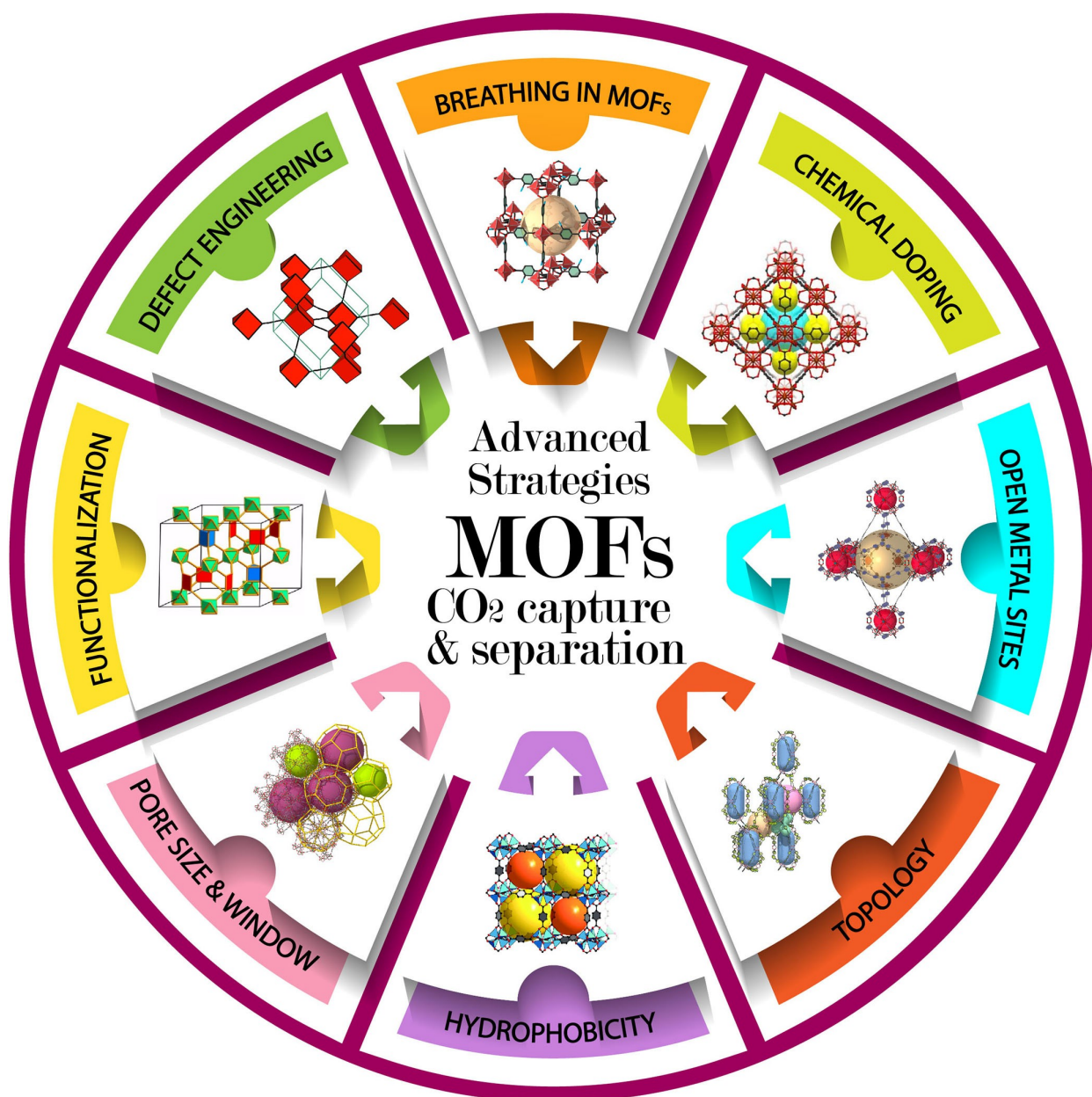# Record Review

THE CHEMICAL RECORD

Advanced Strategies in Metal-Organic Frameworks for CO_2 Capture and Separation

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Abstract: The continuous carbon dioxide (CO_2) gas emissions associated with fossil fuel production, valorization, and utilization are serious challenges to the global environment. Therefore, several developments of CO_2 capture, separation, transportation, storage, and valorization have been explored. Consequently, we documented a comprehensive review of the most advanced strategies adopted in metal-organic frameworks (MOFs) for CO_2 capture and separation. The enhancements in CO_2 capture and separation are generally achieved due to the chemistry of MOFs by controlling pore window, pore size, open-metal sites, acidity, chemical doping, post or pre-synthetic modifications. The chemistry of defects engineering, breathing in MOFs, functionalization in MOFs, hydrophobicity, and topology are the salient advanced strategies, recently reported in MOFs for CO_2 capture and separation. Therefore, this review summarizes MOF materials' advancement explaining different strategies and their role in the CO_2 mitigations. The study also provided useful insights into key areas for further investigations.

Keywords: CO_2, CO_2 separation, CO_2 capture, MOFs, Strategies, Advanced materials

1. Introduction

Anthropogenic activities are critically considered among the major causes of environmental pollution in recent times. Specifically, fossil fuel production and utilization have contributed to global warming and destruction to the environment over the years. These operations are associated with the emission of dangerous gases, including CO_2, CH_4, and many others (including fluorochloro carbons).[1,2] Among these gases, CO_2 has been considered more dangerous due to its huge concentrations in the atmosphere, continuous emissions and resulted hazards. The recent concentration of CO_2 in the atmosphere (shown in Figure 1) recorded by Mauna loa observatory in July-2021 was 416 ppm and is estimated to rise to 500 ppm through the year 2030.[3] This increasing concentration of CO_2 has continued to affect the global plants, animals, and the entire environment. The acidification of oceans due to the associated death of marine organisms and the creation of an imbalance in the ecosystem has greatly and negatively influenced marine species. In addition to the rise in sea-level, the noticed upsurge in the world temperature is a severe issue that directly links with the CO_2 levels. This, in turn, caused a decline in agricultural output and the extinction of useful plant and animal species.[4,5]

In recent times, emission mitigation, capture, and valorization strategies are consistently being evaluated to provide opportunities for handling the situation. Carbon capture and storage (CCS), otherwise called carbon sequestration, is one of these strategies considered by policymakers and oil companies. It typically involved the separation of CO_2 from point sources (e.g. power plants), afterward transportation, and subsequent storage. The three stages of CCS include capture (i.e. isolation and separation), transportation, and storage. Details about these processes have already been documented in earlier publications.[6–18] The major challenges identified are associated with separation difficulties, cost-implications, and leakage problems. Accordingly, successful separation and capture of CO_2 can provide a useful raw material for fuels and chemical manufacture. In another perspective, geological storage for enhanced oil and coal bed methane recovery is also possible. However, due to its chemical properties, separation and
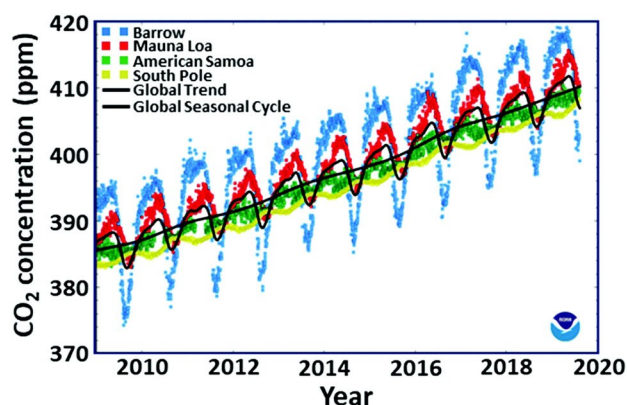
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Figure 1. Global trend for the increase in CO_2 concentration in the last 10 years measured at different observatories contained in the Global Monitoring Division (GMD) of the Earth System Research Laboratory (ESRL). (http://esrl.noaa.gov/gmd/).

capture are becoming problematic to the industry.[19,20] So far, numerous gas separation technologies have been investigated to capture CO_2, i.e. absorption, adsorption, hydrated-based system, cryogenic distillation, and membrane separation.[21]

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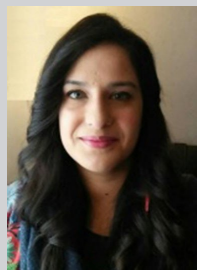
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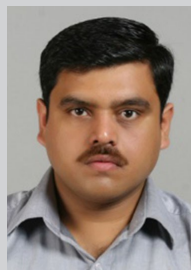
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However, fundamental challenges identified include poor procedures for efficient separation and capture of the CO_2 from emission points.

Similarly, some of the materials explored have poor CO_2 retention stability. These, in turn, rendered the overall process as economically non-feasible. It has been consistently established that, CO_2 massive increase is dangerous to the environment. In practical CCS applications, CO_2 capture from stationary sources is a major concern. Significant quantities of coal and gas combustion to fulfill energy requirements and release of Green house gases (GHGs) into the atmosphere have established an urgent need to produce adsorbent materials to capture CO_2 gas.[22–26] Still, it remains a challenge to improve adsorption and separation performance. Therefore, it is crucial to establish rational strategies to improve CO_2 capture and separation and realistic and urgent implementation plans for their use at industrial scale GHGs capture.[27] CO_2 separation and capture can be enhanced by fine-tuning of pore morphology to an ideal pore size, chemical doping with electronegative/electropositive elements, chemical functionalization by various polar and N-containing groups and by generating open-metal in MOF.[28] The mentioned features The mentioned features are recently reported by few review articles.[29–33] Due to structure flexibility and tunable properties, MOFs also show breathing behavior, defects engineering property, unique toplology, hydrophobicity, and metal chelation. Therefore, a detailed, in-depth study of the structural strategies using MOFs for CO_2 separation and capture is still needed.

MOFs, which contain organic linkers and metal nodes, are promising class of porous materials widely used in storage,[34–40] separation,[41–51] and catalysis.[52–64] These salient features like tunable pore window, pore size, and easy functionalization make these materials incredible, breaking the surface area's record in porous materials. Among several known MOF materials, some of these frameworks produced large internal spaces, creating structures with very high porosity and surface areas.[65–68] Numerous adsorbents have been previously reported in state-of-the-art review articles, including zeolites, MOFs, COFs, carbon based materials, hydroxides, carbonates, ceramics, polymers and amines[69–80] for CO_2 capture and separation. Among these, MOF materials are considered as the best possible alternative to the mentioned adsorbent. Furukawa provided a summary of these porous materials in 2013.[81] Later, NU-110E was prepared by Omar Farha having the maximum BET surface area up to ~7100 $m^2 g^{-1}$ in 2018.[82] Prof. Stefan Kaskel's group reported a new porous MOFs in 2018, known as DUT-60,[83] with an eminent surface area of ~7800. An overview of these high surface areas MOFs[82–92] is presented in Figure 2. The porosity and pore volume enables these materials to capture and allow selective separation of the gas molecule from its mixture.
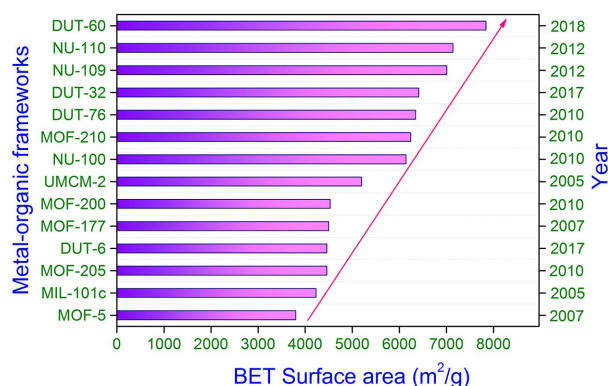

Figure 2. Representative high BET surface areas MOFs.

Besides these unique features, MOFs can be modified for the possible application using pre or post-synthetic modifications of MOFs, use of appropriate organic ligands, metals, and functional groups. Defective engineering of MOFs, chelation in MOFs, imparting hydrophobicity, and dominant crystal structure in MOFs are the salient advanced features reported recently for CO_2 capture and separation shown in Figure 3. All the mentioned highlighted features make MOFs as advanced materials for CO_2 separation and capture. Thus, the leading purpose of this review is to critically analyze relevant literature on the potentials of MOFs as advanced candidates for the separation and capture processes. The exploring of MOFs with advanced structural strategies were carefully discussed. In addition to a strong literature analysis on MOFs modification

Figure 3. Schematic presentation of the most advanced strategies in MOFs for separation and capture of CO_2.

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and application strategies, the paper provides suitable conclusion remarks with further research perspectives.

2. Strategies for Improving CO_2 Capture and Separation in MOFs

2.1. Pore Window and Pore Size Optimization

In MOFs, the pore window and pore size is determined by the type of the organic and inorganic building components. The pore structures in MOF materials are very diverse in size, such as tubular pores, slits, cylindrical or spherical, that link and/or isolate in a zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D). In MOFs, the pore diameters can range from Å to nm, and interior surface areas can vary from a few hundred microns to 7,800 m²/g.[93] Since MOFs have a wide range of pore sizes, they can be used as adsorbent materials for different types of gas capture. Further, inside the porous materials, gases are adsorbed with specific potential energy equal to two interaction potentials: the adsorbate-adsorbent interaction potential and the adsorbate-adsorbate interaction potential. Additionally, pore topology plays a vital role in gas uptake by MOFs.[38] This objective can successfully be attained via varying the pore window and size.[94] Therefore, MOFs adsorbents are typically utilized for CO_2 capture and separation over gas pairs due to their maximum surface area and high pore volume. According to the literature, many MOFs molecular sieving effects are exploited to adsorb a variety of gas molecules that imply only those molecules can crossover the pores with diameters well-matched to the pore window[95–99] However, it is clear that molecules with comparable sizes/shapes are perhaps the most challenging to separate since they need the employment of a separating agent with a very precise size an from a chemistry perspective. Therefore, designing and synthesising a porous material with such fine-tuning of the pore aperture size is also a very difficult task, particularly given the difficulties associated with precisely adjusting the pore aperture size and functionality in the majority of solid-state materials.[100] Therefore, the pore size engineering operations are acknowledged to maximize these solids' adsorption selectivity and capacity. The selective adsorption of CO_2 over N_2 is difficult to achieve of their close kinetic diameter. However, few reports on CO_2 selective adsorption only through controlling the pore size over other gases.[101] Many studies have recently focused on synthesizing MOFs with precise pore engineering, which seems to be perfectly capable of separating different gas mixtures, even when the gas molecules are quite similar in size and characteristics. Li et al.[102] demonstrated the pore shapes, pore size, and their effect on the separation of gases and related applications. Adsorbent materials enhance CO_2 capture and separation is achieved through pore shape exclusive effect, which enhances

the available surface area to offer more adsorption sites and promotes effective screening of molecules over the permeable channel while blocking bigger molecules.[103,104] Li et al.[105] designed single-molecule traps (SMTs) and effectively optimized the synthesis of metal-organic polyhedra with appropriate pore depth, ideal for accurate CO_2 capture and separation. Another study reported[106] the designing of a primitive cubic framework. This comprising on 2D $Cu_2(CO_2)_4$ using fumarate (FMA) connected via three different length organic linkers including 4,4-bipyridine, pyrazine and trans-bis (4-pyridyl)-ethylene(4,4′-Bpe). Among these frameworks, dehydrated [Cu(FMA)(4,4′-bpy)0.5·0.25 H_2O] framework displays small pore size and prohibits the gas molecules entry so they does not take up nitrogen (N_2), (CO_2) and (CH_4). On the other hand a hydrated framework [Cu(FMA)(4,4′-bpe) 0.5·0.5H_2O] exhibits selective adsorption at 195 K for N_2 (3.6 Å), CO_2 (3.3 Å) and CH_4 (3.8 Å) due to the availability of ultramicropores in the framework. In addition, A 2-fold interpenetrated framework, i.e. PCN-5 MOF selectively adsorb more CO_2 over methane because of host framework pores compatibility with the diameter of gas molecules, i.e. 3.3 Å for CO_2 and 3.8 Å for CH4. The uptake of CO_2 at 195 K by MOFs is 4.8 mmol g-1 and 1.9 mmol g-1 for CH4.[108] Another 2- fold interpenetrated framework, i.e. Cd-MOF prepared by Qin and coworkers' via solvothermal method. The following framework shows selective adsorption for CO_2 over methane due to the size-exclusive effects of Cd–MOF framework.[109] The pores surface property of flexible MOFs also indicates selective adsorption. The following MOFs demonstrate breathing phenomena during hydration and dehydration and altered the pore size. In hydrated form, the oxygen atom of the carboxylate of ligands and the hydrogen atom of the H_2O illustrates hydrogen bonding as a result, pores become narrower, and their size is altered correspondingly.[110] However, the pore size is larger in dehydrated form. Moreover, changing the pressure from low to high the pore size tuned from narrower to larger pore and there is an increase in uptake capacity, i.e. 7.2 mmol g^{-1} at high pressure (18 bar). Also, there is an increase in pore volume from 1012.8 Å to 1522.5 Å.[111,112] Another commendable design of this group is [Ni(bpe)$_2$(N(CN)$_2$)](N(CN)$_2$), which has 1D channels with 3D stable interpenetrated framework and adequate pore size. Following MOF exhibits an exceptional behavior for selective adsorption of CO_2. For instance, at 77 K no oxygen and nitrogen molecules get diffused into microspores, but at 195 K it surprisingly adsorb CO_2 and no oxygen and nitrogen molecules could diffuse into pores, though the size of oxygen molecule is closed to CO_2. This uncommon behavior of selective uptake at an elevated temperature would be described via CO_2 strong interaction with host framework pore window.[113] Besides, a rigid 3D MOF, i.e. PCN-26, shows selective adsorption for CO_2 as

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compared to N_2 and CH_4, gases. The selectivity and adsorption for CO_2 is due to their pore diameters (3.68 Å). Moreover, at 800 Torr and 298 K it achieved an adsorption capacity of 109.1 $cm^3 g^{-1}$ for CO_2. As results shows, following MOF (PCN-26) is more suitable for CO_2 adsorption over nitrogen and CH_4.[95] Moreover, Wen et al.[107] reported USTA-120a ([Cu(dpt)$_2$(SiF$_6$)]$_n$) dpt = 3,6-di(4-pyridyl)-1,2,4,5-tetrazine) for discerning uptake of CO_2 over nitrogen. Figure 4a illustrated the structural details of reported MOF, the use of longer linker i.e. dpt offers pore size up to 4.6 Å, the availability of N sites act as lewis base points where it significantly separate and capture CO_2. Additionally, confined pore channels might arrange adsorbed CO_2 with a distance of 4.553 Å (Figure 4b, c). Selective adsorption of CO_2 over methane and nitrogen, studied via transient breakthrough simulations, following experimentations reveal that UTSA-120a be able to adsorb CO_2 gas from the mixture of CO_2/N_2 (15/85, v/v) and CO_2/CH_4 (50/50) (298 K, 1.0 bar) are illustrated in Figure 4d–g. The unusual combination of excessive CO_2 capture capacity and moderate heat of CO_2

adsorption and an extraordinary selective adsorption for CO_2/N_2 make UTSA-120a an incredibly capable contender for CO_2.

For selective adsorption of CO_2, MOFs are considered to be the best candidate. The criteria for selecting suitable MOFs for adsorption are their pore's compatibility with the kinetic diameter of CO_2. ZIF series comparison between pore diameter and corresponding ZIF surface area are reported[114,115] which indicates that ZIFs samples outperformed certain MOFs except for ZIF-68 in terms of CO_2 selectivity over pair gases present in flue gases. Also, to enhance the CO_2 selective adsorption Zn-framework is modified by applying tetrazolate ligand and a new ZIF class is synthesized and showed a significant adsorption capacity for CO_2 of 86 $cm^3 g^{-1}$ at 273 K, respectively. This improvement in gas adsorption results from tetrazolate ligands incorporation provide N-heteroatom sites in framework.[124,125] Furthermore, the MOFs system illustrates nanoscale porosity with high surface area as the promising adsorbate materials for CO_2 adsorption. By turning MOFs' framework to get appropriate pores showing adsorption for CO_2 but not for nitrogen or methane gases present in flue gases[126] i.e. [Al(OH)(ndc)] where ndc = 1,4-napthalenedicarboxylate show high uptake capacity of CO_2 over N_2 with pore diameter 7.7 Å, in addition, due to hydroxyl group presence, it shows favorable interaction with CO_2.[127] One dimensional Mg-based framework, i.e. [Mg$_2$(dobdc)] showing pore diameter up to 11–12 Å with high availability of open metal sites showing high adsorption capacity for CO_2.[128] Table 1 shows the pore size, surface area and CO_2 adsorption capacity by various MOFs. Thus, the advantage of using MOF materials over other functional materials is the ease of tuning pore size by
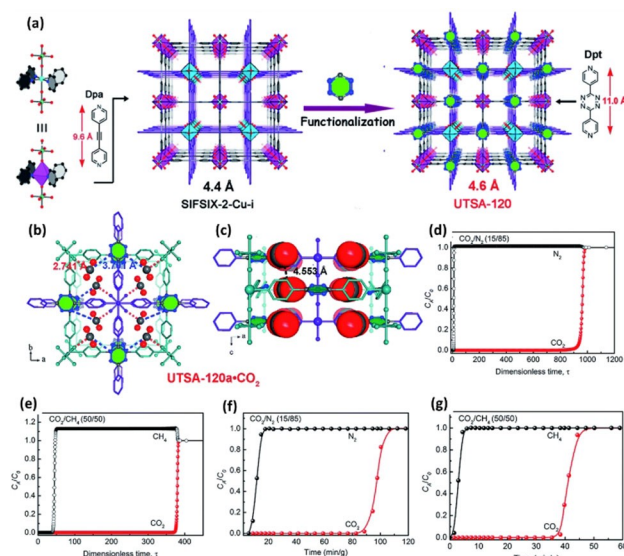

Figure 4. (a) Structural description of UTSA-120a, revealing its pore size (4.6 Å) and dual functionalities of SiF6$^{2−}$ anions and tetrazine rings around the channels. The different nets are highlighted in gray and purple for clarity. Colour code: Cu (turquoise), Si (dark green), F (red), N (blue), and C (grey), (b) Gas adsorption isotherms of UTSA-120a for CO_2, CH_4 and N_2 at 296 K. Filled/empty symbols represent adsorption/desorption. (c) Comparison of CO_2 adsorption isotherms for UTSA-120a and SIFSIX-2-Cu-i at 296 K. (d) Comparison of CO_2 capture capacity for UTSA-120a and other best-performing materials at 0.15 bar and room temperature. (e) IAST selectivity of UTSA-120a (red) for CO_2/N_2 (15/85, v/v) at 296 K, as compared with SIFSIX-2-Cu-i (black). (f) A comparison of the CO_2 uptake (at 0.15 bar) and CO_2/N_2 selectivity at 1.0 bar and room temperature for UTSA-120a and other indicated MOFs. (g) Comparison of heat of CO_2 adsorption for UTSA-120a and other best-performing materials.[107] Copyright © 2019 Royal Society of Chemistry.

Table 1. selected examples of zeolites and MOFs with pore size, surface area and CO_2 adsorption capacity.

Absorbent materials	Surface area (m^2/g)	Pore Size	capacity for CO_2 ($mmol\,g^{-1}$)	Ref.
ZIF-82	1300	0.81 nm	0.41	[116]
ZIF-81	760	0.39 nm	0.27	[116]
ZIF-100	–	3.35 Å	~0.95	[117]
ZIF-79	810	0.4 nm	0.26	[116]
ZIF-79	620	0.38 nm	0.58	[116]
MIL-96	–	2.5~3.5 Å	~3.7	[98]
Ni-MOF-74	1218	1.11 nm	4.34	[118]
Mg-MOF-74	1542	1.11 nm	7.23	[118]
HKUST-1	1571	0.35 nm	0.62	[119]
Zn$_2$(cnc)$_2$(dpt)	–	~3.7 Å	~150	[99]
Zn$_2$(ndc)$_2$(dpni)	–	4~5 Å	~4.3	[120]
MCM-41-DETA	8.1	-	1.87	[121]
MCM-41- AMP	2.2	-	1.14	[121]
MIL-102	–	4.4 Å	~3.4	[122]
MCM-41-TETA	3.4	–	2.2	[121]
Zn$_3$(OH)(pcdc)$_{2.5}$	–	3x5 Å	~0.568	[123]

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modifying organic ligand within the coordination covalent network.

2.2. Post-Synthetic Modification in MOFs

Post-synthetic modification (PSM) is a technique to enhance the properties of the parent MOF after its synthesis. Recently, PSM has gained enormous attention and is considered a flexible tool to obtain the best MOF properties. Coordination chemists recently proved that PSM is the most systematic approach for structural and functional modification, which was otherwise impossible with direct synthesis techniques. Roughly, more than three hundred post synthetically modified MOFs are available on the Scifinder database. Chemical functionalization usually enhances the contact between quadrupole CO_2 molecule and interaction between basic functional group entity and electrostatic potential; thereby, absorbent achieves a strong tendency to absorb CO_2.[129] In 2007 Cohen and his coworkers[130] modified IRMOF-3 using acetic anhydride; the newly modified MOF material had amide group attachment successfully incorporated throughout MOF network.

Due to the strong attraction of CO_2 with amine groups, the functional group $-NH_2$ is commonly used in different adsorbent materials. Many polar functional classes such as – halogen atoms, hydroxyl, carboxyl, cyano and nitro groups have proven effects on MOFs' carbon-dioxide uptake capacity.[131] Gaikwad et al.[132] reported the amine functionalization effects on MOF-177 for CO_2 adsorption capacity at varying temperatures such as from 298–328 K. In contrast to parent MOF-177 an amine functionalized MOF-177 show CO_2 adsorption capacity of 4.6 mmol/g at 328 K.

PSM allows accomplishing the following goals. (A) PSM can introduce functional groups into a MOF structure. (B) To modify and exchange organic linkers in a coordination polymer network. (C) MOFs cation exchanging. These techniques help to add desirable characteristics to MOF networks. For example, CO_2 molecules being acidic are attracted to basic functional groups. Here grafting amine functional groups on open metal sites of MOF enhances CO_2 uptake tendency by a MOF. In a water-stable MOF the coordinated unsaturated Copper (II) sites were decorated with ethylenediamine; however, resultant pores of MOF materials became narrow, leading towards reduced CO_2 uptakes at relatively high CO_2 pressure. Nevertheless, isosteric heats of adsorption values and selectivity of CO_2/N_2 increased dramatically in contrast to the pristine MOF. Also a similar technique was effectively employed to more related MOFs like MOF-99.[133] DOBDC linker-based MOF i.e. Mg–MOF-74 found to have maximum adsorption capacities for CO_2 at very low CO_2 pressures (6 mmolg^{-1} at 0.15 bar pressure and 298 K).[27] Here one-dimensional narrow pores development and bulky

amine groups incorporation into MOF network negatively affected the overall surface area of MOF, therefore MOF-74 structures like $Mg_2(dotpdc)$, $Mg_2(dondc)$ and $Mg_2(dobpdc)$, were developed and tested as post synthetically amine modification. Newly developed amine doped MOFs showed higher CO_2 capturing tendency and selectivity than parent without amine MOFs.[134] The CO_2 capture tendency and selectivity of MOF enhanced thermal and water stability of these coordination polymers were also remarkably increased. BET surface areas of most of the amine modified MOFs decreased however, attraction towards amine-modified MOFs increased. Scientists then explored PSM with smaller amine molecules like hydrazine e.g. Mg-MOF-74 (N_2H_4). This approach helped achieve higher CO_2 uptake values with similar chemical properties yet smaller amine size, without compromising pore size expansion. Here amine molecules were attached at larger distances from each other due to smaller sizes with weak hydrogen bonds. This MOF gave a much higher uptake of CO_2 values (1.8 mmolg^{-1} at 0.4 mbar and at 298 K) than Mg–MOF-74. However, Qst values were found to be really high, this indicating difficult MOF regeneration as stronger bonds between adsorbent and adsorbate typically need harsh regeneration conditions like higher regeneration temperatures.[27] Gas capture with MOFs and strong bonds between gas molecules and MOF greatly challenge regeneration. To overcome this challenge a new functionalization strategy i.e. solvent assisted ligand incorporation (SALI) was designed.[149] Fluorinated chains were attached on Zirconium secondary basic units of NU-1000. Attractive forces were developed between OH and COOH groups of linkers to assist higher CO_2 uptake values than parent NU-1000; it is attributed to attraction between the quadrupole moment of CO_2 molecule and C–F dipoles. It also resulted in moderate isosteric heat of adsorption values for CO_2 capture thus providing easy regeneration of framework.[149]

Moreover, hafnium-based MOFs such as UiO-66(Hf) MOFs execute improved gas adsorption, prepared through solvothermal methods. Amongst all the prepared MOFs like UiO-66(Hf)-$(OH)_2$ show eminent uptake of CO_2 gravimetrically such as of 1.81 mmolg^{-1} at pressure of 0.15 bar and temperature of 298 K, in comparison to UiO-66(Hf) is up to 0.36 mmolg^{-1}, it shows 400% more enhanced uptake and at 298 K and 1 bar it exhibits i.e. 4.06 mmolg^{-1}, which is equivalent to PPN-SO_3Li with capacity upto 3.7 mmolg^{-1}. Also, UiO66(Hf)-NH_2 show second highest CO_2 uptake capacity up to 0.93 mmolg^{-1}, consequently UiO-66(Hf)-$(COOH)_2$ exhibits CO_2 uptake capacity up to 0.40 mmolg^{-1}, followed by UiO-66(Hf)-$(F)_4$ exhibits uptake of CO_2 0.28 mmolg^{-1} as illustrated in Figure 5.[148]

Many desirable characteristics can be incorporated in coordination polymers using PSM like enhancing gas uptake
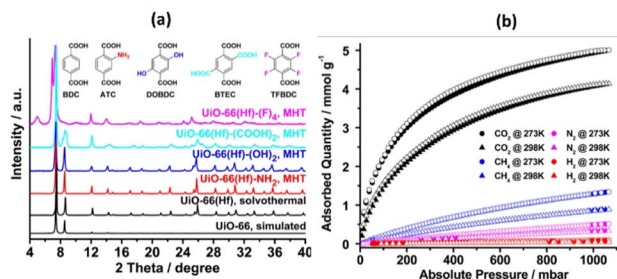
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Figure 5. a). PXRD of UiO-66(Hf)-type MOFs. b). Gas adsorption isotherms of UiO-66(Hf)-(OH)$_2$.[148] Copyright © 2016 American Chemical Society.

values and gas selectivity. PSM not only achieves functional group addition in selected MOF materials and cation exchange, but researchers have also recently reported insertion, modification and organic linker exchanging to develop new and improved frameworks.[150] Thus post-synthetic modification can introduce specific functional groups into MOF networks by adding CO_2-loving molecules and overall enhancing CO_2 uptake value.[20]

Organic linkers in Cr-MIL 101-SO$_3$H were modified using PSM technique for linker modification to Cr-MIL-101-SO$_3$H-TAEA (TAEA = tris (2-aminoethyl) amine) by incorporation of tris-amine ethyl amine (TAEA). The resultant framework showed higher CO_2 uptake tendency had a high CO_2 (2.3 mmol g^{-1} at 313 K and 150 mbar).[151] Qst calculated was 87 KJ/mol that indicates strong chemisorption. One famous MOF UiO-66-alkyl was post-synthetically modified with amino alcohol and demonstrated good CO_2 adsorption of 11.6 mmol g^{-1} at 20 bar and 308 k. It showed a lesser amount of nitrogen adsorption in similar conditions so it's good MOF choice for N_2/CO_2 selectivity.[152]

Adding a bridging linker in MOF by post-synthetically incorporated 3,6-di(4-pyridyl)-1,2,4,5- tetrazine (bpta) into SNU-30. After PSM the pore size reduced by 6% but CO_2 uptake by framework compared to prestine SNU-30 showed almost negligible CO_2, methane and nitrogen gas uptake values. moreover it showed very moderated Qst values so found an excellent candidate for gas uptake and regeneration.[153] Another MOF LIFM-28 demonstrated fine-tuning of its pore size by the addition of organic linker through post-synthetic modification strategy. Amine group addition enhanced CO_2 uptake levels as a result of acid-base attraction among basic amine functional groups and acidic CO_2. Pore tuning not only improves BET surface area rather this framework shows better thermal and structural stability. Nevertheless, Qst values calculated here were bit higher, indicating strong CO_2-amine group interactions.[154] Table 2 illustrates the MOF-based sorbent and subsequent uptake capacity of various MOFs for CO_2.

2.3. Pre-Synthetic Modification in MOFs

Functionalization in organic linkers before the MOF synthesis is known as pre-synthetic modification (PSM) in MOFs. The functionality may be applied in a process by changing the organic linker before the MOF synthesis. The overall strategy of PSM technique is the decorate the pore by adding functionality within the framework in such a way to achieve maximum affinity toward CO_2 gas molecules without enhancing regeneration energies. In addition to the MOFs, functional groups will substantially restrict the number of suitable substituents. So it's very important to choose the substituents attached carefully.[155] Metal atom and choice of ligand in MOFs have potential effects on framework's overall structure and adsorption capacities. Here targeted groups incorporation can alter overall MOF networks so potentially changing MOFs applications.[156] Newly modified MOFs can be used successfully in catalysis, drug delivery, gas adsorption and storage applications.[157,158] In Pre-synthetic MOF modification groups (like hydroxyl[159] and carboxyl are widely used for grafting on MOF ligands.[160] Solvothermal techniques have shown the best potentials for pre-synthetic modifications of some best MOFs studies so far, including ZIFs,[161] MOF-5,[162] and MIL-53(Fe).[163] Here, a newly developed ligand with or without functionalization can produce better and high-performance novel framework. In a study by Lu et al.[164] incorporated cellulose solution with metal ions using conventional synthesis method, cellulose-modified MOFs (ZIF-8@CA) obtained thus showed better performance than prestine MOF.

Deng and his coworkers[165] in 2010 added a variety of functional groups like −(Cl)$_2$, −NH$_2$, −Br, , −C$_4$H$_4$, −NO$_2$, (OC$_7$H$_7$)$_2$, −(CH$_3$)$_2$, −(OC$_3$H$_5$)$_2$, and -with benzene dicarboxylic acid linker to produce 18 novel structures. They found complex arrangement of functionalities within framework like one the MOF thus produced in this series i. e. MTV-MOF-5-EHI, showed about 400% improved CO_2 gas selectivity over CO related to similar counterparts. Moghaddam and his team reported pre synthetic functionalization of Zr-MOF. The adsorption capacity of new MOF was calculated to be around 47.5 mg g^{-1}. They claimed that the proposed technique can be implicated to real water sample analysis.[166] Various functionalized linkers were incorporated with MOFs like UiO-66-NO$_2$ and UiO-66-NO$_2$–N (N = −NH$_2$, −(OH)$_2$, and −COOH)$_2$), using hydrothermal synthesis techniques by Rada and his coworkers in 2015. The effect of various solvents for washing and MOF activation was also studied here. MOFs activated with methanol and chloroform demonstrated much higher CO_2 uptake values.[146] Pre-synthetic functionalization of the Cd based MOF build with 1,3,5-tris(4-carboxyphenyl) ligand performed using amine (NH$_2$-H$_3$BTB) and hydroxy (HO-H$_3$BTB) groups. Resultant MOFs showed pillared-layer MOFs

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Table 2. MOF-based sorbent and related CO_2 uptake capacity.

Materials	BET (m²/g)	Temperature (K)	Pressure (bar)	CO₂ capture (wt. %)	Qst (KJmol⁻¹)	Ref.
$Fe_2(DOBDC)$		298	1	30.8	33	[135]
	1345	308		27.3		
		318		22.9		
Pie-Ni-DOBDC	409	298	1	12	–	[136]
Ni-MOF 74	1252	298	1	19.4	–	[136]
Mg-MOF-74	1416	298	1	30.1	–	[137]
Amino Zr-MOF	1220	273	1	19.62	29.3	[138]
	1395	296		12.54		
$Zn_2(NH_2BDC)_2$ (dpNDI)	897	273	1	29.04	46.5	[133]
$Mg(DOBDC)$	1525	298	10	37.4	-	[27]
		313		32.6		
		328		29.9		
$Cu_2(H_2O)_2BDPO$	2447	273	1	40.1	25.4	[139]
Co-DOBDC	1089.3	298	1	21.6	37	[135]
UiO-66-aminoalcohol		308	20	11.6		[140]
$[Cu_2(TCMBT)].6H_2O$	808	298	20	25.5	26.7	[141]
Mn-DOBDC	1256	273	1	33	29	[20]
		298	15	57.3		
			1	26.4		
			15	44.5		
EDA–Mn-DOBDC	1203	273	1	49	32	[20]
		298	15	70.4		
			1	33.5		
			15	57.2		
Cu (TATB)	3360	293	–	–	61	[139]
$Mg_2(DOBDC)$	–	313	1	30.8	–	[27]
Mg(DOBDC) EDA	–	298	1	7.04	30	[27]
$[Cu_3(TDPAT)]$	1938	273	1	25.8	42.2	[139]
$Cu(pia)_2(SiF_6)(H_2O)_{12}$	285	296	1	5.5	30	[139]
$[Cu_3(BTC)^{-6}]_n$	3288	273	20	157	–	[142]
$[Cu_3L_2(H_2O)_5]$	2690	273	1	27.3	–	[141]
Ni-DOBDC	1017.5	298	1	20.5	42	[135]
Cu-BDC⊃HMTA	730	273	1	21.2	29.8	[20]
			14	52.8		
Amino MIL 53	262	273	1	18	28	[143]
Eu-NH₂-BDC	605.8	273	1	35.59	25.4	[144]
		298		4.10		
Mg-ABDC	63	273	1.3	6.18	–	[145]
Co-ABDC	71	273	1.3	34.97	–	[145]
$Cu_2(BDPT^{4-})(H_2O)_2$	1400	273	1	30.7	22.5	[142]
Cu-BDC	708	273	1	5.28	–	[20]
			14	17.4		
Amino MIL 101	2100	298	29.6	62	–	[143]
UIO-66-NH₂-NO₂	868	273	1	3.88	–	[146]
Mn-H₂ABDC	1453	273	1	40.9	32	[147]
		273	15	92.4		
		298	1	27.3		
		273	15	74.8		

and showed great fluorescence emission. When activated these frameworks showed excellent gas separation and storage possessions for CO_2.[167] The synthesis of flexible functionalized MOF, i.e. MIL-53(Fe), was performed along with introducing many functional groups like $-CO_2H$, $-Cl$, $-CF_3$, $-Br$, $-CH_3$, $-OH$, $-NH_2$. Scientists concluded that the pore geometry is largely interrelated with the intra framework interactions.[168] Still, there is sufficient room for enhancement of pre-synthetic modification technique for MOF materials by selecting organic ligand, functional groups and optimizing synthesis conditions and parameters.

2.4. MOFs Topology

The structural network formed by the metal nodes and linkers in a MOF is called MOFs topology. Understanding the role and effect of the MOF topology on the selective capture and separation of CO_2 is a crucial key to design the optimum MOF material. For example, the construction of MOFs with a topological cage structure with large cavities for the gas storage and small and defined pore windows is considered a unique characteristic of MOF design for the selective capture and trapping of the specific gas molecule.[169,170] To convict a solid sorbent material for the CO_2 selective separation and capture from other gases, scientists and researchers should consider the adjustment between the gas selectivity toward the targeted gas molecules and its adsorption capacity. MOFs that feature well-defined structural versatility and modularity have been examined for CO_2 selective capture. Designing a MOF with a specific active site for CO_2 based on the MOF's crystal structure and topology is a unique strategy for the selective CO_2 capture that MOFs are capable of. Two main strategies to design a selective MOF with targeted topology based on the secondary building units (SBUs) of the MOFs, (i) based on the design and selection of the organic linker or (ii) based on the selection of the metal cluster SBU.[170,171] For instance, Yu et al.[141] designed and synthesized multi-cage MOF termed NUM-3 from a tetracarboxylic acid linker (3,3', 5,5'-azobenzenetetracarboxylic acid) mixed with 2,4,6-tri(4-pyridinyl)- 1,3,5-triazine)to play as more coordination sites with the Ni atom. The two linkers worked as the surface and edges of the polyhedral cage. NUM-3 with (3,4,5)- connected topology has four different cagees in the order of ABCDDCBA minimum repeating uint with a 1 D channel. The activated NUM-3 exhibted good selective capture of CO_2 campared with C_2H_2 and C_2H_6 based on the sieving effect, in addition to high CO_2/N_2 and CO_2/CH_4 selectivity.

Luo et al.[173] synthesized a MOF-74 isomer $Zn_2(H_2O)$-(dobdc).0.5(H_2O) called UTSA-74 from the same metal and linker of the original Zn-MOF-74 (Zn salt, and 2,5-dioxido-1,4-benzenedicarboxylic acid). UTSA-74 has a new **fgl** topology with 8.0 Å one dimensional channels. Compared to the original MOF-74, UTSA-74 contains two different Zn^{2+} sites in its secondary building units (SBU) one is an octahedral and other is tetrahedral coordination geometry. Thus, the new MOF-74 isomer here contains two open metal active sites after activating and removing the water guest molecules. These active sites are binding to the CO_2 molecules through bridging instead of terminal binding in case of the Zn-MOF-74. Another example of MOF-pore-sieving gas separation is NbOFFIVE-1Ni developed by Eddaoudi and coworkers.[174,175] NbOFFIVE-1Ni is a 3D microporous framework constructed from Ni(II) pyrazine with $(NbOF5)^{2-}$ as pillars connecting the framework square-grid layers. The developed NbOFFIVE-1Ni

(also known as KAUST-7) is considered an isostructure of the previously explored SIFSIX series. The substitution of the inorganic pillars of SIFSIX, which is $(SiF6)^{2-}$ with a larger cation $(NbOF5)^{2-}$ in the NbOFFIVE-1Ni structure, leads to reducing the pore aperture from (5.0–7.3 Å) to (3.0–4.8 Å).[176] NbOFFIVE-1Ni exhibited the record of CO_2 uptake from air at 400 ppm with adsorption capacity of 1.3 mmol g^{-1} at 298 K. Selective physical binding of CO_2 inside the confined pore structure is proved using the single XRD study of NbOFFIVE-1Ni with CO_2. Under both dry and wet conditions, NbOFFIVE-1Ni offers highly selective CO_2/N_2 dynamic separation in a mixed gas breakthrough measurement. In another study, Eddauodi and coworkers have developed a series of cage-based MOFs with different topologies based on the linker used. They utilized the Rare-Earth hexanuclear RE cluster $RE6(OH)_8(COO)_{12}$ with a 2-fluorobenzoic acid modulator. When linear linker was used *fcu* MOF topology was explored while *pek*, *aea*, and *gea* nets were discovered with tricarboylate linkers, and *ftw* and *shp*-MOFs with a quadrangular tetracarboxylate linkers and alb MOFs with haxacarboxylates. These variations in the MOF topology and the tuning of the pore window and cage sized have shown great promise in the selective CO_2 separation from different gas streams.[177–179] Although the great promise from the design of MOFs is based on the topology point of view, functionality/topology selection should be considered for designing the new MOFs for selective CO_2 capture. Combining experimental research with computational modeling is critical to fully understand the structure relationship assuming the topology control. Anderson et al.[172] investigated the role of the different chemical functionalities and topology analysis in the CO_2 adsorption using a multi-scale density functional theory (DFT) approach and grand canonical Monte Carlo (GCMC) combined with machine learning (ML). The proposed algorisms based on the MOF organic linkers and topological features assist in determining these MOF characteristics in the CO_2 capture and separation (Figure 6).[172]

Depending on the crystal structure, Zhai et al.[180] prepared mixed metal MOFs with a combination of divalent metal (Mg^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}) and trivalent (Ga^{3+}, V^{3+}, Sc^{3+}, Fe^{3+}, In^{3+}), called CMP-200 series. It was found that at 1 bar and 273 K a high level uptake of CO_2 is 9.27 cm^3/g was obtained in case of a heterometallic MOF of Mg^{2+} and Fe^{3+} as shown in Figure 7. In another work Botas et al.[181] partially exchanged the Zn^{2+} of the MOF-5 with the Co^{2+}. The CO_2 adsorption capacity at 10 bar pressure and 273 K increase from 48 % to 67 % by weight. Michael O'Keeffe reported the synthesis of rod MOF based on Mn metal such as ROD-6. It signifies an uncommon topology comprising both a polytopic linker (1,3,6,8-tetrakis(p-benzoic acid)pyrene) and a secondary building unit (rod SBU).
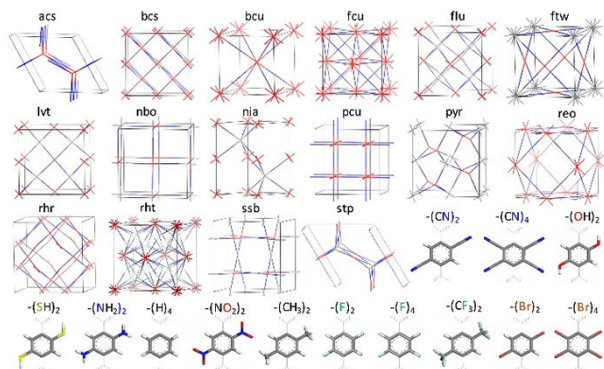
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Figure 6. Representative MOF topologies used in the construction of over 400 MOF. Along with the common functional groups in the substituted terephthalate linker.[172] Copyright © 2018, American Chemical Society.
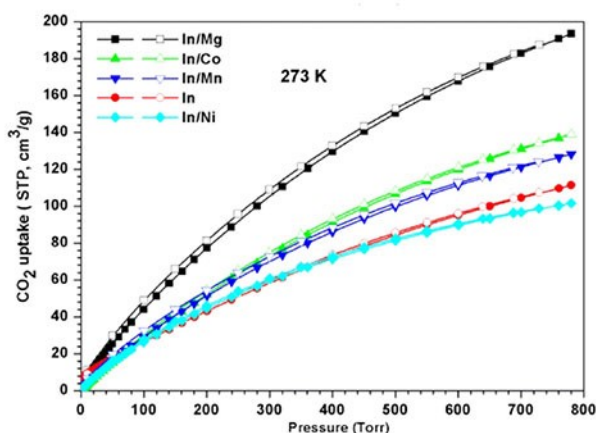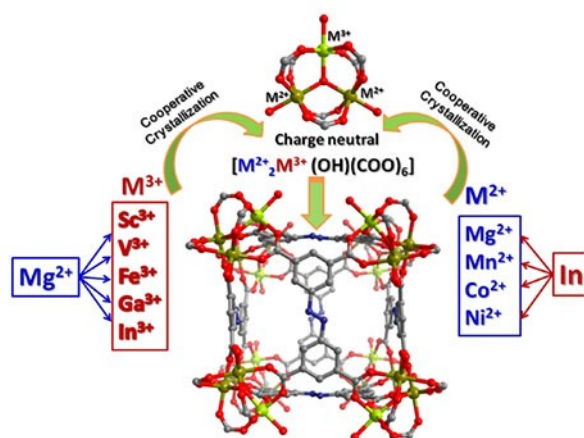

Figure 7. Structure of CMP-200-M^{2+}/M^{3+} series and CO_2 uptake capacity.[180] Copyright © 2016 American Chemical Society.

The topology in ROD-6 is organized inside two interconnecting planes, offering a considerable closer contact of

4.32 Å among the pyrene centers. Before employing a recommended deconstruction method, the SBU was a zigzag ladder, and two branches containing tetratopic linker is shortened to a two linked triangles. This MOF CO_2 uptake was 60 cc/g at 1 bar and 273 K temperature.[182] Liu et al.[183] reported $[Cu(L)(4,4'\text{-bipy})(H_2O)]_n$ $1.5nCH_3CN$ (H_2L = diphenylmethane-4,4'-dicarboxylic acid) MOF. They illustrate the $CdSO_4$ as a net and apparent 1D channel. More significantly, at low pressure 1 demonstrate high CO_2 selectivity, which inveterates through computational calculations via applying the Connolly algorithm to disclose the shape and size of available cavities. Thus it shows a high CO_2 adsorption of $86.5\ cc\,g^{-1}$ under 195 K and 1 bar pressure conditions. Pal et al.[184] reported a 3D MOF, {[Zn-$(OBA)(L)_{0.5}]$. DMA}$_n$ has been prepared by combining of linker (H_2OBA = 4, 4'-oxybisbenzoic acid) with N,N donor spacer (L = 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene). The framework presents rhombus-molded channels of estimated size 5.3 Å × 6.4 Å with 31.8% of prospective solvent in an available volume. Evacuated framework gas sorption measurements showing 40 $cc\,g^{-1}$ of CO_2 uptake at 1 bar pressure and 273 K temperature.

2.5. Functionalization

2.5.1. Functionalized Ligands in sMOFs

Synthetically tuning of the MOFs structural frameworks with the different functional group are called functionalization. MOFs are porous network materials comprised of inorganic units connected by appropriately functionalized organic ligands, which have been considered a suitable material for storing and capturing CO_2.[185] Ligand functionalization improves the selective adsorption of CO_2 over the mixture of gases and improves the stability of frameworks. Many families of porous materials have been prepared with high thermal and chemical stability, producing a capable candidate for adsorption of CO_2 as a mixture of gases.[186] In MOFs, the CO_2 interaction with organic linkers is particularly significant since linkers play a prevailing role in CO_2 adsorption. Moreover, improving gas uptake, selectivity, and the attraction for CO_2 by MOF can be achieved through tuning the interaction of CO_2 and introducing different functional groups in linkers, i.e. OSO_3H, $-NO_2$, $-OH$, $-NH_2$ etc..[187] Other polar groups such as $-N=C\,(R)-$, $-OH$, $-NH_2$, $-N=N-$ in their framework show substantial selective adsorption of CO_2 from other gases. In this perspective, sulphonate and phosphonate functionalized ligands must be considered. The functional group has a considerable effect on framework water stability as flue gas comprises small amounts of water vapors that surprisingly affect the uptake of CO_2, specifically in MOFs.

The water stability of MOF plays an essential role in gas molecules adsorption technology.[188]

In this context, Taddei et al.[189] prepared MOF based on water-stable phosphonate ligands (Cu_3 (H_2L_2) (bipy)$_2$. $11H_2O$) [H_2L_2:N,N,N′,N′tetrakis (phosphonomethyl)hexamethylenediamine]. According to their consideration, at ambient temperature, this MOF uptakes CO_2 up to 73 cm^3/g signify a high value of gas adsorption and show considerable CO_2/N_2 selectivity and this denote two consequences, first ligands polarity induced by P–O group presence that boost the uptake of CO_2 (due to their quadruple movement), secondly in activation process pores were filled from CO_2 and no pores would persist to take up nitrogen.

A few other water-stable MOFs CALF-25 and CALF-30 were designated by Tayler et al.[173] and Gelfend et al.[174] demonstrated high CO_2 adsorption capacity. They showed considerable stability even after in 90 % humid environment it retains their structure. The stability arises because of steric group presence on ligands that lead to the formation of a hydrophobic framework.

Considering the amines affinity towards CO_2, amine functionalized linkers have been incorporated into frameworks for improving the selectivity and adsorption of CO_2 over range of pair gases i. e. CO_2/CH_4; CO_2/N_2. Aluminum and amino based framework such as [Al(OH)(NH_2bdc)], the amino groups incorporation lessens the quantity of polar sites thus at lower pressure, i. e. below 2 bar resulting in negligible methane adsorption in the following framework. Amino and hydroxyl groups′ existence significantly boosts the framework selectivity towards CO_2 adsorption.[190]

Amongst the functional groups that were investigated, OSO_3H shows maximum interaction energy of -5.4 kcal/mol with CO_2, which is nearly two times higher than the benzene binding energy (-2.9 kcal/mol).[186] Likewise, CO_2 selective adsorption over H_2, CH_4 and N_2 due to a material that is sulfone-functionalized, i. e. H_3O [$Zn_7(m_3-OH)_3(bbs)_6$] by preferential interaction of CO_2 with polar sulfone group.

Functionalization enhances the uptake of CO_2, in contrast to N_2 with low pressure, i. e. 0–1 bar, i. e. Frameworks grafted through groups that partake great attraction for CO_2. For instance, [Zn_2(bttb)(py-CF_3)$_2$] where bttb^{-4} (4,4,4,4-benzene-1,2,4,5-tetrayltetrabenzoate) integrates the pyridine based linker such as py-CF_3 (4-(trifluoromethyl)pyridine). Certainly, the CO_2/N_2 selectivity calculated using py-CF_3 amended framework was found higher than zeolites and activated carbons.[191,192]

Moreover, during the modification of ligands via amine groups to enhance uptake capacity, the chain length also affects porosity, surface area, and uptake capacity of MOFs for CO_2. With respect to the eminence of following parameters, Keceli et al.[193] described the functionalization of linker with amide possessing diverse chain lengths, i. e. R; CH_3, C_2H_5, C_3H_7, and

C_4H_9; it was observed that MOF functionalized with amide having shorter chain length (R; CH_3) exhibits high adsorption capacity for CO_2 such as 4.65 mmol/g in comparison to C_4H_9, exhibits lower CO_2 adsorption capacity, i. e. 2.95 mmol/g. Serra et al.[194] performed a contrasting study between amine functionalized MIL-101(Al) and MIL-101 (Al) MOFs. The observed amine-functionalized MIL-101(Al) displays improved CO_2 adsorption selectivity and capacity over other gases. Due to high thermal stability and fast regenerability, MOF also acts as a potential candidate for natural gas separation. Also, IRMOF-74, and IRMOF-74-III-CH_2 NH_2 structures were modified by inserting different functional groups within the frameworks i. e. $-NH_2$, CH_2NH_2. CH_2NHMe shows 3.2 mmol g^{-1} CO_2 uptake capacity at pressure up to 1 bar.[195] Further investigations are still needed to test moisture stability, mechanical stresses, high temperatures and the regeneration ability of MOFs in the presence of various functional groups. Table 3 shows the selectivity of various reported MOFs for CO_2/CH_4, CO_2/N_2, or CO_2/H_2 separations.

2.5.2. MOFs with Multiple Functional Groups

Another strategy to boost the uptake of CO_2 by MOFs is to employ mixed ligands in MOF synthesis. Several functional groups combinations enhance MOF′s adsorption and selectivity capacity and increase the MOF′s thermal and mechanical stability. For instance, Zhang et al.[196] prepared multifunctional MOF [Zn_2(Atz)$_2$(ox)] via solvothermal technique by employing mixed ligands i. e. 3 amino-1,2,4-triazole (3-AT) and oxalic acid. According to the results in Figure 8, the prepared MOF demonstrates a significant increase in CO_2
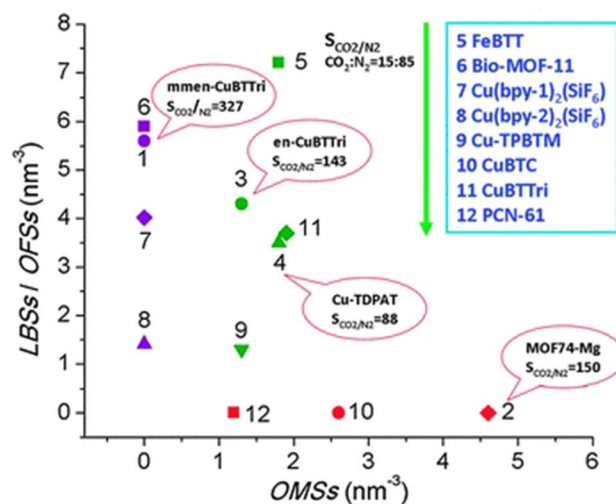

Figure 8. The effect of dual-functionality (OMSs and LBSs/OFSs) on the MOF adsorption selectivity (*S*) for CO_2/N_2 (15/85) at room temperature and 1 atm.[196] Copyright © 2013 Royal Society of Chemistry.

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Table 3. Reported MOFs for CO_2/N_2, CO_2/H_2 or CO_2/CH_4 separations in post-combustion and pre-combustion CO_2 capture.

Materials	Condition for CO_2 uptake	Separation selectivity applications	Ref
$[Zn_4O(btb)_2]$ (MOF-177)	33.5 mmol/g, 298 K, 32 bar	CO_2/CH_4	[202]
$[Zn_4O(bdc)_3]$ (MOF-5)	2.10 mmol/g, 9.24 wt%, 295 K, 1 atm	CO_2/CH_4	[202]
$[Zn_4O(NH_2bdc)_3]$		CO_2/CH_4	[202]
$[Zn_4O(fma)_3]$	69 wt% CO_2 vs. 8.6 wt% CH_4, 300 K, 28 bar	CO_2/CH_4	[203]
$[Cr_3F(H_2O)_2O(btc)]_3$ (MIL-100)	18 mmol/g vs. 7.5 mmol/g CH_4, 303 K, 48.7 bar	CO_2/CH_4	[204]
$[Cr_3F(H_2O)_2O(bdc)]_3$ (MIL-101)	40 mmol/g vs. 12 mmol/g	CO_2/CH_4	[204]
$[Cu_3(btc)_2]$	12.7 mmol/g, 15 bar vs.4 mmol/g	CO_2/CH_4; CO_2/N_2	[202, 205]
$[Cu_2(BPnDC)_2(bpy)]$ (SNU-6)	25.8 mmol/g, 114 wt%, 195 K, 1 bar, 2.50 mmol/g	CO_2/CH_4; CO_2/N_2	[206]
$[Ni_2(NH_2bdc)_2(dabco)]$	14 wt%, 298 K, 1 atm, 60 wt%, 25 atm	CO_2/CH_4	[207]
$[Ni_2(bdc)_2(dabco)]$	10 wt%, 298 K, 1 atm,	CO_2/CH_4	[207]
$[In(OH)(NH_2bdc)]$	8 wt%, 298 K, 1 atm	CO_2/CH_4	[207]
$[In(OH)(bdc)]$	4 wt%,298 K, 1 atm	CO_2/CH_4	[207]
$[Mg(tcpbda)]$	1.49 mmol/g, 6.5 wt%, 298 K, 1 atm vs. 0.45 mmol/g % CH_4 and negligible N_2	CO_2/CH_4; CO_2/N_2	[119, 208]
$[Mg_2(dobdc)]$	23.6 wt%, 298 K, 0.1 atm, 35.2 wt% at 1 atm, 63 wt% at 50 bar	CO_2/CH_4	[209]
IRMOF-74CH$_2$ –NH$_2$–	3.2 mmol/g CO_2 adsorption at 1 bar	–	[195]
en-Cu-BTTir	0.366 mmol/g CO_2 adsorption at 0.06 bar	–	[210]
Mmen-CuBTTir	2.38 mmol/g CO_2 adsorption at 0.06 bar	CO_2/N_2	[211]
MIL-101-PEI (Polyethylene imine)	4.2 mmol/g CO_2 adsorption at 0.15 bar	CO_2/N_2	[212]
Mg-MOF-74 TEPA (Tetraethylenepentamine)	26.9 wt% at 760 torr	–	[213]

adsorption to 4.35 mmol/g under 273 K temperature and 1 bar of pressure. The remarkable CO_2 uptake by MOF is due to the availability of two active sites in the framework such as the presence of free amine group and lone pair availability on nitrogen, CO_2 interacts with amine group via hydrogen bonding (N–H….O) and interaction of lone pair of nitrogen with carbon of CO_2. Moreover, oxalic acid ligand oxygen of multifunctional ligands enhances the stability and uptake capacity and increases the MOF affinity for CO_2.[197] Besides, Luo et al.[198] reported zinc-based MOFs decorated with multi-functional groups, i.e. –COOH, –NH$_2$, –OH, –NO$_2$ and –H.

According to their results, mixed functional MOFs show remarkable enhancement in uptake capacity at 273 K and 1 bar. Thet prepared five structural isomorphs, and 1-D hexagonal channels functionalized with a variety of organic shutters capable of tunable properties and selective gas adsorption. The research findings indicate that the selective CO_2 adsorption capacity of 3 is due to the combined action of the acylamide and amide groups. Recently seal et al.[199] developed the CSMCRI-9, a dual functional Cd(II) MOF using electron-rich tricarboxylate ligands, functionalized pyridyl linkers, and $[Cd_3(COO)_6]$ SBUs. The prepared activated

MOF showed physisorbed CO_2 affinity ($Q_{st} = 28.21$ kJ mol^{-1}) with highl CO_2/N_2 selectivity (343.05) with multicyclic CO_2 sorption stability. These multi-functional MOFs not only capture the CO2 but also behave as catalysts in CO_2 fixation.

2.6. Introduction of Open-metal Sites in MOFs

MOFs containing open metal sites (OMS) are potential CO_2 capture candidates. The metal ion used to generate the open metal site in MOFs ought to be a component of the metal node or metal structural building unit. In many applications, activating of open metal sites in MOFs is seen as significant. Further, when comparing MOFs with completely occupied metal sites, the OMS in MOFs often constitute the stronger binding sites, resulting in enhanced interaction with various sorbate molecules and have higher binding energy.[200] Also, to some extent, increased porosity of OMS-MOFs results in a greater gas absorption. Further, CO_2 and OMS have interaction energy of more than 30 kJ/mol, resulting in a strong CO_2 absorption at relatively low pressure and the OMS-CO_2 adsorbate binding affinity is linked with electrostatic interactions.

Accordingly, Sayo et al. demonstrated that for Mg-MOF-74, the predicted zero-coverage adsorption energy (47.9 kJ/mol) for CO_2 adsorbed at the open Mg^{2+} sites is in good accordance with the actual finding (45 kJ/mol).[201] Likewise, According to Brown et al., the CO_2 adsorption capacity is determined by the CO_2 molecule's bond strength to the OMS. There is some evidence to suggest that CO_2 adsorption capacity is dependent on OMS-CO_2 molecule bond strength, according to Brown et al. When it came to Cu^{2+}, the M-MOF-74 series had the lowest binding enthalpy because the oxygen atoms along the axial ligand were too lengthy, which made it difficult for CO_2 to reach the Cu^{2+} site[214]

In addition, a study by Matzger et al. found that the metal oxide nanoparticles (Zn-MOF-74) and three of their isostructural counterparts (Co-MOF-74) were effective in CO_2 adsorption. At 0.1 and 1 bar, Mg-MOF-74 absorbed 236 and 352 mg/g of magnesium, respectively. During sorption study for different gases, Grajciar et al. found that CO_2 molecules preferably adsorb low-covered, coordinated unsaturated Cu-BTC sites.[215] Yazaydn et al. discovered that adding a few water molecules co-ordinated to Cu-open-metal BTC's sites substantially improved CO_2 absorption as well as its selectivity over N_2 and CH_4 [216]

Similarly, an open metal sites containing framework i.e. $[Zn_3(OH)(p\text{-}cdc)_{2.5}(DMF)_4]$ where p-cdcH$_2$ = 1,12-dihydroxydicarbonyl-1,12- dicarba-closo- where p-cdcH$_2$ = 1,12-dihydroxydicarbonyl-1,12-dicarba-closo-dodecaborane, comprises on unsaturated coordinated Zn^{2+} sites. Unsaturated open metal sites showed greater adsorption capacity because of favorable interaction between Zn^{2+} and CO_2 quadrupole moment.[120] Related improvements have been reported for $[Ni_2(NH_2bdc)_2(dabco)]$ where dabco = 1,4-diazabicyclo [2.2.2] octane an amine-functionalized frameworks. Alkylamine-functionalized frameworks have shown improved selectivity towards CO_2 adsorption, specifically for the separation of flue gas. Plainly, wide possibilities can be envisioned to tune amine-functionalized framework adsorption capacity and their through incorporating sterically hindered, secondary and tertiary amines at bridging ligands or unsaturated open metal sites.[207]

Thus, the presence of OMS in the MOF enables the metal site and guest molecules to interact more effectively and enables the MOF to efficiently adsorb the CO_2 molecules,incorporating sterically hindered, secondary and tertiary amines at bridging ligands or unsaturated open metal sites.[207] Thus, the presence of OMS in the MOF enables the metal site and guest molecules to interact more effectively and enables the MOF to efficiently adsorb the CO_2 molecules.

2.7. Basicity in MOFs

CO_2, being an acidic molecule, has a great affinity towards basic metal oxides nodes in MOFs. A metal oxide with a small charge to radius ratio is more ionic in character, and CO_2 molecules adsorb on available positive and negative metal oxide sites. It would present more basic sites for CO_2 to absorb. Although acidity in zeolites and metal-oxides plays a crucial role in catalysis,[217–224] it also plays an essential role in CO_2 capture and separation. The adsorption capacity for CO_2 is removed reversibly for metal based oxides i.e. CaO and MgO.[225] In comparison, MOFs retaining Lewis acid sites which derive from metal centers, i.e. Al^{3+}, Mg^{+2}, Cr^{3+}, Cu^{2+}, Co^{2+}, and Zn^{2+} to which ligands coordinate via the particular functional group. Moreover, it can be precisely premeditated by modifying its structural features by decorating it with particular functional groups i.e. −OH, NO_2, −NH_2, etc for exploiting its CO_2 selectivity.[226,227] CO_2 either act as Lewis acid or Lewis base varies on the nature of functional group. The electrostatic attraction accelerates the prepared framework and affects the CO_2 site in the augmented geometries.[228] In addition, the CO_2 capability to act as weak Lewis base or acid by the oxygen atom site which is electron rich and carbon site which is electron deficient.[229] In comparison to reported frameworks its metal sites i.e. Al^{3+}, Mg^{+2}, Cr^{3+}, Cu^{2+}, Co^{2+}, and Zn^{2+} retaining Lewis acid sites, whereas, its ligand sites having particular functional group such as pyridyl, carboxylate act as Lewis base sites.[36]

For enhancing MOFs adsorption capacity for CO_2, MOFs structure is modified by introducing amine-functionalized ligands that exhibit a considerably high adsorption capacity for CO_2 amine groups act as Lewis base show high affinity for CO_2, which act as Lewis acid. Such as, Pachfule et al.[230] reported amine-functionalized penetrated isostructural MOFs; Cd-ANIC-1 and Co-ANIC-1 (where ANIC: 2-amino-isonicotinic acid) exhibits considerably high CO_2 uptake capacity such as 4.72 mmol/g for Cd-ANIC-1 and 4.22 mmol/g for Co-ANIC-1, respectively. This desirable high adsorption capacity for CO_2 is attributed by amine-functionalized ligands Lewis basic effect, as shown in Figure 9.

In MOFs, the presence of unsaturated metal sites offers a superior separation of gas pairs, such as CO_2/CH_4. Among the reported instances, HKUST-1 which comprises of $Cu_2(COO^{-1})_4$ paddle wheels connected via btc^{-3} ligands (1,3,5-benzenetricarboxylate), The framework favorably adsorbs CO_2 with enthalpy of adsorption 30–35 KJ/mol over a mixture of gases i.e. CH_4 and N_2.The adsorption mechanism can be explained via coordinating CO_2 to the metal center i.e. O=C=O···Cu^{2+} in an end-n fashion.[231] The absorption and selectivity of material dependent on inorganic building structures and metal, for instance, Mg comprising MOF, have established the prevalent interface strength between other
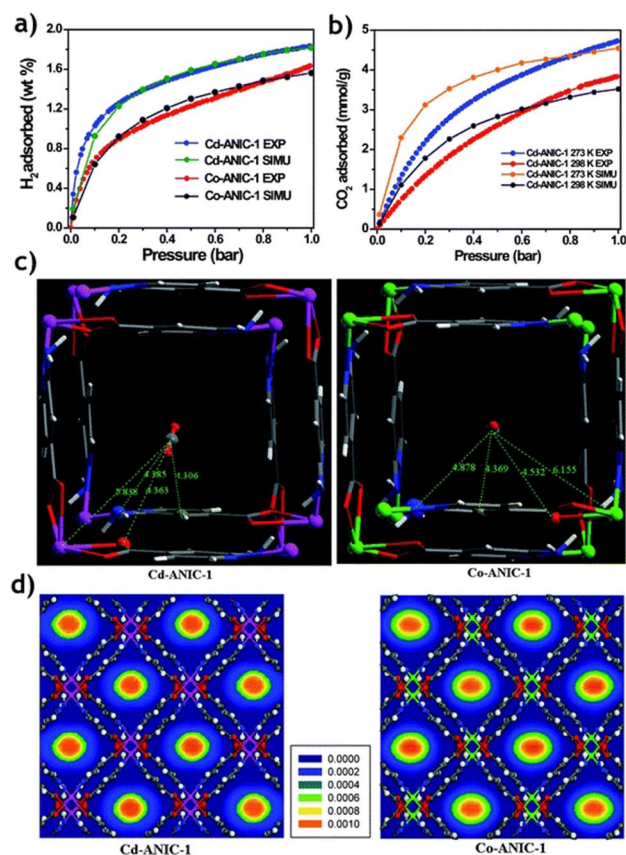
Figure 9. Simulation results for Cd-ANIC-1 and Co-ANIC-1. (a) Experimental and simulated H_2 adsorption isotherms for Cd-ANIC-1 (blue and green circles) and Co-ANIC-1 (red and black circles). (b) Experimental and simulated CO_2 adsorption isotherms for Cd-ANIC-1 at 273 K (brown and blue circles) and 298 K (black and red circles). (c) Distances between CO_2 and framework atoms C_2, Cd, O and N_2 in Cd-ANIC-1 and C_2, Co, O and N_2 in Co-ANIC-1. (d) Density contours of H_2 adsorption at 1 kPa in Cd-ANIC-1 and Co-ANIC-1. (Color code: Cd: pink, Co: green, O: red, H: white, N: blue, C: grey).[230] Copyright 2016 Royal Society of Chemistry.

studied metals. The uptake capacity of CO_2 by $[Mg_2(dobdc)]$ is 47 KJ/mol is double then that of any isostructural framework series i. e. for M=Co and Ni show uptake capacity for CO_2 41 and 37 mmol/g correspondingly, recommends CO_2 preferential adsorption on Mg^{2+}.[207,208] Adsorption of CO_2 investigated in MIL series i. e. MIL-100 $[Cr_3F(H_2O)_2O(btc)]_3$, MIL-101 $[Cr_3F(H_2O)_2O(bdc)]_3$ have Cr^{3+} with coordinatively unsaturated sites and have higher capacity for CO_2 adsorption involving $O=C=O\cdots Cr^{3+}$ endwise coordination.[232]

2.8. Chemical Doping in MOFs

Doping is the introduction of foreign entities into MOFs structure for enhanced properties. The doping technique has been established effectively in MOFs to improve the selective separation and high uptake of CO_2. The doped metal cations

essentially trigger the adsorption site and change the CO_2 molecule structure pattern in pore space by virtue of the influence of thermodynamic balance and electrostatic influence. The metal atoms which can be used for metal doping include Pd, Li, Na and Cd. Owing to high electro-positivity and lightweight, lithium is commonly the best candidate for metal doping. Li-doped MOF-5 with a very high electronegative value across aromatic rings has been proven to be the preferred CO_2 adsorption site and doping of Li atoms on MOF-5, in strong accordance with the substantial rise in electrostatic contribution and improve the selectivity of CO_2 over methane. Xu et al.[233] analyzed the Li-MOF-5 systemically to attain strong CO_2 discernment over CH_4, owing to Li atoms' inclusion that ascribed to the enhanced electrostatic potential. Smith et al.[234] in their study with Titanium exchanged UiO-66, reported the rise in the CO_2 adsorption from 2.3 mmol/g to 4.0 mmol/g by the substitution of Zr^{4+} with the Ti^{4+}. The titanium introduction decreases the pore size and increases the interaction with titanium, causing an increase in the CO_2 uptake (Figure 10). Chemically, CO_2 is an acidic gas that could best interact with surface abundant in Lewis sites. In this perspective, the introduction of metallic species such as Pd, Li, Co, etc. provides additional Lewis sites that can preferentially interact with the CO_2. This phenomenon consequently upgrades the capture capacity of the MOFs materials. Although metal doping procedures onto the MOF structures are recent areas of interest with few studies documented, strategies for metal doping on oxides and zeolites have been well-established.[235] Therefore, such strategies should be escalated by employing numerous other metals like Cd, Zn, Ni, etc. These species have good potentials to create extra-framework Lewis sites and consequently escalate the CO_2 capture capacity.

Key issues that must be considered here include the pathways for enhancing active sites stability, timely retention of the captured CO_2 and the chances to regenerate the doped-MOFs after interaction with the captured CO_2.
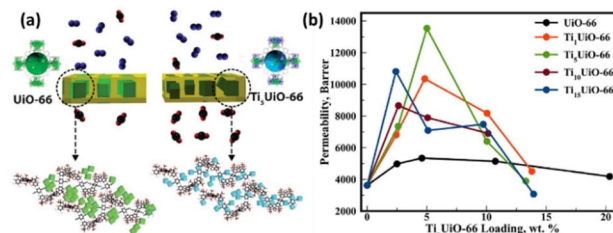

Figure 10. a) Ti-exchange of UiO-66 MOF increases the interaction with PIM-1 polymer, leading to a drastic increase in CO_2 permeability compared to a UiO-66 PIM-1 membrane. b) CO_2 Permeability of PIM-1 TixUiO-66 mixed matrix membranes. Permeability measurement recorded with a pressure differential of 2 Bar, at 298 K and within 1/2 5% deviation adopted with permission from Ref..[234] Copyright © 2015 Springer Nature.

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Adhikari et al.[236] reported MOF-74 with cobalt and nickel doped with palladium loaded on activated carbon (AC) show remarkable CO_2 uptake capacity, such as MOF-74 (Co)-Pd exhibits 11.42 mmol/g adsorption capacity and MOF-74(Ni)-Pd exhibits 12.24 mmol/g at 32 bar and 298 K. The uptake of CO2 was facilitated by a partially negative charge carrying oxygen atoms interaction with artially positive charge Pd because of its low electronegativity.

Cao et al.[237] reported alkali metal-doped HKUST-1 for selective and high uptake of CO_2. The results demonstrate that the HKUST-1 doped K^+, Na^+ and Li^+ storage capacity for CO_2, was larger than undoped HKUST-1. The CO_2 uptake at 18 bar and 298 K was 8.64 mmol/g was shown by 1 K-HKUST-1 than in contrast to HKUST-1 with an adsorption capacity of 7.72 mmolg^{-1}. Following remarkable uptake of CO_2 via 1 K-HKUST-1 was reliant on high pore volume, surface area, charge and size of cation and cations distribution inside the framework of prepared materials. All these studies demonstrated that chemical doping in MOFs materials remarkably improves MOF′s capacity to capture CO_2 gas; However, it′s worth noting that there is a lot of room to develop efficient metal doping methods technique.

2.9. MOF Composites Formation

Composites with enhanced superficial properties are employed for CO_2 capturing, prepared by combining two or more MOF materials. They are mainly considered to fulfill the demands of technology concerning to different applications. For composites materials fabrication, numerous preparation methods have been used, i.e. Microemulsion, hydrothermal, co-precipitation and sol-gel, etc..[59,70,239–241]

One of the superlative methods of enhancing CO_2 adsorption has stimulated the researchers to fabricate MOF composites.[242] According to literature, MOF composites comprising graphene, graphite and carbon nanotube show a magnificent adsorption capacity for CO_2. Graphite and graphene should be employed in the form of reduced graphene oxide and graphene oxide for composites synthesis, as the functional groups on GO and rGO such as carboxylic, hydroxylic and epoxy, form a strong bond with metal sites in the framework results in the100 kPa, respectively. The enhancement of adsorption capacity is due to available metal sites present in the MOF. Also, because of cupper ions and carboxylate groups of graphite oxides strong coordination, GO@MOF-505 has demonstrated 80 % thermal stability.[238] adsorbent with ultra-high surface area. Several MOF composites has been synthesized to date adsorption of gases. For instance, Chen et al. reported GO@MOF-505 composites synthesized from copper-based MOF and graphite oxide from the solvothermal method as illustrated in Figure 11.
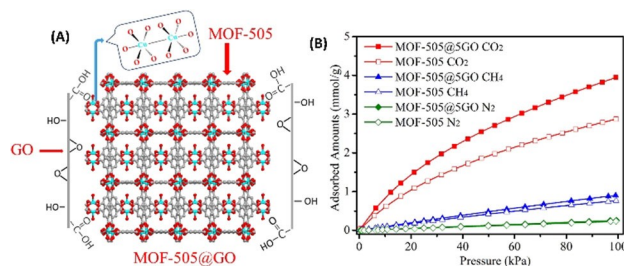

Figure 11. (A) MOF-505@GO composites formation (B) N_2, CO_2 and CH_4 fitted isotherms of MOF-505 and MOF-505@5GO at 298 K.[238] Copyright © 2016 Elsevier.

In contrast to parent MOF, Composites illustrate adsorption capacity up to 3.94 mmol/g and selectivity were up to 8.6 for CO_2/CH_4 and 37.2 for CO_2/N_2 at temperature 298 K and pressure

Furthermore, graphene oxide-based Cu–MOF effect on adsorption capacity of CO_2 was investigated by Huang et al..[243] They reported GrO@Cu-BTC MOF prepared by hydrothermal method. The results showed a remarkable improvement in CO_2 selective adsorption over methane in contrast to parent MOF Cu-BTC show uptake capacity 8.19 mmol/g at 1 bar and 273 K. This enhancement occurs because of the strong interaction of CO_2 to the framework of GrO@Cu-BTC. Analogous to graphene oxide, CNTs is an admirable candidate for the preparation of composites of MOFs. Anbia et al.[244] designed multi carbon nanotube composites such as MWCNT@MIL-101 (Cr) and investigate the composites adsorption capacity for CO_2 at temperature 298 K and pressure 10 bar. The result shows 60 % improvement in CO_2 adsorption than parent MOF, i. e. MIL-101 (Cr) from 0.84–1.35 mmol/g. The enhancement in adsorption capacity is related to the higher micropore volume achieved by MWCNT incorporation. In addition to carbon nanotubes composites, the effect of functionalized carbon nanotubes based composites were also investigated in the adsorption study of CO_2.[245] Yang et al. synthesized a functionalized CNT (hydroxyl-CNT) based new composite such as ZIF-8/CNT. According to their observations, there is a considerable enhancement in the CO_2 adsorption and thermal stability due to functionalized CNT presence. It is remarkable to note that crystal structure and morphology of ZIF-8/CNT is comparable to the parent ZIF-8 MOF but presented significantly high thermal stability.[252] Also, Cao et al.[253] reported graphene oxide-based MOFs UiO-66-NH$_2$/GO, UiO-66/GO. The composites exhibit an enhanced adsorption capacity for CO_2 at a temperature of 273 K up to 6.41 mmol/g in comparison to UiO-66/GO) having adsorption capacity 6.10 mmol/g and show CO_2/N_2 selectivity. With appreciable thermal stability. In addition, Zhao et al.[248] reported AGO and MOF-5 based composites for capturing of CO_2. The result shows MOF-5/

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AGO-H has high CO_2 uptake capacity i.e. 1.06 mmol/g at 25 °C and 1 bar. Abid et al.[254] reported MIL-96(Al), its capacity for CO_2 is boosts up by incorporating a second metal such as calcium. Adsorption studies analysis prove that prepared materials such as MIL-96(Al)-Ca1 & 2 at 950 kPa show enhanced uptake capacity for CO_2 compared to MIL-96(Al) due to its improved efficiency pore volume. These materials show CO_2 uptake in the given sequence such as 8.09, 9.38 and 10.22 mmol/g. However, the uptake for CO_2 decreases to 5.26 mmol g^{-1} for MIL-96(Al)-Ca4. Moreover, N_2 adsorption is considerably reduced by 90 % for MIL-96(Al)-Ca4 compared to MIL-96(Al)-Ca1 at comparable operating conditions. Besides, at pressure of 28.8 and 100 kPa, the selectivity is 841.42 and 67 for CO_2/N_2 by MIL-96(Al)-Ca4, respectively.

Table 4 illustrates the performance of the different composites at specific conditions for CO_2 capture.[248] Another strategy is the composite of second metal atoms into the MOF frameworks (M-MOF) are considered as one crucial feature for capture, separation and conversion. Due to facile functionalization in MOFs, it allows metal atoms to accommodate in the framework. This strategy of adding another metal to the MOF structure enhanced the parent MOFs′ characteristics and functionalities.[254] Eric D. Bloch and co-workers reported MOF′s synthesis with Aluminium and 2,2′-bipyridine-5,5′-dicarboxylic acid, which had the bipyridine coordination places. This on binding with Copper enhances the CO_2 uptake from 6 to 12 wt%.[255] Metal-cyclam Zirconium MOFs such as VPI-100 (Cu & Ni) showed an enhanced CO_2 uptake because of the copper and nickel metals presence. Metal-cyclam based MOF with copper demonstrated a CO_2 uptake of 33.8 cc/g and with nickel 28.2 cc/g. This was only possible due to the metal cyclam's presence with the Zirconium clusters.[256]

2.10. Hydrophobicity in MOFs

The water molecule in the post-combustion of CO_2 separation and capture is a daunting challenge. In this regard, the introduction of hydrophobic nature in MOFs plays a vital role in CO_2 capture during humid conditions. Besides pore window, stability and affinity, hydrophobicity is another main feature exploit in MOF membrane recently. Huang et al.[257] prepared a Zn(BDC)(TED)0.5 MOF membrane, which displays high stability and selectivity during on-stream humid CO_2/H_2 separation. The pore window did not block by the steam due to the hydrophobic nature of MOF. Two alkyl hydrophobic group were implanted in UiO-66 MOF, which realty enhanced its stability under the moisture condition for gas separation application.[258] Furthermore, a DFT calculation examined 15 different MOFs having different hydrophobic nature shed light on the possible utilization of these materials for industrial CO_2 capture in humid conditions.[258] Gupta et al.[259] choose two MOFs (hydrophobic and hydrophilic) having the same topology with 1-*n*-butyl-3-methylimidazolium thiocyanate ionic liquid for membrane fabrication. He concluded that the hydrophilic support is superior to the hydrophobic support during CO_2 capture. Following the advantages of hydrophobicity and controlled pore windows in MOFs several isoritucular MOFs were developed for harmful volatile organics capture.[260] Two isoretucular MOFs named UiO-66(Zr)-(OAc)$_2$ & (OPr)$_2$, were tested for CO_2 capture. The breakthrough analysis at wet flue gas show that UiO-66(Zr)-(OPr)$_2$ has adsorption selectivity up to 229 % for CO_2/N_2 compare to UiO-66(Zr)-(OH)$_2$ as illustrated in Fig-

Table 4. List of MOFs composites, conditions and properties reported for CO_2 adsorption.

Composites	Surface area (m²/g)	Adsorption Temp (°C)	Adsorption capacity (mmol/g)	Adsorption pressure bar)	Ref.
HKUST-1/ GO	1015.2	32	2.5	5	[246]
Aminated graphite oxide MOF/GO-U3	1367	4	7.27	1	[247]
MOF-Aminated graphite oxide MOF-5/AGO-H	430	25	1.06	4	[248]
MOF-Aminated graphite oxide MOF-5/AGO-O	294	25	0.54	4	[248]
Mixed amine composite MCM-41-TEPA30%-AMP30%	133	70	3.01	1	[249]
Aminated Cu-BTCgraphite oxide	1367	25	13.41	15	[247]
GO@MOF-505	1279	25	3.94	1	[238]
GrO@MIL-101	2950	25	22.4	25	[250]
GrO@Cu-BTC	1677	0	8.19	1	[243]
GO@HKUST-1	1554	0	9.02	1	[251]
MWCNT@MIL-101	1243	25	1.35	10	[244]
ZIF-8/CNT	1997	0	2.210	1	[252]
UiO-66-NH$_2$/GO	1052	0	6.41	-	[253]
UiO-66/GO	1184	0	6.10	-	[253]

ure 12.[261] This strategy of hydrophobicity successfully demonstrates to engineer MOF materials for practical capture and separation processes of CO_2 under wet conditions. Controlling the hydrophobicity of the MOFs not only is needed to enhance the water stability of the material but also will lead to precise control in many other applications. This tuning of the pore hydrophobicity of the MOF can be achieved by the post-synthetic modification of the exiting stable MOF. Li et al.[262]
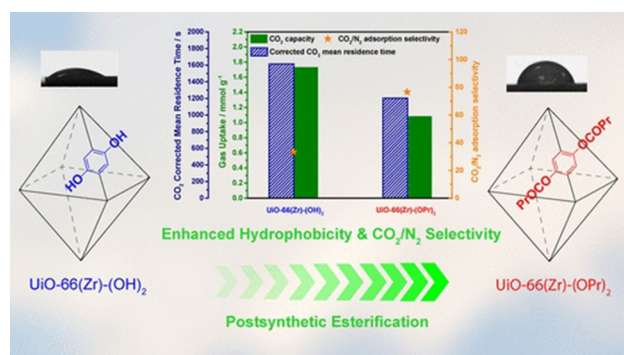

Figure 12. Effect of hydrophobicity for post-combustion CO_2 capture from wet flue gas.[261] Copyright © 2018 American Chemical Society

have investigated the systematic control of the hydrophobicity and water adsorption properties of the well studied MIL-101 (Cr) by the post-synthetic modification of the organic linker using primary amines with different alkyl chain lengths. The amine groups are coordinated with the Cr^{3+} cluster, and the alkyl chain will be hanging in the pore. As proved by the contact angle measurements, increasing the number of carbons of the alkyl chain has exponentially increased the contact angle. The water uptake capacity showed a positive shift in the pressure step by increasing the carbon chains' hydrophobicity.

2.11. MOF as Additive

Membrane technology surpasses the problems associated with the thermal and non-thermal adsorption separation of CO_2 from its mixture gases. The membranes technology further boosts the CO_2 separation performance after the discovery of novel porous MOFs. The addition of MOFs into polymer membranes solves the issue of permselectivity trade-off by the polymeric membrane. The high performance of these materials is contingent on the MOF loading and interaction with the polymer matrix.[263] Table 5 gives an overview of the role of MOFs additive as a unique strategy for CO_2 separation.

Table 5. MOFs as an additive for CO_2 selective adsorption.

MOF additive	Polymer	Loading Wt%	$P(CO_2)$	CO_2/CH_4	CO_2/N_2	H_2/CO_2	Ref.
HKUST	PI	30	22.1	29.8	–	3.0	[264]
MOF-5	PI	30	20.2	44.7	38.8	2.7	[265]
IRMOF-1	Ultem	10	2.8	27.8	–	–	[264]
HKUST-1	Pdms	10	3000	34	8.9	0.2	[266]
HKUST-1	Psf	5	6.5	18	20	1.5	[266]
ZIF-8	PPEEs	30	50	20.8	24.5	1.8	[267]
MIL-53(Al)	PMDA-ODA	5	0.3	72.1	34.8	1.1	[268]
ZIF-8	PIM-1	43	6300	14.7	18.0	1.1	[269]
ZIF-90	PBI	10				8.9	[270]
HKUST-1	PPO	10	68.7	16.4	16	1.1	[271]
ZIF-8	6FDA-durene	33.3	486.5	15.6	13.4	1.1	[272]
MIL-68	Psf	4	4.7	32	–	2.3	[273]
NH_2-MIL-53(Al)	PSF/PI	25	5.4	27.5	–	–	[274]
ZIF-8	PBI-BuI	30	5.2	43.6	16	4.2	[275]
ZIF-8	DMPBI-BuI	30	53.9	15.7	11.3	2.4	[275]
ZIF-8	DBzPBI-BuI	20	89.8	11.6	14.3	2	[275]
c-MOF-5	PEI	25	5.4	23.4	28.4	5.3	[276]
ZIF-71	6FDA-durene	30	7750	9.53	11.5	0.59	[277]
ZIF-8	PI/PSF	30	19	42		–	[278]
UiO-66	PIM-1	30	4500	22	28	–	[279]
ZIF-11	6FDA-DAM	30	73	30	–	1	[280]
ZIF-90	6FDA-TP	50	63	36	20	2.8	[281]
NH_2-MIL-53	VTEC	1			–	5	[282]
FeBTC	PEBAX	5	80	19.3	–	–	[283]
NH_2-MIL-53(Al)	Cellulose Acetate	30	1000	–	17.8	–	[284]
ZIF − 94	6FDA-DAM	40	2000	–	22.9	–	[285]
UiO-66	6FDA-Bisp	17	57	48	–	–	[286]
Cu-BPY − HFS	PI	30	10.4	25.5	–	–	[287]
ZIF-L	PI	20	19.4	4.6	3	13.4	[288]

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2.12. Defects Engineering

Defects in MOFs are the sites that locally break the regular periodic arrangement of atoms and linkers of the parent crystalline framework. The CO_2 adsorption influenced by the defect engineering depends on the two main factors (a) the density of the coordinatively unsaturated sites and (b) surface area and distribution of pore size. One of the interesting examples is the NOTT-202 that is made of $[In(COO)_4]$ units connected with biphenyl-3, 3′, 5, 5′-tetra (phenyl-4-carboxylate) linker. It has a disordered second net due to the symmetry relationship. This network fragmentation and defects help NOTT-202 to attain a high surface area and pore volume. The CO_2 adsorption, in this case, was found to occur in three steps indicating stepwise filling of the pores at 195 K. This study NOTT-202 has a greater affinity for CO_2 adsorption and trapping.[289] Wu and coworkers found that the linker vacancies lead to defects that increase the surface area and pore size in some cases the adsorption of CO_2.[290] There were also reports that the functionalization of these defects in case of PCN-125 leads to an increase in the affinity towards the CO_2 adsorption (Figure 13).[291] Synthesis of MOF-5 with DBA develops defects that result in the macro and mesopores with enhanced CO_2 uptake than MOF-5.[211,292] Guiyang Zhang and coworkers synthesized organosulfonate-based MOF with an imperfect primitive cubic topology. The MOF′s microporous nature showed the highest permanent porosity (~43 %) in sulfonate-MOFs with the highest CO_2 uptake of 102 cc/g and 74 cc/g at 273 K and 298 K under 1 bar among the organosulfonate based MOFs. This was mainly due to a large number of coordinated and dangling sulfonate groups

Figure 13. (A). Missing-Linker Defects in Zr based MOF UiO-66 and its significant Effects on Gas Adsorption,[290] Copyright © 2013 American Chemical Society. (B). Coassembly strategy for the induction of mesopores functionalized with a variety of substituent groups on the ligand.[291] Copyright © 2012 American Chemical Society.

which increases the affinity for the CO_2.[293] A. Koutsianos et al.[294] used post-synthetic defect exchange to create amino functionalities in the cluster defects in formic acid curtailed UiO-66 that were integrated with the picolinic and nicotinic acids (pyridine containing) and aminobenzoic acid and anthranilic acid. It was concluded that the defective sites having different nitrogen increases the overall CO_2 capture of the defective MOF. Moreover, the NH_2-functionalized MOFs presented improved functioning in comparison to materials carrying heterocyclic nitrogen group. In another study[295] UiO-66 was prepared under modified microwave assisted solvothermal method that produces changes in the defects concentration leading to pronounced effect on the CO_2 adsorption at low and the high pressure. They observed that under the use of HCl as the missing linker defects modulators the CO_2 adsorption decreases at 1 bar while it increases at 35 bar. Similarly, by using formic acid as the modulator for the generation of missing linker defects the CO_2 adsorption decreases both at 1 and 35 bar. At low pressure the decrease is mainly due to the CO_2-sorbent interactions. The difference in the adsorption between the formic acid and the HCl is mainly caused by the different interaction of the CO_2 with the OH^-, Cl^-, and /or $HCOO^-$.

2.13. Flexibility/Breathing in MOFs

Unlike the robust MOFs, Flexible MOFs are susceptible to structure change and change in the pore structure and surface area upon the effect of exterior stimuli, for instance, temperature or pressure or removing the dust molecules from the pore, also called breathing MOFs.[296,297] The pressure induced the Kitagawa group firstly discovered gate opening effect in 2003.[299] Due to this framework's flexibility in breathing MOFs, most of them behave non-porous frameworks when there are no pores′ gest molecules. Simultaneously, an induced gate opening and gas adsorption will happen after stimulation by temperature or high pressure, which allows the adsorption of gas molecules that can diffuse through this gate. Therefore, this unique class of flexible MOFs with their structure transformation, behave a gate opening mechanism that allows selective adsorption and separation of the targeted gas molecules via the molecular sieving effect.[300] Utilization of the flexible MOFs′ structural transformation and tuning the pore aperture is a unique strategy for selective CO_2 uptake from other gas blend in the stream.[301] For example, the selective capture of CO_2 from a blend of gases of industrial flue gas has been achieved by the 3D flexible framework called $[Zn(bpdc)(bpee)].2DMOF$ constructed from 4,4-biphenyl-dicarboxylate and 1,2-bis(4-pyridylethene) and Zn metal.[298] As shown in the single-component gas isotherms Figure 14 the material has an exceptional affinity toward
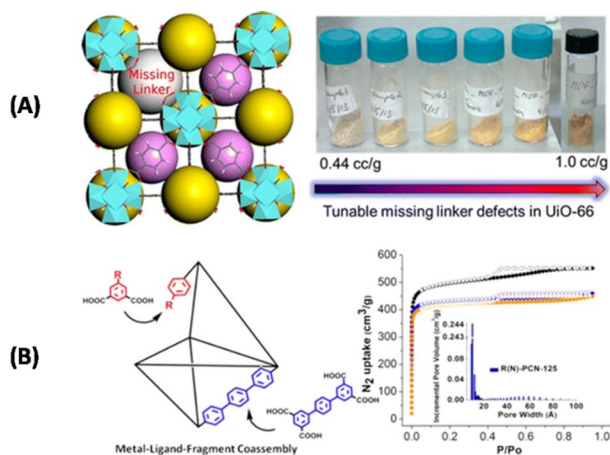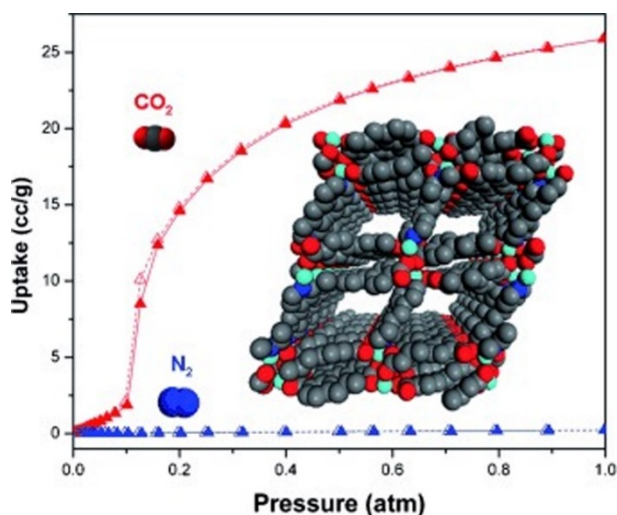
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Figure 14. Single component gas isotherms for N_2 (blue) and CO_2 (red) for the flexible MOF [Zn(bpdc)(bpee)].2DMF showing the ultrahigh CO_2/N_2 selectivity governed by the flexible MOF reprinted from ref.[298] Copyright © 2010 WILEY-VCH.

CO_2 compared to the N_2 with a practical step in the CO_2 isotherm at 0.1 bar for the gate opening effect. The [Zn(bpdc)(bpee)].2DMF flexible MOF exhibited CO_2 uptake of 5.4 wt% at 298 K and 1 bar with a selectivity of 294 of CO_2/N_2 at the same condition.

He et al.[302] followed the ligand exchange strategy to convert a three-dimensional rigid MOF into a new two dimensional flexible MOF. In this study, the rigid parent framework is first synthetized to form the solvothermal reaction of zinc acetate as the metal precursor with 4,4-biphenyldicarboxylate and 4,4-bipyridine as the linkers. Then the solid crystals were socked at 105 °C with a solution of the flexible linker 4,4-1,3-bis(4-pyridyl)propane, producing the daughter MOF. Although the parent 3D rigid MOF has a nitrogen uptake of 12 mmol g^{-1}, the daughter flexible MOF does not have any nitrogen uptake at 1 bar pressure and 77 K temperature. Interestingly, the flexible MOF exhibited a structural transformation from nonporous into porous frameworks upon the induction of a CO_2 and CH_4 molecules at 10 bar, indicating the structure flexibility. The resulting flexible MOF showed significant improvement in the selectivity of CO_2/N_2 mixture at 273 K and 1 bar related to the parent MOF with only CO_2/N_2 of 8 at the same conditions.[302]

The selective adsorption via flexible MOFs has shown great potential for separation-specific gas based on particular gate opening pressure. Chen et al.[303] reported the selective capture of CO_2 and C_2H_2 from the C_2H_4 polymer feedstock using the gate opening pressure strategy. They investigated the tuning of pore aperture of the flexible framework of NTU-65 for the

efficient separation of the gases mixtures of CO_2, C_2H_2 and C_2H_4. NTU-65 exhibited selective adsorption of C_2H_2 and CO_2 with large uptake capacities of 86.3 and 79.5 cm^3/g, respectively while slight uptake of C_2H_4 of 2.2 cm^3/g 263 K.[303] The dynamic breakthrough experiments for the ternary mixture of $CO_2/C_2H_2/C_2H_4$ proved the practical production of high purity polymer grade C_2H_4 with 99.95% at the optimized temperature of 263 K.

The predesign of the breathing MOF based on the stimulation of a flexible or controlled functional linker is considered a promising strategy for the selective capture of CO_2. Azo-based linker is one of the well-known organic linkers that undergo structure isomerization and cis-trans transformation upon the light or heat treatment. For instance, Park et al.[304] have developed a breathing MOF called PCN-13, constructed from azobenzene linker. The photo-stimulation of the PCN-13 showed a significant effect on the adsorption of CO_2. Similar results we investigated in azo-based MOF reported by Kitagawa group in which the adsorption of N_2 can be tuned under UV light.[305] Gong et al.[306] synthesized a breathing MOF called ECUT-15 in which they studied the photoswitching behavior and its direct effect in the CO_2 adsorption. The novel flexible MOF showed good adsorption of CO_2 and excellent selectivity over the other gases for example, N_2, O_2, CO and CH_4.

3. Summary and Outcomes

The review carefully demonstrated that there are several strategies that could be employed to design MOFs for CO_2 separation and capture application. Designing of MOFs with adequate pore windows and size will allow the accommodation of large quantities of CO_2 without destruction to the MOFs integrity.

Apart from designing MOFs with excellent pore properties, post-synthetic and pre-synthetic modifications could also be applicable in upgrading their CO_2 uptake. This review has established that modification with metals such as Fe, Cu, Zn, Mg, etc. can give rise to advanced MOFs structures with enhanced stability and gas adsorption properties. As a post-synthesis approach, the metals are incorporated systematically at balanced concentrations. This way, the original MOFs integrity is retained whereas the CO_2 capacity is strongly elevated. An alternative to this method involved the use of organic modifiers like amino alcohols. These substrates work like the metals but must carefully be employed to avoid structural ruptures when contact with large gas volumes. This could be due to the acidic nature of the gas. Therefore, the functionality must be carefully modified

On the other hand, the pre-synthesis modification requires the change of organic linker before the MOFs preparation. Available literature demonstrated solvothermal method as the

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most appropriate in designing stable structures with enhanced CO_2 adsorption capacities.

Despite all of these strategies' certain features of the original MOFs must be considered at the design stages. These include the original functional groups of the MOFs, crystal structures and acidity properties. Eventually, CO_2 is an acidic and very volatile gas with some handling difficulties. Therefore, any MOF design must consider adequate crystallinity development to prevent structural ruptures and ensure acidity-basicity properties compatible with the CO_2 stability within the MOF structures. Doping strategies and the flexibility evaluations must also be carefully considered at both the stages of preparations and applications. Large quantities of dopants can produce MOFs structures with low CO_2 adsorption capacity. Accordingly, the MOFs structures must be flexible for re-engineering and CO_2 separation at appropriate stages.

From a wider perspective, although other CO_2 captures and separations strategies that none-MOFs based have been evaluated at the trial stages. There are indications that the materials already tested have poor capacity, low stability, and associated regeneration challenges. Some of the reasons are due to their unique physicochemical properties, apparent stability under acidic conditions and the chances to promote efficiency via simple modification procedures as already demonstrated. While some key published works have considered some laboratory-scale works as so far feasible, many documented works have identified the separation and capture aspects of the technologies as seriously challenging. In the prior sections, we have undoubtedly emphasized how MOFs could be employed (with or without modifications) to serve as better replacement separation and capture materials. However, in an attempt to promote research in this direction, the paper is highlighting the following issues as areas for further investigation:

1. Evaluation of different MOFs structures under variable conditions of CO_2 pressure and temperature. Since the approach is new in the literature, various models must be developed and evaluated by considering different temperature and pressure conditions. This way, the most suitable capture/separation conditions would be appropriately established.

2. Formulating eco-efficient strategies for acidity modification in MOFs that capture CO_2 would be feasibly achieved at low cost. Since the CO_2 gas is acidic in nature, the development of MOFs structures that are resistant to rupture by the influence of acidity must carefully be considered. Accordingly, the possibility of gas chemisorption under advanced experimental conditions cannot be ruled out. Thus, proper acidity-basicity design of the MOF compounds is essential.

3. Considering the chances to design MOFs with distinct functionalities, it becomes imperative to establish the functional groups more susceptible to CO_2 capture, with consequent stability under severe conditions. This should consider the volatile nature of the gas and its diffusional characteristics within the MOFs. Invariably, any leakage can trigger serious process challenges with consequent negative effects of the overall process eco-scientific feasibilities.

4. Exploring the possibilities of using other dopants such as Ni, La, Cd, etc. During MOFs design and the chances of creating better Lewis sites for the CO_2 capture. This alternative can provide a good way of comparison between the already evaluated metals and their corresponding alternatives in terms of chemical stability, retention of structural integrity, capture/separation capacities and the eco-scientific feasibilities for large scale considerations.

5. Careful investigations of pre-synthetic or post-synthetic MOFs modification would be more effective for designing efficient CO_2 separation and separation structures. This should cover the suitable selection of modifiers, the conditions during modifications and the stability of the modified MOFs strictures both at the prior and posterior stages of the CO_2 capture and separation.

Certainly, when these issues are adequately addressed and the eco-efficiency of the overall process established, MOFs′ application will escalate the chances for CO_2 valorization and environmental protection in line with globalization requirements.

Author Contributions

Muhammad Usman: Supervision, Conceptualization, Writing- Original draft preparation, Writing- Reviewing, and Editing. **Naseem Iqbal**: Supervision, Writing- Original draft preparation, Validation. Writing- Reviewing Software and Editing. **Tayyaba Noor**: Methodology, Writing- Original draft preparation, Validation. **Neelam Zaman**: Software, Data curation, Writing- Reviewing, and Editing. **Aisha Asghar**: Data curation, Software, Writing- Original draft preparation. **Mahmoud M. Abdelnaby**: Writing- Reviewing and Editing. **Ahmad Galadima**: Data curation, Writing- Original draft preparation. **Aasif Helal**: Writing- Reviewing, Editing, and Validation.

Acknowledgments

References

[1] D. A. Lashof, D. R. Ahuja, *Nature* **1990**, *344*, 529–531.

[2] J. K. Donald, in *Building STEM Skills Through Environmental Education*, ed. by T. S. Stephen, D. Janese, IGI Global, Hershey, PA, USA, **2021**, pp. 172–218.

[3] T. D. Burns, K. N. Pai, S. G. Subraveti, S. P. Collins, M. Krykunov, A. Rajendran, T. K. Woo, *Environ. Sci. Technol.* **2020**, *54*, 4536–4544.

[4] S. Agostini, B. P. Harvey, S. Wada, K. Kon, M. Milazzo, K. Inaba, J. M. Hall-Spencer, *Sci. Rep.* **2018**, *8*, 11354.

[5] F. Gervais, *Earth-Sci. Rev.* **2016**, *155*, 129–135.

[6] S. Ó. Snæbjörnsdóttir, B. Sigfússon, C. Marieni, D. Goldberg, S. R. Gislason, E. H. Oelkers, *Nat. Rev. Earth Environ.* **2020**, *1*, 90–102.

[7] S. Chu, *Science* **2009**, *325*, 1599.

[8] K. S. Lackner, *Science* **2003**, *300*, 1677.

[9] M. D. Garba, M. Usman, S. Khan, F. Shehzad, A. Galadima, M. F. Ehsan, A. S. Ghanem, M. Humayun, *J. Environ. Chem. Eng.* **2021**, *9*, 104756.

[10] C. Molina-Fernández, P. Luis, *J. CO2 Util.* **2021**, *47*, 101475.

[11] S. Kumar, R. Srivastava, J. Koh, *J. CO2 Util.* **2020**, *41*, 101251.

[12] A. Dindi, D. V. Quang, L. F. Vega, E. Nashef, M. R. M. Abu-Zahra, *J. CO2 Util.* **2019**, *29*, 82–102.

[13] Z. Ahmed, F. Rehman, U. Ali, A. Ali, M. Iqbal, K. H. Thebo, *ChemBioEng Rev.* **2021**, *8*, 110–120.

[14] A. Ali, R. Pothu, S. H. Siyal, S. Phulpoto, M. Sajjad, K. H. Thebo, *Mater. Sci. Technol.* **2019**, *2*, 83–88.

[15] O. T. Qazvini, R. Babarao, S. G. Telfer, *Nat. Commun.* **2021**, *12*, 197.

[16] O. T. Qazvini, S. G. Telfer, *ACS Appl. Mater. Interfaces* **2021**, *13*, 12141–12148.

[17] H. Yamada, *Polym. J.* **2021**, *53*, 93–102.

[18] S. O. Adio, S. A. Ganiyu, M. Usman, I. Abdulazeez, K. Alhooshani, *Chem. Eng. J.* **2020**, *382*, 122964.

[19] A. Nawar, M. Ali, A. Waqas, A. Javed, N. Iqbal, R. Khan, *Energy Fuels* **2019**, *34*, 2035–2044.

[20] A. Asghar, N. Iqbal, T. Noor, M. Ali, T. L. Easun, *Nanomaterials* **2019**, *9*, 1063.

[21] M. Songolzadeh, M. Soleimani, M. Takht Ravanchi, R. Songolzadeh, *Sci. World J* **2014**, *2014*, 828131.

[22] T. Ghanbari, F. Abnisa, W. M. A. Wan Daud, *Sci. Total Environ.* **2020**, *707*, 135090.

[23] A. Nawar, H. Ghaedi, M. Ali, M. Zhao, N. Iqbal, R. Khan, *Process Saf. Environ. Prot.* **2019**, *132*, 214–225.

[24] C. J. E. Bajamundi, J. Koponen, V. Ruuskanen, J. Elfving, A. Kosonen, J. Kauppinen, J. Ahola, *J. CO2 Util.* **2019**, *30*, 232–239.

[25] N. Jiang, Y. Shen, B. Liu, D. Zhang, Z. Tang, G. Li, B. Fu, *J. CO2 Util.* **2020**, *35*, 153–168.

[26] A. a. F. Eftaiha, A. K. Qaroush, A. K. Hasan, K. I. Assaf, F. a. M. Al-Qaisi, M. E. Melhem, B. A. Al-Maythalony, M. Usman, *New J. Chem.* **2021**, *45*, 16452–16460.

[27] S. Choi, T. Watanabe, T. H. Bae, D. S. Sholl, C. W. Jones, *J. Phys. Chem. Lett.* **2012**, *3*, 1136–41.

[28] A. Asghar, N. Iqbal, T. Noor, B. M. Kariuki, L. Kidwell, T. L. Easun, *Green Chem.* **2021**, *23*, 1220–1227.

[29] C. G. Piscopo, S. Loebbecke, *ChemPlusChem* **2020**, *85*, 538–547.

[30] M. Ding, R. W. Flaig, H.-L. Jiang, O. M. Yaghi, *Chem. Soc. Rev.* **2019**, *48*, 2783–2828.

[31] Q. Xue, Z. Zhang, B. K. Ng, P. Zhao, B. T. Lo, *Top. Curr. Chem.* **2021**, *379*, 1–22.

[32] X. Deng, J.-Y. Hu, J. Luo, W.-M. Liao, J. He, *Top. Curr. Chem.* **2020**, *378*, 1–50.

[33] R. Aniruddha, I. Sreedhar, B. M. Reddy, *J. CO2 Util.* **2020**, *42*, 101297.

[34] B. M. Connolly, M. Aragones-Anglada, J. Gandara-Loe, N. A. Danaf, D. C. Lamb, J. P. Mehta, D. Vulpe, S. Wuttke, J. Silvestre-Albero, P. Z. Moghadam, *Nat. Commun.* **2019**, *10*, 1–11.

[35] O. T. Qazvini, R. Babarao, Z.-L. Shi, Y.-B. Zhang, S. G. Telfer, *J. Am. Chem. Soc.* **2019**, *141*, 5014–5020.

[36] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724–781.

[37] G. Zhang, H. Fei, *Top. Curr. Chem.* **2020**, 203–214.

[38] T. Pham, B. Space, *Top. Curr. Chem.* **2020**, 215–279.

[39] N. A. A. Qasem, N. U. Qadir, R. Ben-Mansour, S. A. M. Said, *J. CO2 Util.* **2017**, *22*, 238–249.

[40] T. Noor, M. Mohtashim, N. Iqbal, S. R. Naqvi, N. Zaman, L. Rasheed, M. Yousuf, *J. Electroanal. Chem.* **2021**, *890*, 115249.

[41] J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2011**, *112*, 869–932.

[42] A. S. Ghanem, M. Ba-Shammakh, M. Usman, M. F. Khan, H. Dafallah, M. A. Habib, B. A. Al-Maythalony, *J. Appl. Polym. Sci.* **2020**, *137*, 48513.

[43] A. M. Bassem, M. Usman, KFUPM, U. Patent US16/720,535 **2020**.

[44] M. Usman, M. M. Abdelnaby, S. Shafiq, A. M. Alloush, A. Helal, Z. H. Yamani, in *Book A metal-organic framework membrane for olefin-paraffin separation*, ed., ed. by Editor, Engineers Australia, City, **2020**, Chap. Chapter, pp. 329.

[45] M. Usman, M. Ali, B. A. Al-Maythalony, A. S. Ghanem, O. W. Saadi, M. Ali, M. A. Jafar Mazumder, S. Abdel-Azeim, M. A. Habib, Z. H. Yamani, W. Ensinger, *ACS Appl. Mater. Interfaces* **2020**, *12*, 49992–50001.

[46] J. Pei, K. Shao, L. Zhang, H. M. Wen, B. Li, G. Qian, *Top. Curr. Chem.* **2020**, 305–338.

[47] B. Qian, Z. Chang, X.-H. Bu, *Top. Curr. Chem.* **2020**, 135–173.

[48] C. Xue, Q. Zhang, E. Wang, R. Huang, J. Wang, Y. Hao, X. Hao, *J. CO2 Util.* **2020**, *36*, 1–8.

[49] M. Usman, B. A. Al-Maythalony, US Patents, KFUPM US20210138433 A1 **2021**.

[50] M. Usman, A. Helal, US Patents, KFUPM US20210187475 A1 **2021**.

[51] B. A. Al-Maythalony, A. S. Ghanem, M. Ba-Shammakh, M. Usman, US Patents, KFUPM US16/285,724 **2020**.

[52] E. M. Miner, L. Wang, M. Dincă, *Chem. Sci.* **2018**, *9*, 6286–6291.

[53] K. M. Choi, K. Na, G. A. Somorjai, O. M. Yaghi, *J. Am. Chem. Soc.* **2015**, *137*, 7810–7816.

[54] M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2011**, *112*, 1196–1231.

[55] A. Helal, K. E. Cordova, M. E. Arafat, M. Usman, Z. H. Yamani, *Inorg. Chem. Front.* **2020**, *7*, 3571–3577.

[56] Y. Shi, S. Hou, X. Qiu, B. Zhao, *Top. Curr. Chem.* **2020**, 373–426.

[57] L. Yaqoob, T. Noor, N. Iqbal, H. Nasir, M. Sohail, N. Zaman, M. Usman, *Renewable Energy* **2020**, *156*, 1040–1054.

[58] L. Ullah, G. Zhao, Z. Xu, H. He, M. Usman, S. Zhang, *Sci. China Chem.* **2018**, *61*, 402–411.

[59] D. Israf Ud, N. Qazi, D. G. Mustapha, I. A. Abdulrahman, A. A. Mshari, U. Muhammad, *Mini-Rev. Org. Chem.* **2021**, *18*, 1–1.

[60] M. Humayun, H. Ullah, M. Usman, A. Habibi-Yangjeh, A. Ali Tahir, C. Wang, W. Luo, *J. Energy Chem.* **2021**.

[61] M. Usman, M. Humayun, M. D. Garba, L. Ullah, Z. Zeb, A. Helal, M. H. Suliman, B. Y. Alfaifi, N. Iqbal, M. Abdinejad, A. A. Tahir, H. Ullah, *Nanomaterials* **2021**, *11*, 2029.

[62] N. A. Khan, M. Humayun, M. Usman, Z. A. Ghazi, A. Naeem, A. Khan, A. L. Khan, A. A. Tahir, H. Ullah, *Energies* **2021**, *14*, 2267.

[63] A. Helal, M. Usman, M. E. Arafat, M. M. Abdelnaby, *J. Ind. Eng. Chem.* **2020**, *89*, 104–110.

[64] I. U. Din, M. Usman, S. Khan, A. Helal, M. A. Alotaibi, A. I. Alharthi, G. Centi, *J. CO2 Util.* **2021**, *43*, 101361.

[65] U. Salahuddin, N. Iqbal, T. Noor, S. Hanif, H. Ejaz, N. Zaman, S. Ahmed, *Catalysts* **2021**, *11*, 92.

[66] S. Ashraf, R. Mehek, N. Iqbal, T. Noor, G. Ali, A. Wahab, A. A. Qayyum, A. Ahmad, *Mater. Chem. Phys.* **2021**, 124824.

[67] M. D. Haider, N. Iqbal, S. A. M. Rizvi, T. Noor, S. Hanif, R. Anwar, *J. Electrochem. Energy Convers. Storage* **2021**, *18*, 021001.

[68] L. Yaqoob, T. Noor, N. Iqbal, H. Nasir, A. Mumtaz, *Sci. Rep.* **2021**, *11*, 13402.

[69] A. Aziz, S. S. Shah, A. Kashem, *Chem. Rec.* **2020**, *20*, 1074–1098.

[70] S. S. Shah, M. N. Shaikh, M. Y. Khan, M. A. Alfasane, M. M. Rahman, M. A. Aziz, *Chem. Rec.* **2021**, *21*, 1631–1665.

[71] M. Ashraf, I. Khan, M. Usman, A. Khan, S. S. Shah, A. Z. Khan, K. Saeed, M. Yaseen, M. F. Ehsan, M. N. Tahir, N. Ullah, *Chem. Res. Toxicol.* **2020**, *33*, 1292–1311.

[72] M. Usman, M. Humayun, S. S. Shah, H. Ullah, A. A. Tahir, A. Khan, H. Ullah, *Energies* **2021**, *14*, 2281.

[73] A. A. Olajire, *J. CO2 Util.* **2017**, *17*, 137–161.

[74] C.-H. Yu, C.-H. Huang, C.-S. Tan, *Aerosol Air Qual. Res* **2012**, *12*, 745–769.

[75] B. Li, Y. Duan, D. Luebke, B. Morreale, *Appl. Energy* **2013**, *102*, 1439–1447.

[76] E. I. Koytsoumpa, C. Bergins, E. Kakaras, *J. Supercrit. Fluids* **2018**, *132*, 3–16.

[77] M. Usman, A. Helal, M. M. Abdelnaby, A. M. Alloush, M. Zeama, Z. H. Yamani, *Chem. Rec.* **2021**, *21*, 1771–1791.

[78] M. A. Jafar Mazumder, P. H. Raja, A. M. Isloor, M. Usman, S. H. Chowdhury, S. A. Ali, Inamuddin, A. Al-Ahmed, *Sci. Rep.* **2020**, *10*, 7049.

[79] R. Razzaq, H. Zhu, L. Jiang, U. Muhammad, C. Li, S. Zhang, *Ind. Eng. Chem. Res.* **2013**, *52*, 2247–2256.

[80] R. Razzaq, C. Li, M. Usman, K. Suzuki, S. Zhang, *Chem. Eng. J.* **2015**, *262*, 1090–1098.

[81] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.

[82] O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. O. z. r. Yazaydın, J. T. Hupp, *J. Am. Chem. Soc.* **2012**, *134*, 15016–15021.

[83] I. M. Hönicke, I. Senkovska, V. Bon, I. A. Baburin, N. Bönisch, S. Raschke, J. D. Evans, S. Kaskel, *Angew. Chem. Int. Ed.* **2018**, *57*, 13780–13783; *Angew. Chem.* **2018**, *130*, 13976–13979.

[84] S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 14176–14177.

[85] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040–2042.

[86] H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim, *Science* **2010**, *329*, 424–428.

[87] C. A. Trickett, A. Helal, B. A. Al-Maythalony, Z. H. Yamani, K. E. Cordova, O. M. Yaghi, *Nat. Rev. Mater.* **2017**, *2*, 17045.

[88] H. Furukawa, M. A. Miller, O. M. Yaghi, *J. Mater. Chem.* **2007**, *17*, 3197–3204.

[89] K. Koh, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2009**, *131*, 4184–4185.

[90] O. K. Farha, A. Ö. Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr, J. T. Hupp, *Nat. Chem.* **2010**, *2*, 944–948.

[91] U. Stoeck, I. Senkovska, V. Bon, S. Krause, S. Kaskel, *Chem. Commun.* **2015**, *51*, 1046–1049.

[92] Y.-B. Huang, J. Liang, X.-S. Wang, R. Cao, *Chem. Soc. Rev.* **2017**, *46*, 126–157.

[93] R.-B. Lin, S. Xiang, W. Zhou, B. Chen, *Chem* **2020**, *6*, 337–363.

[94] W. Fan, X. Wang, X. Zhang, X. Liu, Y. Wang, Z. Kang, F. Dai, B. Xu, R. Wang, D. Sun, *ACS Cent. Sci.* **2019**, *5*, 1261–1268.

[95] W. Zhuang, D. Yuan, D. Liu, C. Zhong, J.-R. Li, H.-C. Zhou, *Chem. Mater.* **2012**, *24*, 18–25.

[96] B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky, H.-C. Zhou, *Inorg. Chem.* **2007**, *46*, 1233–1236.

[97] D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, K. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 32–33.

[98] T. Loiseau, L. Lecroq, C. Volkringer, J. Marrot, G. Férey, M. Haouas, F. Taulelle, S. Bourrelly, P. L. Llewellyn, M. Latroche, *J. Am. Chem. Soc.* **2006**, *128*, 10223–10230.

[99] M. Xue, S. Ma, Z. Jin, R. M. Schaffino, G.-S. Zhu, E. B. Lobkovsky, S.-L. Qiu, B. Chen, *Inorg. Chem.* **2008**, *47*, 6825–6828.

[100] K. Adil, Y. Belmabkhout, R. S. Pillai, A. Cadiau, P. M. Bhatt, A. H. Assen, G. Maurin, M. Eddaoudi, *Chem. Soc. Rev.* **2017**, *46*, 3402–3430.

[101] D. Aaron, C. Tsouris, *Sep. Sci. Technol.* **2005**, *40*, 321–348.

[102] Y. Li, R. T. Yang, *Langmuir* **2007**, *23*, 12937–44.

[103] R. Babu, R. Roshan, A. C. Kathalikkattil, D. W. Kim, D. W. Park, *ACS Appl. Mater. Interfaces* **2016**, *8*, 33723–33731.

[104] G. Avci, S. Velioglu, S. Keskin, *ACS Appl. Mater. Interfaces* **2018**, *10*, 33693–33706.

[105] J.-R. Li, J. Yu, W. Lu, L.-B. Sun, J. Sculley, P. B. Balbuena, H.-C. Zhou, *Nat. Commun.* **2013**, *4*, 1538.

[106] B. Li, B. Chen, *Sci. China Chem.* **2016**, *59*, 965–969.

[107] H.-M. Wen, C. Liao, L. Li, A. Alsalme, Z. Alothman, R. Krishna, H. Wu, W. Zhou, J. Hu, B. Chen, *J. Mater. Chem. A* **2019**, *7*, 3128–3134.

[108] S. Ma, X.-S. Wang, E. S. Manis, C. D. Collier, H.-C. Zhou, *Inorg. Chem.* **2007**, *46*, 3432–3434.

[109] L. Qin, Z.-M. Ju, Z.-J. Wang, F.-D. Meng, H.-G. Zheng, J.-X. Chen, *Cryst. Growth Des.* **2014**, *14*, 2742–2746.

[110] M. Alhamami, H. Doan, C.-H. Cheng, *Materials* **2014**, *7*, 3198–3250.

[111] P. L. Llewellyn, S. Bourrelly, C. Serre, Y. Filinchuk, G. Férey, *Angew. Chem. Int. Ed.* **2006**, *45*, 7751–7754; *Angew. Chem.* **2006**, *118*, 7915–7918.

[112] S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 13519–13521.

[113] T. K. Maji, R. Matsuda, S. Kitagawa, *Nat. Mater.* **2007**, *6*, 142–148.

[114] G. Sneddon, A. Greenaway, H. H. Yiu, *Adv. Energy Mater.* **2014**, *4*, 1301873.

[115] M. D. Haider, N. Iqbal, S. A. M. Rizvi, T. Noor, S. Hanif, R. Anwar, *J. Electrochem. Energy Convers. Storage* **2020**, 1–16.

[116] K. Chue, J. Kim, Y. Yoo, S. Cho, R. Yang, *Ind. Eng. Chem. Res.* **1995**, *34*, 591–598.

[117] B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nature* **2008**, *453*, 207–211.

[118] R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 3875–3877.

[119] P. D. Dietzel, V. Besikiotis, R. Blom, *J. Mater. Chem.* **2009**, *19*, 7362–7370.

[120] Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, R. Q. Snurr, *Langmuir* **2008**, *24*, 8592–8598.

[121] E. E. Ünveren, B. Ö. Monkul, Ş. Sarıoğlan, N. Karademir, E. Alper, *Petroleum* **2017**, *3*, 37–50.

[122] S. Surblé, F. Millange, C. Serre, T. Düren, M. Latroche, S. Bourrelly, P. L. Llewellyn, G. Férey, *J. Am. Chem. Soc.* **2006**, *128*, 14889–14896.

[123] Y.-S. Bae, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, J. T. Hupp, R. Q. Snurr, *Chem. Commun.* **2008**, 4135–4137.

[124] B. A. Al-Maythalony, O. Shekhah, R. Swaidan, Y. Belmabkhout, I. Pinnau, M. Eddaoudi, *J. Am. Chem. Soc.* **2015**, *137*, 1754–1757.

[125] M. Eddaoudi, D. F. Sava, J. F. Eubank, K. Adil, V. Guillerm, *Chem. Soc. Rev.* **2015**, *44*, 228–249.

[126] O. K. Farha, J. T. Hupp, *Acc. Chem. Res.* **2010**, *43*, 1166–1175.

[127] A. Comotti, S. Bracco, P. Sozzani, S. Horike, R. Matsuda, J. Chen, M. Takata, Y. Kubota, S. Kitagawa, *J. Am. Chem. Soc.* **2008**, *130*, 13664–13672.

[128] D. Britt, H. Furukawa, B. Wang, T. G. Glover, O. M. Yaghi, *Proc. Nat. Acad. Sci.* **2009**, *106*, 20637–20640.

[129] A. Asghar, N. Iqbal, T. Noor, J. Khan, in *Book Ethylendiamine (EDA) loading on MOF-5 for enhanced carbon dioxide capture applications*, ed., ed. by Editor, IOP Publishing, City, **2020**, Vol. 471, Chap. Chapter, pp. 012009.

[130] Z. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2007**, *129*, 12368–12369.

[131] J. Khan, N. Iqbal, A. Asghar, T. Noor, *Mater. Res. Express* **2019**, *6*, 105539.

[132] S. Gaikwad, Y. Kim, R. Gaikwad, S. Han, *J. Environ. Chem. Eng.* **2021**, *9*, 105523.

[133] V. Agostoni, P. Horcajada, M. Noiray, M. Malanga, A. Aykac, L. Jicsinszky, A. Vargas-Berenguel, N. Semiramoth, S. Daoud-Mahammed, V. Nicolas, C. Martineau, F. Taulelle, J. Vigneron, A. Etcheberry, C. Serre, R. Gref, *Sci. Rep.* **2015**, *5*, 7925.

[134] A. Gheorghe, I. Imaz, J. I. van der Vlugt, D. Maspoch, S. Tanase, *Dalton Trans.* **2019**, *48*, 10043–10050.

[135] L. J. Wang, H. Deng, H. Furukawa, F. Gándara, K. E. Cordova, D. Peri, O. M. Yaghi, *Inorg. Chem.* **2014**, *53*, 5881–5883.

[136] J. Liu, D. M. Strachan, P. K. Thallapally, *Chem. Commun.* **2014**, *50*, 466–8.

[137] X. L. Zhang, S. M. Li, S. Chen, F. Feng, J. Q. Bai, J. R. Li, *Ecotoxicol. Environ. Saf.* **2020**, *187*, 109821.

[138] J. Wu, J. Zhou, S. Zhang, A. Alsaedi, T. Hayat, J. Li, Y. Song, *J. Colloid Interface Sci.* **2019**, *555*, 403–412.

[139] S. Kazemi, V. Safarifard, *Nanochem Res* **2018**, *3*, 62–78.

[140] A. Kronast, S. Eckstein, P. T. Altenbuchner, K. Hindelang, S. I. Vagin, B. Rieger, *Chem. Eur. J.* **2016**, *22*, 12800–12807.

[141] M. H. Yu, P. Zhang, R. Feng, Z. Q. Yao, Y. C. Yu, T. L. Hu, X. H. Bu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 26177–26183.

[142] N. Stock, S. Biswas, *Chem. Rev.* **2012**, *112*, 933–69.

[143] R. Goswami, N. Seal, S. R. Dash, A. Tyagi, S. Neogi, *ACS Appl. Mater. Interfaces* **2019**, *11*, 40134–40150.

[144] D. Lee, J. Zhao, C. J. Oldham, G. W. Peterson, G. N. Parsons, *ACS Appl. Mater. Interfaces* **2017** *9*, 44847–44855.

[145] Y. Yang, R. Lin, L. Ge, L. Hou, P. Bernhardt, T. E. Rufford, S. Wang, V. Rudolph, Y. Wang, Z. Zhu, *Dalton Trans.* **2015**, *44*, 8190–7.

[146] Z. H. Rada, H. R. Abid, H. Sun, S. Wang, *J. Chem. Eng. Data* **2015**, *60*, 2152–2161. .

[147] A. Asghar, N. Iqbal, L. Aftab, T. Noor, B. M. Kariuki, L. Kidwell, T. L. Easun, *R. Soc. Open Sci.* **2020**, *7*, 191934.

[148] Z. Hu, A. Nalaparaju, Y. Peng, J. Jiang, D. Zhao, *Inorg. Chem.* **2016**, *55*, 1134–1141.

[149] P. Deria, S. Li, H. Zhang, R. Q. Snurr, J. T. Hupp, O. K. Farha, *Chem. Commun.* **2015**, *51*, 12478–81.

[150] H. Hintz, S. Wuttke, *Chem. Commun.* **2014**, *50*, 11472–5.

[151] M. Fujiwara, H. Ando, M. Tanaka, Y. Souma, *Appl. Catal. A* **1995**, *130*, 105–116.

[152] J. Mehta, S. Dhaka, A. K. Paul, S. Dayananda, A. Deep, *Environ. Res.* **2019**, *174*, 46–53.

[153] H. J. Park, Y. E. C. Cheon, M. Pail Suh, *Chem. Eur. J 16* 11662–11669.

[154] C. X. Chen, Z. Wei, J. J. Jiang, Y. Z. Fan, S. P. Zheng, C. C. Cao, Y. H. Li, D. Fenski, C. Y. Su, *Angew. Chem. Int. Ed.* **2016**, *55*, 9932–9936; *Angew. Chem.* **2016**, *128*, 10086–10090.

[155] F. Marpaung, M. Kim, J. H. Khan, K. Konstantinov, Y. Yamauchi, M. S. A. Hossain, J. Na, J. Kim, *Chem. Asian J.* **2019**, *14*, 1331–1343.

[156] A. Asghar, N. Iqbal, L. Aftab, T. Noor, B. M. Kariuki, L. Kidwell, T. L. Easun, *R. Soc. Open Sci.* **2020**, *7*, 191934.

[157] A. Ahmad, N. Iqbal, T. Noor, A. Hassan, U. A. Khan, A. Wahab, M. A. Raza, S. Ashraf, *J. CO2 Util.* **2021**, *48*, 101523.

[158] N. Zaman, T. Noor, N. Iqbal, *RSC Adv.* **2021**, *11*, 21904–21925.

[159] M. Mihaylov, S. Andonova, K. Chakarova, A. Vimont, E. Ivanova, N. Drenchev, K. Hadjiivanov, *Phys. Chem. Chem. Phys.* **2015**, *17*, 24304–14.

[160] J. R. Karra, B. E. Grabicka, Y. G. Huang, K. S. Walton, *J. Colloid Interface Sci.* **2013**, *392*, 331–336.

[161] J. P. Durholt, G. Fraux, F. X. Coudert, R. Schmid, *J. Chem. Theory Comput.* **2019**, *15*, 2420–2432.

[162] D. Saha, Z. Bao, F. Jia, S. Deng, *Environ. Sci. Technol.* **2010**, *44*, 1820–6.

[163] L. Hamon, P. L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G. D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. van Beek, E. Jolimaitre, A. Vimont, M. Daturi, G. Ferey, *J. Am. Chem. Soc.* **2009**, *131*, 17490–9.

[164] G. Lu, O. K. Farha, W. Zhang, F. Huo, J. T. Hupp, *Adv. Mater.* **2012**, *24*, 3970–4.

[165] H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science* **2010**, 846–850.

[166] Z. S. Moghaddam, M. Kaykhaii, M. Khajeh, A. R. Oveisi, *Acta Part A Mol. Biomol. Spectrosc.* **2018**, *194*, 76–82.

[167] H. R. Fu, F. Wang, J. Zhang, *Dalton Trans.* **2014**, *43*, 4668–4673.

[168] T. Devic, P. Horcajada, C. Serre, F. Salles, G. Maurin, B. Moulin, D. Heurtaux, G. Clet, A. Vimont, J. M. Grená, *J. Am. Chem. Soc.* **2010**,, *132*,, 1127–1136. .

[169] B. Li, D. Ma, Y. Li, Y. Zhang, G. Li, Z. Shi, S. Feng, M. J. Zaworotko, S. J. Ma, *Chem. Mater.* **2016**, *28*, 4781–4786.

[170] V. Guillerm, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah, M. Eddaoudi, *Chem. Soc. Rev.* **2014**, *43*, 6141–6172.

[171] Y. He, B. Li, M. O'Keeffe, B. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5618–5656.

[172] R. Anderson, J. Rodgers, E. Argueta, A. Biong, D. A. Gómez-Gualdrón, *Chem. Mater.* **2018**, *30*, 6325–6337.

[173] F. Luo, C. Yan, L. Dang, R. Krishna, W. Zhou, H. Wu, X. Dong, Y. Han, T.-L. Hu, M. O'Keeffe, L. Wang, M. Luo, R.-B. Lin, B. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 5678–5684.

[174] A. Cadiau, K. Adil, P. M. Bhatt, Y. Belmabkhout, M. Eddaoudi, *Science* **2016**, *353*, 137–140.

[175] P. M. Bhatt, Y. Belmabkhout, A. Cadiau, K. Adil, O. Shekhah, A. Shkurenko, L. J. Barbour, M. Eddaoudi, *J. Am. Chem. Soc.* **2016**, *138*, 9301–9307.

[176] H. Wang, Y. Liu, J. Li, *Adv. Mater.* 2002603.

[177] P. M. Bhatt, Y. Belmabkhout, A. H. Assen, Ł. J. Weseliński, H. Jiang, A. Cadiau, D.-X. Xue, M. Eddaoudi, *Chem. Eng. J.* **2017**, *324*, 392–396.

[178] D.-X. Xue, A. J. Cairns, Y. Belmabkhout, L. Wojtas, Y. Liu, M. H. Alkordi, M. Eddaoudi, *J. Am. Chem. Soc.* **2013**, *135*, 7660–7667.

[179] L. Zhang, Y. Feng, H. He, Y. Liu, J. Weng, P. Zhang, W. Huang, *Catal. Today* **2021**, *374*, 38–43.

[180] Q.-G. Zhai, X. Bu, C. Mao, X. Zhao, P. Feng, *J. Am. Chem. Soc.* **2016**, *138*, 2524–2527.

[181] J. A. Botas, G. Calleja, M. Sánchez-Sánchez, M. G. Orcajo, *Langmuir* **2010**, *26*, 5300–5303.

[182] R.-J. Li, M. Li, X.-P. Zhou, D. Li, M. O'Keeffe, *Chem. Commun.* **2014**, *50*, 4047–4049.

[183] J.-Q. Liu, J. Wu, Z.-B. Jia, H.-L. Chen, Q.-L. Li, H. Sakiyama, T. Soares, F. Ren, C. Daiguebonne, O. Guillou, S. W. Ng, *Dalton Trans.* **2014**, *43*, 17265–17273.

[184] A. Pal, A. Mitra, S. Chand, J.-B. Lin, M. C. Das, *CrystEngComm* **2019**, *21*, 535–543.

[185] A. Asghar, N. Iqbal, T. Noor, *Polyhedron* **2020**, *181*, 114463.

[186] M. G. Frysali, E. Klontzas, E. Tylianakis, G. E. Froudakis, *Micrpor. Mesopor. Mat* **2016**, *227*, 144–151.

[187] R. Serna-Guerrero, A. Sayari, *Chem. Eng. J.* **2010**, *161*, 182–190.

[188] G. K. Shimizu, R. Vaidhyanathan, J. M. Taylor, *Chem. Soc. Rev.* **2009**, *38*, 1430–1449.

[189] M. Taddei, F. Costantino, A. Ienco, A. Comotti, P. V. Dau, S. M. Cohen, *Chem. Commun.* **2013**, *49*, 1315–1317.

[190] S. Couck, J. F. Denayer, G. V. Baron, T. Rémy, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.* **2009**, *131*, 6326–6327.

[191] Y.-S. Bae, O. K. Farha, J. T. Hupp, R. Q. Snurr, *J. Mater. Chem.* **2009**, *19*, 2131–2134.

[192] F. Dreisbach, R. Staudt, J. Keller, *Adsorption* **1999**, *5*, 215–227.

[193] E. Keceli, M. Hemgesberg, R. Grünker, V. Bon, C. Wilhelm, T. Philippi, R. Schoch, Y. Sun, M. Bauer, S. Ernst, *Micrpor. Mesopor. Mat* **2014**, *194*, 115–125.

[194] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, F. Kapteijn, *Chem. Mater.* **2011**, *23*, 2565–2572.

[195] A. M. Fracaroli, H. Furukawa, M. Suzuki, M. Dodd, S. Okajima, F. Gándara, J. A. Reimer, O. M. Yaghi, *J. Am. Chem. Soc.* **2014**, *136*, 8863–8866.

[196] Z. Zhang, Y. Zhao, Q. Gong, Z. Li, J. Li, *Chem. Commun.* **2013**, *49*, 653–661.

[197] R. Vaidhyanathan, S. S. Iremonger, K. W. Dawson, G. K. Shimizu, *Chem. Commun.* **2009**, 5230–5232.

[198] F. Luo, M.-S. Wang, M.-B. Luo, G.-M. Sun, Y.-M. Song, P.-X. Li, G.-C. Guo, *Chem. Commun.* **2012**, *48*, 5989–5991.

[199] N. Seal, M. Singh, S. Das, R. Goswami, B. Pathak, S. Neogi, *Mater. Chem. Front.* **2021**, *5*, 979–994.

[200] Ü. Kökçam-Demir, A. Goldman, L. Esrafili, M. Gharib, A. Morsali, O. Weingart, C. Janiak, *Chem. Soc. Rev.* **2020**, *49*, 2751–2798.

[201] G. Alonso, D. Bahamon, F. Keshavarz, X. Giménez, P. Gamallo, R. Sayós, *J. Phys. Chem. C* **2018**, *122*, 3945–3957.

[202] A. R. Millward, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 17998–17999.

[203] M. Xue, Y. Liu, R. M. Schaffino, S. Xiang, X. Zhao, G.-S. Zhu, S.-L. Qiu, B. Chen, *Inorg. Chem.* **2009**, *48*, 4649–4651.

[204] P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, *Langmuir* **2008**, *24*, 7245–7250.

[205] Z. Liang, M. Marshall, A. L. Chaffee, *Energy Fuels* **2009**, *23*, 2785–2789.

[206] Y. E. Cheon, M. P. Suh, *Chem. Eur. J.* **2008**, *14*, 3961–3967.

[207] B. Arstad, H. Fjellvåg, K. O. Kongshaug, O. Swang, R. Blom, *Adsorption* **2008**, *14*, 755–762.

[208] S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.

[209] Y. E. Cheon, J. Park, M. P. Suh, *Chem. Commun.* **2009**, 5436–5438.

[210] W. R. Lee, S. Y. Hwang, D. W. Ryu, K. S. Lim, S. S. Han, D. Moon, J. Choi, C. S. Hong, *Energy Environ. Sci.* **2014**, *7*, 744–751.

[211] S. Gadipelli, Z. Guo, *Chem. Mater.* **2014**, *26*, 6333–6338.

[212] Y. Lin, Q. Yan, C. Kong, L. Chen, *Sci. Rep.* **2013**, *3*, 1859.

[213] X. Su, L. Bromberg, V. Martis, F. Simeon, A. Huq, T. A. Hatton, *ACS Appl. Mater. Interfaces* **2017**, *9*, 11299–11306.

[214] M. Sai Bhargava Reddy, D. Ponnamma, K. K. Sadasivuni, B. Kumar, A. M. Abdullah, *RSC Adv.* **2021**, *11*, 12658–12681.

[215] L. Grajciar, O. Bludský, P. Nachtigall, *J. Phys. Chem. Lett.* **2010**, *1*, 3354–3359.

[216] C. Chen, Y.-R. Lee, W.-S. Ahn, *J. Nanosci. Nanotechnol.* **2016**, *16*, 4291–4301.

[217] G. Xu, P. Nie, H. Dou, B. Ding, L. Li, X. Zhang, *Mater. Today* **2017**, *20*, 191–209.

[218] T. Kan, X. Sun, H. Wang, C. Li, U. Muhammad, *Energy Fuels* **2012**, *26*, 3604–3611.

[219] M. Usman, J. Zhu, K. Chuiyang, M. T. Arslan, A. Khan, A. Galadima, O. Muraza, I. Khan, A. Helal, B. A. Al-Maythalony, Z. H. Yamani, *Catalysts* **2019**, *9*, 919.

[220] H. Wang, Y. Cao, D. Li, U. Muhammad, C. Li, Z. Li, S. Zhang, *J. Renew. Sustain. Energy* **2013**, *5*, 053114.

[221] H. H. Zhang, Y. M. Cao, M. Usman, L. J. Li, C. S. Li, *Adv. Mat. Res* **2012**, *531*, 263–267.

[222] M. Usman, D. Li, R. Razzaq, M. Yaseen, C. Li, S. Zhang, *J. Ind. Eng. Chem.* **2015**, *23*, 21–26.

[223] M. Yaseen, M. Humayun, A. Khan, M. Usman, H. Ullah, A. A. Tahir, H. Ullah, *Energies* **2021**, *14*, 1278.

[224] M. Usman, D. Li, R. Razzaq, U. Latif, O. Muraza, Z. H. Yamani, B. A. Al-Maythalony, C. Li, S. Zhang, *J. Environ. Chem. Eng.* **2018**, *6*, 4525–4530.

[225] M. B. Jensen, L. G. Pettersson, O. Swang, U. Olsbye, *J. Phys. Chem. B* **2005**, *109*, 16774–16781.

[226] S. D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A. G. Russell, Q. Wei, M. Fan, *RSC Adv.* **2013**, *3*, 22739–22773.

[227] P. Jadhav, R. Chatti, R. Biniwale, N. Labhsetwar, S. Devotta, S. Rayalu, *Energy Fuels* **2007**, *21*, 3555–3559.

[228] K. M. K. Yu, I. Curcic, J. Gabriel, S. C. E. Tsang, *ChemSusChem* **2008**, *1*, 893–899.

[229] D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* **2010**, *49*, 6058–6082; *Angew. Chem.* **2010**, *122*, 6194–6219.

[230] P. Pachfule, Y. Chen, J. Jiang, R. Banerjee, *J. Mater. Chem.* **2011**, *21*, 17737–17745.

[231] S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P. Wheatley, R. Morris, A. Zecchina, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2676–2685.

[232] P. Chowdhury, C. Bikkina, S. Gumma, *J. Phys. Chem. C* **2009**, *113*, 6616–6621.

[233] Q. Xu, D. Liu, Q. Yang, C. Zhong, J. Mi, *J. Mater. Chem.* **2010**, *20*, 706–714.

[234] S. J. D. Smith, B. P. Ladewig, A. J. Hill, C. H. Lau, M. R. Hill, *Sci. Rep.* **2015**, *5*, 7823.

[235] T. Noor, U. Raffi, N. Iqbal, L. Yaqoob, N. Zaman, *Mater. Res. Express* **2019**, *6*, 125088.

[236] A. K. Adhikari, K.-S. Lin, *Chem. Eng. J.* **2016**, *284*, 1348–1360.

[237] Y. Cao, Y. Zhao, F. Song, Q. Zhong, *J. Energy Chem.* **2014**, *23*, 468–474.

[238] Y. Chen, D. Lv, J. Wu, J. Xiao, H. Xi, Q. Xia, Z. Li, *Chem. Eng. J.* **2017**, *308*, 1065–1072.

[239] M.-S. Yen, M.-C. Kuo, *Dyes Pigm.* **2012**, *94*, 349–354.

[240] R. Safi, H. Shokrollahi, *Prog. Solid State Chem.* **2012**, *40*, 6–15.

[241] S. M. Abu Nayem, S. Shaheen Shah, N. Sultana, M. A. Aziz, A. J. Saleh Ahammad, *Chem. Rec.* **2021**, *21*, 1039–1072.

[242] J. Begum, Z. Hussain, T. Noor, *Mater. Res. Express* **2020**, *7*, 015083.

[243] W. Huang, X. Zhou, Q. Xia, J. Peng, H. Wang, Z. Li, *Ind. Eng. Chem. Res.* **2014**, *53*, 11176–11184.

[244] M. Anbia, V. Hoseini, *Chem. Eng. J.* **2012**, *191*, 326–330.

[245] R. Ahmad, N. Iqbal, M. M. Baig, T. Noor, G. Ali, I. H. Gul, *Electrochim. Acta* **2020**, *364*, 137147.

[246] Y. Zhao, Y. Cao, Q. Zhong, *J. clean energy tech* **2014**, *2*, 34–37.

[247] A. Policicchio, Y. Zhao, Q. Zhong, R. G. Agostino, T. J. Bandosz, *ACS Appl. Mater. Interfaces* **2014**, *6*, 101–108.

[248] Y. Zhao, H. Ding, Q. Zhong, *Appl. Surf. Sci.* **2013**, *284*, 138–144.

[249] X. Wang, Q. Guo, J. Zhao, L. Chen, *Int. J. Greenhouse Gas Control* **2015**, *37*, 90–98.

[250] X. Zhou, W. Huang, J. Miao, Q. Xia, Z. Zhang, H. Wang, Z. Li, *Chem. Eng. J.* **2015**, *266*, 339–344.

[251] F. Xu, Y. Yu, J. Yan, Q. Xia, H. Wang, J. Li, Z. Li, *Chem. Eng. J.* **2016**, *303*, 231–237.

[252] Y. Yang, L. Ge, V. Rudolph, Z. Zhu, *Dalton Trans.* **2014**, *43*, 7028–7036.

[253] Y. Cao, H. Zhang, F. Song, T. Huang, J. Ji, Q. Zhong, W. Chu, Q. Xu, *Materials* **2018**, *11*, 589.

[254] H. R. Abid, Z. H. Rada, Y. Li, H. A. Mohammed, Y. Wang, S. Wang, H. Arandiyan, X. Tan, S. Liu, *RSC Adv.* **2020**, *10*, 8130–8139.

[255] E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long, O. M. Yaghi, *J. Am. Chem. Soc.* **2010**, *132*, 14382–14384.

[256] J. Zhu, P. M. Usov, W. Xu, P. J. Celis-Salazar, S. Lin, M. C. Kessinger, C. Landaverde-Alvarado, M. Cai, A. M. May, C. Slebodnick, *J. Am. Chem. Soc.* **2018**, *140*, 993–1003.

[257] A. Huang, Y. Chen, Q. Liu, N. Wang, J. Jiang, J. Caro, *J. Membr. Sci.* **2014**, *454*, 126–132.

[258] S. Li, Y. G. Chung, R. Q. Snurr, *Langmuir* **2016**, *32*, 10368–10376.

[259] K. M. Gupta, Y. Chen, J. Jiang, *J. Phys. Chem. C* **2013**, *117*, 5792–5799.

[260] N. M. Padial, E. Quartapelle Procopio, C. Montoro, E. López, J. E. Oltra, V. Colombo, A. Maspero, N. Masciocchi, S. Galli, I. Senkovska, S. Kaskel, E. Barea, J. A. R. Navarro, *Angew. Chem. Int. Ed.* **2013**, *52*, 8290–8294; *Angew. Chem.* **2013**, *125*, 8448–8452.

[261] Y. Wang, Z. Hu, T. Kundu, Y. Cheng, J. Dong, Y. Qian, L. Zhai, D. Zhao, *ACS Sustainable Chem. Eng.* **2018**, *6*, 11904–11912.

[262] Y. Li, H.-T. Wang, Y.-L. Zhao, J. Lv, X. Zhang, Q. Chen, J.-R. Li, *Inorg. Chem. Commun.* **2021**, *130*, 108741.

[263] X. Shi, N. Iqbal, S. Kunwar, G. Wahab, H. Kasat, A. M. Kannan, *Int. J. Hydrogen Energy* **2018**, *43*, 3520–3526.

[264] C. Liu, B. McCulloch, S. T. Wilson, A. I. Benin, M. E. Schott, US Patents, **2009**.

[265] E. V. Perez, K. J. Balkus, J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2009**, *328*, 165–173.

[266] A. Car, C. Stropnik, K.-V. Peinemann, *Desalination* **2006**, *200*, 424–426.

[267] K. Díaz, M. López-González, L. F. del Castillo, E. Riande, *J. Membr. Sci.* **2011**, *383*, 206–213.

[268] H. Ren, J. Jin, J. Hu, H. Liu, *Ind. Eng. Chem. Res.* **2012**, *51*, 10156–10164.

[269] A. F. Bushell, M. P. Attfield, C. R. Mason, P. M. Budd, Y. Yampolskii, L. Starannikova, A. Rebrov, F. Bazzarelli, P. Bernardo, J. Carolus Jansen, M. Lanč, K. Friess, V. Shantarovich, V. Gustov, V. Isaeva, *J. Membr. Sci.* **2013**, *427*, 48–62.

[270] T. Yang, T.-S. Chung, *J. Mater. Chem. A* **2013**, *1*, 6081–6090.

[271] L. Ge, W. Zhou, V. Rudolph, Z. Zhu, *J. Mater. Chem. A* **2013**, *1*, 6350–6358.

[272] S. N. Wijenayake, N. P. Panapitiya, S. H. Versteeg, C. N. Nguyen, S. Goel, K. J. Balkus, I. H. Musselman, J. P. Ferraris, *Ind. Eng. Chem. Res.* **2013**, *52*, 6991–7001.

[273] B. Seoane, V. Sebastian, C. Tellez, J. Coronas, *CrystEngComm* **2013**, *15*, 9483–9490.

[274] T. Rodenas, M. van Dalen, P. Serra-Crespo, F. Kapteijn, J. Gascon, *Micrpor. Mesopor. Mat* **2014**, *192*, 35–42.

[275] A. Bhaskar, R. Banerjee, U. Kharul, *J. Mater. Chem. A* **2014**, *2*, 12962–12967.

[276] M. Arjmandi, M. Pakizeh, *J. Ind. Eng. Chem.* **2014**, *20*, 3857–3868.

[277] S. Japip, H. Wang, Y. Xiao, T. Shung Chung, *J. Membr. Sci.* **2014**, *467*, 162–174.

[278] S. Shahid, K. Nijmeijer, *Sep. Purif. Technol.* **2017**, *189*, 90–100.

[279] M. R. Khdhayyer, E. Esposito, A. Fuoco, M. Monteleone, L. Giorno, J. C. Jansen, M. P. Attfield, P. M. Budd, *Sep. Purif. Technol.* **2017**, *173*, 304–313.

[280] M. Safak Boroglu, A. B. Yumru, *Sep. Purif. Technol.* **2017**, *173*, 269–279.

[281] Q. Zhang, S. Luo, J. R. Weidman, R. Guo, *Polymer* **2017**, *131*, 209–216.

[282] E. V. Perez, G. J. D. Kalaw, J. P. Ferraris, K. J. Balkus, I. H. Musselman, *J. Membr. Sci.* **2017**, *530*, 201–212.

[283] F. Dorosti, A. Alizadehdakhel, *Chem. Eng. Res. Des.* **2018**, *136*, 119–128.

[284] M. Mubashir, Y. F. Yeong, K. K. Lau, T. L. Chew, J. Norwahyu, *Sep. Purif. Technol.* **2018**, *199*, 140–151.

[285] M. Etxeberria-Benavides, O. David, T. Johnson, M. M. Łozińska, A. Orsi, P. A. Wright, S. Mastel, R. Hillenbrand, F. Kapteijn, J. Gascon, *J. Membr. Sci.* **2018**, *550*, 198–207.

[286] M. Zamidi Ahmad, M. Navarro, M. Lhotka, B. Zornoza, C. Téllez, V. Fila, J. Coronas, *Sep. Purif. Technol.* **2018**, *192*, 465–474.

[287] Y. Zhang, I. Musselman, J. Ferraris, K. Balkus Jr, *J. Membr. Sci.* **2008**, *313*, 170.

[288] S. Kim, E. Shamsaei, X. Lin, Y. Hu, G. P. Simon, J. G. Seong, J. S. Kim, W. H. Lee, Y. M. Lee, H. Wang, *J. Membr. Sci.* **2018**, *549*, 260–266.

[289] S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, *Nat. Mater.* **2012**, *11*, 710–716.

[290] H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim, W. Zhou, *J. Am. Chem. Soc.* **2013**, *135*, 10525–10532.

[291] J. Park, Z. U. Wang, L.-B. Sun, Y.-P. Chen, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 20110–20116.

[292] K. M. Choi, H. J. Jeon, J. K. Kang, O. M. Yaghi, *J. Am. Chem. Soc.* **2011**, *133*, 11920–11923.

[293] G. Zhang, H. Yang, H. Fei, *ACS Catal.* **2018**, *8*, 2519–2525.

[294] A. Koutsianos, E. Kazimierska, A. R. Barron, M. Taddei, E. Andreoli, *Dalton Trans.* **2019**, *48*, 3349–3359.

[295] W. Liang, C. J. Coghlan, F. Ragon, M. Rubio-Martinez, D. M. D'Alessandro, R. Babarao, *Dalton Trans.* **2016**, *45*, 4496–4500.

[296] S. Krause, V. Bon, I. Senkovska, U. Stoeck, D. Wallacher, D. M. Többens, S. Zander, R. S. Pillai, G. Maurin, F.-X. Coudert, S. Kaskel, *Nature* **2016**, *532*, 348–352.

[297] Q. Dong, X. Zhang, S. Liu, R.-B. Lin, Y. Guo, Y. Ma, A. Yonezu, R. Krishna, G. Liu, J. Duan, R. Matsuda, W. Jin, B. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 22756–22762; *Angew. Chem.* **2020**, *132*, 22944–22950.

[298] H. Wu, R. S. Reali, D. A. Smith, M. C. Trachtenberg, J. Li, *Chem. Eur. J.* **2010**, *16*, 13951–13954.

[299] R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem. Int. Ed.* **2003**, *42*, 428–431; *Angew. Chem.* **2003**, *115*, 444–447.

[300] A. Raza, S. Farrukh, A. Hussain, I. U. Khan, T. Noor, M. H. D. Othman, M. F. Yousaf, *Int. J. Energy Res.* **2020**, *44*, 7989–7999.

[301] J. Wang, Y. Zhang, P. Zhang, J. Hu, R.-B. Lin, Q. Deng, Z. Zeng, H. Xing, S. Deng, B. Chen, *J. Am. Chem. Soc.* **2020**, *142*, 9744–9751.

[302] Y. He, J. Shang, Q. Gu, G. Li, J. Li, R. Singh, P. Xiao, P. A. Webley, *Chem. Commun.* **2015**, *51*, 14716–14719.

[303] B. Chen, Q. Dong, X. Zhang, S. Liu, R.-B. Lin, Y. Guo, Y. Ma, A. Yonezu, R. Krishna, G. Liu, J. Duan, R. Matsuda, W. Jin, *Angew. Chem. Int. Ed.* **2020**.

[304] J. Park, D. Yuan, K. T. Pham, J.-R. Li, A. Yakovenko, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 99–102.

[305] N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda, S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 4501–4504.

[306] L. L. Gong, X. F. Feng, F. Luo, *Inorg. Chem.* **2015**, *54*, 11587–11589.