2016**, *307*, 342-360, DOI 10.1016/j.ccr.2015.08.008.
33. Wang, X.-J.; Li, J.; Li, P.-Z.; Xing, L.-B.; Lu, H.; Wu, H.; Shi, Y.; Zou, R.; Zhao, Y. An Amine Functionalized rht-Type Metal-Organic Framework with the Improved Performance for Gas Uptake. Inorg. *Chem. Commun.* **2014**, *46*, 13-16, DOI 10.1016/j.inoche.2014.04.027.
34. Choi, S.; Watanabe, T.; Bae, T.-H.; Sholl, D. S.; Jones, C. W. Modification of the Mg/DOBDC MOF with Amines to Enhance CO_2 Adsorption from Ultradilute Gases. *J. Phys. Chem. Lett.* **2012**, *3*, 1136-1141, DOI 10.1021/jz300328j.
35. Wang, X.; Li, H.; Hou, X.-J. Amine-Functionalized Metal Organic Framework as a Highly Selective Adsorbent for CO_2 over CO. *J. Phys. Chem. C* **2012**, *116*, 19814-19821, DOI 10.1021/jp3052938.
36. Chen, C.; Kim, J.; Park, D.-W.; Ahn, W.-S. Ethylenediamine Grafting on a Zeolite-Like Metal Organic Framework (ZMOF) for CO_2 Capture. *Mater. Lett.* **2013**, *106*, 344-347, DOI 10.1016/j.matlet.2013.05.078
37. Das, A.; Choucair, M.; Southon, P. D.; Mason, J. A.; Zhao, M.; Kepert, C. J.; Harris, A. T.; D'Alessandro, D. M. Application of the Piperazine-Grafted CuBTTri Metal-Organic Framework in Postcombustion Carbon Dioxide Capture. *Microporous Mesoporous Mater.* **2013**, *174*, 74-80, DOI 10.1016/j.micromeso.2013.02.036.
38. Andreoli, E.; Dillon, E. P.; Cullum, L.; Alemany, L. B.; Barron, A. R. Cross-Linking Amine-Rich Compounds into High Performing Selective CO_2 Absorbents. *Sci. Rep.* **2014**, *4*, 7304, DOI 10.1038/srep07304.
39. Qiao, Z.; Zhou, J.; Lu, X. Designing New Amine Functionalized Metal-Organic Frameworks for Carbon Dioxide/Methane Separation. *Fluid Phase Equilib.* **2014**, *362*, 342-348, DOI 10.1016/j.fluid.2013.10.050.
40. Kim, Y. K.; Hyun, S. M.; Lee, J. H.; Kim, T. K.; Moon, D.; Moon, H. R. Crystal-Size Effects on Carbon Dioxide Capture of a Covalently Alkylamine-Tethered Metal-Organic Framework Constructed by a One-Step Self-Assembly. *Sci. Rep.* **2016**, *6*, 19337, DOI 10.1038/srep19337.
41. Shekhah, O.; Belmabkhout, Y.; Chen, Z.; Guillerm, V.; Cairns, A.; Adil, K.; Eddaoudi, M. Made-to-Order Metal-Organic Frameworks for Trace Carbon Dioxide Removal and Air Capture. *Nat. Commun.* **2014**, *5*, 4228, DOI 10.1038/ncomms5228.
42. McDonald, T. M.; Mason, J. A.; Kong, X. Q.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocella, V.; Giordanino, F.; Odoh, S. O.; Drisdell, W. S.; Vlaisavljevich, B.; Dzubak, A. L.; Poloni, R.; Schnell, S. K.; Planas, N.; Lee, K.; Pascal, T.; Wan, L. F.; Prendergast, D.; Neaton, J. B.; Smit, B.; Kortright, J. B.; Gagliardi, L.; Bordiga, S.; Reimer, J. A.; Long, J. R. Cooperative Insertion of CO_2 in Diamine-Appended Metal-Organic Frameworks. *Nature* **2015**, *519*, 303-308, DOI 10.1038/nature14327.
43. Darunte, L. A.; Walton, K. S.; Sholl, D. S.; Jones, C. W. CO_2 Capture via Adsorption in Amine-Functionalized Sorbents. *Curr. Opin. Chem. Eng.* **2016**, *12*, 82-90, DOI 10.1016/j.coche.2016.03.002.
44. Liu, J.; Thallapally, P. K.; McGrail, B. P.; Brown, D. R.; Liu, J. Progress in Adsorption-Based CO_2 Capture by Metal-Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41*, 2308-2322, DOI 10.1039/C1CS15221A.
45. Lin, Y.; Kong, C.; Chen, L. Amine-Functionalized Metal-Organic Frameworks: Structure, Synthesis and Applications. *RSC Adv.* **2016**, *6*, 32598-32614, DOI 10.1039/C6RA01536K.
46. Qiao, Z.; Wang, N.; Jiang, J.; Zhou, J. Design of Amine-Functionalized Metal-Organic Frameworks for CO_2 Separation: The More Aamine, the Better? *Chem. Commun.* **2016**, *52*, 974-977, DOI 10.1039/C5CC07171B.
47. Braun, M. E.; Steffek, C. D.; Kim, J.; Rasmussen, P. G.; Yaghi, O. M. 1,4-Benzenedicarboxylate Derivatives as Links in the Design of Paddlewheel Units and Metal-Organic Frameworks. *Chem. Commun.* **2001**, 2532-2533, DOI: 10.1039/B108031H.
48. Liu, Q.; Ning, L.; Zheng, S.; Tao, M.; Shi, Y.; He, Y. Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants. *Sci. Rep.* **2013**, *3*, 2916, DOI 10.1038/srep02916.
49. Boutin, A.; Coudert, F.-X.; Springuel-Huet, M.-A.; Neimark, A. V.; Férey, G.; Fuchs, A. H. The Behavior of Flexible MIL-53(Al) upon CH_4 and CO_2 Adsorption. *J. Phys. Chem. C* **2010**, *114*, 22237-22244, DOI 10.1021/jp108710h.
50. Llewellyn, P. L.; Bourrelly, S.; Serre, C.; Vimont, A.; Daturi, M.; Hamon, L.; De Weireld, G.; Chang, J.-S.; Hong, D.-Y.; Hwang, Y. K.; Jhung, S. H.; Férey, G. High Uptakes of CO_2 and CH_4 in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101. *Langmuir* **2008**, *24*, 7245-7250, DOI 10.1021/la800227x.
51. Kumar, A.; Madden, D. G.; Lusi, M.; Chen, K.-J.; Daniels, E. A.; Curtin, T.; Perry, J. J.; Zaworotko, M. J. Direct Air Capture of CO_2 by Physisorbent Materials. *Angew. Chem. Int. Ed.* **2015**, *54*, 14372-14377, DOI 10.1002/anie.201506952.
52. Bhatt, P. M.; Belmabkhout, Y.; Cadiau, A.; Adil, K.; Shekhah, O.; Shkurenko, A.; Barbour, L. J.; Eddaoudi, M. A Fine-Tuned Fluorinated MOF Addresses the Needs for Trace CO_2 Removal and Air Capture Using Physisorption. *J. Am. Chem. Soc.* **2016**, *138*, 9301-9307, DOI 10.1021/jacs.6b05345.
53. Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. Strong CO_2 Binding in a Water-Stable, Triazolate-Bridged Metal−Organic Framework Functionalized with Ethylenediamine. *J. Am. Chem. Soc.* **2009**, *131*, 8784-8786, DOI 10.1021/ja903411w.
54. McDonald, T. M.; D'Alessandro, D. M.; Krishna, R.; Long, J. R. Enhanced Carbon Dioxide Capture upon Incorporation of N,N[Prime or Minute]-Dimethylethylenediamine in the Metal-Organic Framework CuBTTri. *Chem. Sci.* **2011**, *2*, 2022-2028, DOI 10.1039/C1SC00354B.
55. Montoro, C.; Garcia, E.; Calero, S.; Perez-Fernandez, M. A.; Lopez, A. L.; Barea, E.; Navarro, J. A. R. Functionalisation of MOF Open Metal Sites with Pendant Amines for CO_2 Capture. *J. Mater. Chem.* **2012**, *22*, 10155-10158, DOI 10.1039/C2JM16770K.
56. Cabello, C. P.; Berlier, G.; Magnacca, G.; Rumori, P.; Palomino, G. T. Enhanced CO_2 Adsorption Capacity of Amine-Functionalized MIL-100(Cr) Metal-Organic Frameworks. *CrystEngComm* **2015**, *17*, 430-437, DOI 10.1039/C4CE01265H.
57. Darunte, L. A.; Oetomo, A. D.; Walton, K. S.; Sholl, D. S.; Jones, C. W., Direct Air Capture of CO_2 Using Amine Functionalized MIL-101(Cr). *ACS Sustain. Chem. Eng.* **2016**, *4*, 5761-5768, DOI 10.1021/acssuschemeng.6b01692.
58. McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R. Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal–Organic Framework mmen-Mg_2(dobpdc). *J. Am. Chem. Soc.* **2012**, *134*, 7056-7065, DOI 10.1021/ja300034j.
59. Cao, Y.; Song, F.; Zhao, Y.; Zhong, Q. Capture of Carbon Dioxide from Flue Gas on TEPA-Grafted Metal-Organic Framework Mg_2(dobdc). *J. Environ. Sci.* **2013**, *25*, 2081-2087, DOI 10.1016/S1001-0742(12)60267-8.
60. Planas, N.; Dzubak, A. L.; Poloni, R.; Lin, L.-C.; McManus, A.; McDonald, T. M.; Neaton, J. B.; Long, J. R.; Smit, B.; Gagliardi, L. The Mechanism of Carbon Dioxide Adsorption in an Alkylamine-Functionalized Metal–Organic Framework. *J. Am. Chem. Soc.* **2013**, *135*, 7402-7405, DOI 10.1021/ja4004766.
61. Lee, W. R.; Hwang, S. Y.; Ryu, D. W.; Lim, K. S.; Han, S. S.; Moon, D.; Choi, J.; Hong, C. S. Diamine-Functionalized Metal-Organic Framework: Exceptionally High CO_2 Capacities from Ambient Air and Flue Gas, Ultrafast CO_2 Uptake Rate, and Adsorption Mechanism. *Energ. Environ. Sci.* **2014**, *7*, 744-751, DOI 10.1039/C3EE42328J.
62. Lee, W. R.; Jo, H.; Yang, L.-M.; Lee, H.; Ryu, D. W.; Lim, K. S.; Song, J. H.; Min, D. Y.; Han, S. S.; Seo, J. G.; Park, Y. K.; Moon, D.; Hong, C. S. Exceptional CO_2 Working Capacity in a

Heterodiamine-Grafted Metal-Organic Framework. *Chem. Sci.* **2015**, *6*, 3697-3705, DOI 10.1039/c5sc01191d.
63. Mason, J. A.; McDonald, T. M.; Bae, T.-H.; Bachman J. E.; Sumida, K.; Dutton, J. J.; Kaye, S. S.; Long, J. R. Application of a High-Throughput Analyzer in Evaluating Solid Adsorbents for Post-Combustion Carbon Capture via Multicomponent Adsorption of CO_2, N_2, and H_2O. *J. Am. Chem. Soc.* **2015**, *137*, 4787-4803, DOI 10.1021/jacs.5b00838.
64. Siegelman, R. L.; McDonald, T. M.; Gonzalez, M. I.; Martell, J. D.; Milner, P. J.; Mason, J. A.; Berger, A. H.; Bhovvn, A. S.; Long, J. R. Controlling Cooperative CO_2 Adsorption in Diamine-Appended Mg_2(dobpdc) Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2017**, *139*, 10526-10538, DOI 10.1021/jacs.7b05858.
65. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science* **2002**, *295*, 469-472, DOI 10.1126/science.1067208.
66. Vermoortele, F.; Ameloot, R.; Vimont, A.; Serre, C.; De Vos, D. An Amino-Modified Zr-Terephthalate Metal-Organic Framework as an Acid-Base Catalyst for Cross-Aldol Condensation. *Chem. Commun.* **2011**, *47*, 1521-1523, DOI 10.1039/C0CC03038D.
67. Ghalei, B.; Sakurai, K.; Kinoshita, Y.; Wakimoto, K.; Isfahani, A. P.; Song, Q. L.; Doitomi, K.; Furukawa, S.; Hirao, H.; Kusuda, H.; Kitagawa, S.; Sivaniah, E. Enhanced Selectivity in Mixed Matrix Membranes for CO_2 Capture through Efficient Dispersion of Amine-Functionalized MOF Nanoparticles. *Nat. Energy* **2017**, *2*, 17086, DOI 10.1038/nenergy.2017.86.
68. Huang, X.; Lu, J.; Wang, W.; Wei, X.; Ding, J. Experimental and Computational Investigation of CO_2 Capture on Amine Grafted Metal-Organic Framework NH_2-MIL-101. *Appl. Surf. Sci.* **2016**, *371*, 307-313, DOI 10.1016/j.apsusc.2016.02.154.
69. Ge, J.; Liu, L.; Qiu, L.; Jiang, X.; Shen, Y. Facile Synthesis of Amine-Functionalized MIL-53(Al) by Ultrasound Microwave Method and Application for CO_2 Capture. *J. Porous Mater.* **2016**, *23*, 857-865 DOI 10.1007/s10934-016-0142-y.
70. Zarate, A.; Peralta, R. A.; Bayliss, P. A.; Howie, R.; Sanchez-Serratos, M.; Carmona-Monroy, P.; Solis-Ibarra, D.; Gonzalez-Zamora, E.; Ibarra, I. A. CO_2 Capture under Humid Conditions in NH_2-MIL-53(Al): The Influence of the Amine Functional Group. *RSC Adv.* **2016**, *6*, 9978-9983, DOI 10.1039/C5RA26517G.
71. Li, P.-Z.; Wang, X.-J.; Zhao, Y. L. Click Chemistry as a Versatile Reaction for Construction and Modification of Metal-Organic Frameworks. *Coord. Chem. Rev.* **2019**, *380*, 484-518, DOI 10.1016/j.ccr.2018.11.006.
72. Li, H.; Wang, K.; Feng, D.; Chen, Y.-P.; Verdegaal, W.; Zhou, H.-C. Incorporation of Alkylamine into Metal–Organic Frameworks through a Brønsted Acid–Base Reaction for CO_2 Capture. *ChemSusChem* **2016**, *9*, 2832-2840, DOI 10.1002/cssc.201600768.
73. Flaig, R. W.; Osborn Popp, T. M.; Fracaroli, A. M.; Kapustin, E. A.; Kalmutzki, M. J.; Altamimi, R. M.; Fathieh, F.; Reimer, J. A.; Yaghi, O. M. The Chemistry of CO_2 Capture in an Amine-Functionalized Metal–Organic Framework under Dry and Humid Conditions. *J. Am. Chem. Soc.* **2017**, *139*, 12125-12128, DOI 10.1021/jacs.7b06382.
74. Guo, X.; Huang, H.; Ban, Y.; Yang, Q.; Xiao, Y.; Li, Y.; Yang, W.; Zhong, C. Mixed Matrix Membranes Incorporated with Amine-Functionalized Titanium-Based Metal-Organic Framework for CO_2/CH_4 Separation. *J. Membr. Sci.* **2015**, *478*, 130-139, DOI 10.1016/j.memsci.2015.01.007.
75. Darunte, L. A.; Terada, Y.; Murdock, C. R.; Walton, K. S.; Sholl, D. S.; Jones, C. W. Monolith-Supported Amine-Functionalized Mg_2(dobpdc) Adsorbents for CO_2 Capture. *ACS Appl. Mate. Interfaces* **2017**, *9*, 17042-17050, DOI 10.1021/acsami.7b02035.
76. Yeon, J. S.; Lee, W. R.; Kim, N. W.; Jo, H.; Lee, H.; Song, J. H.; Lim, K. S.; Kang, D. W.; Seo, J. G.; Moon, D.; Wiers, B.; Hong, C. S. Homodiamine-Functionalized Metal-Organic Frameworks with a MOF-74-Type Extended Structure for Superior Selectivity of CO_2 over N_2. *J. Mater. Chem. A* **2015**, *3*, 19177-19185, DOI 10.1039/C5TA02357B.
77. Wang, N.; Mundstock, A.; Liu, Y.; Huang, A.; Caro, J. Amine-Modified Mg-MOF-74/CPO-27-Mg Membrane with Enhanced H_2/CO_2 Separation. *Chem. Eng. Sci.* **2015**, *124*, 27-36, DOI 10.1016/j.ces.2014.10.037.
78. Cui, X.; Chen, K.; Xing, H.; Yang, Q.; Krishna, R.; Bao, Z.; Wu, H.; Zhou, W.; Dong, X.; Han, Y.; Li, B.; Ren, Q.; Zaworotko, M. J.; Chen, B. Pore Chemistry and Size Control in Hybrid Porous Materials for Acetylene Capture from Ethylene. *Science* **2016**, *353*, 141-144, DOI 10.1126/science.aaf2458.
79. Lin, Y.; Lin, H.; Wang, H.; Suo, Y.; Li, B.; Kong, C.; Chen, L. Enhanced Selective CO_2 Adsorption on Polyamine/MIL-101(Cr) Composites. *J. Mater. Chem. A* **2014**, *2*, 14658-14665, DOI 10.1039/C4TA01174K.

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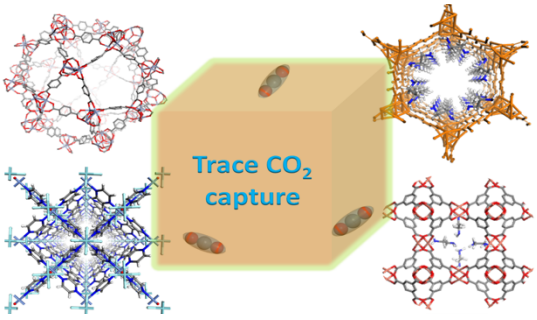
TOC Graphic



Synopsis: This review highlights the design, capacity, selectivity, stability and mechanisms of metal-organic frameworks for trace CO_2 capture.