

**Carbon capture and conversion using metal-organic frameworks and MOF-based materials**

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Carbon capture and conversion using metal-organic frameworks and MOF-based materials

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Rapidly increasing atmospheric CO₂ concentrations threaten human society, the natural environment, and the synergy between the two. In order to ameliorate the CO₂ problem, carbon capture and conversion techniques have been proposed. Metal-organic framework (MOF)-based materials, a relatively new class of porous materials with unique structural features, high surface areas, chemical tunability and stability, have been extensively studied with respect to their applicability to such techniques. Recently, it has become apparent that the CO₂ capture capabilities of MOF-based materials significantly boost their potential toward CO₂ conversion. Furthermore, MOF-based materials' well-defined structures greatly facilitate the understanding of structure-property relationships and their roles in CO₂ capture and conversion. In this review, we provide a comprehensive account of significant progress in the design and synthesis of MOF-based materials, including MOFs, MOF composites and MOF derivatives, and their application to carbon capture and conversion. Special emphases on the relationships between CO₂ capture capacities of MOF-based materials and their catalytic CO₂ conversion performances are discussed.

1. Introduction

Energy demands of the global society are being met largely by combustion of fossil fuels including coal, petroleum, and natural gas. A major greenhouse gas (GHG), carbon dioxide (CO₂) is a key by-product of such combustion. The immense quantity of CO₂ emissions has resulted in serious environmental issues, such as global warming, ocean acidification, extreme weather, and species extinction.^{1, 2} Since the early 19th century, a steep and continuous increase has been observed in atmospheric CO₂ concentrations from approximately 280 ppm in the early 1800s to over 400 ppm in 2018. With little to no mitigative action, the Intergovernmental Panel on Climate Change (IPCC) has predicted that atmospheric CO₂ concentrations could reach 950 ppm by 2100.³⁻⁵ Elevated atmospheric CO₂ levels serve to directly increase the global mean temperature (around 1.9 °C at atmospheric CO₂ concentrations of 570 ppm) by absorbing outgoing longwave radiation (i.e. the greenhouse effect).³ Therefore, decreasing emissions and mitigating atmospheric

CO₂ concentrations are imperative tasks that require drastic, immediate attention. With the understanding that fossil fuels will remain a major source of energy for the foreseeable future, the most straightforward strategy to reduce anthropogenic CO₂ emissions lies in removing CO₂ from point sources, such as the flue gas from fossil-fuel burning power plants. This can be accomplished using suitable carbon capture and storage (CCS) technologies. Key drawbacks in such technologies lie in the energy consumption associated with separation, purification, compression, transportation, and storage processes.⁶ This consumption is likely to be accompanied by further CO₂ emission, and thus will not adequately address the issue. Moreover, various adsorbents have been developed in order to capture and store CO₂, but their high regeneration temperatures and/or limited CO₂ adsorption capacities still hinder the development of CCS technologies.^{2, 6, 7} Beyond CCS, another strategy involves capture and subsequent conversion of CO₂ into high value-added chemicals and fuels (i.e. CO₂ capture and conversion). In doing so, CO₂ capture and conversion serves as an anthropogenic carbon cycle, is more sustainable, and thus lies further within the realm of "green chemistry".

In the past decades, several classes of materials, including ionic liquids (ILs), zeolites, porous carbons, porous organic polymers, covalent organic frameworks (COFs) and metal-organic frameworks (MOFs), have been developed for CO₂ capture and conversion applications.⁸⁻¹⁶ In particular, MOFs signify a relatively new class of crystalline porous materials constructed from multimetallic units called secondary building units (SBUs) and organic linkers.¹⁷⁻²¹ By designing and functionalizing SBUs, linkers and pore environments, MOFs'

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physical and chemical properties can be finely tuned, making them promising materials for a variety of applications, such as gas storage and separation, heterogeneous catalysis, sensing, drug delivery, to mention a few.^{14-19, 22-92} With respect to CO₂ capture and conversion, MOFs serve as promising adsorbents and catalysts because of their unique advantages: 1) Predictable, functionalizable structures; it is possible to predict the structures of many MOFs and the structural designability and chemical tunability of the materials allow for incorporation of different type of accessible capture and catalytically active sites. 2) Hybrid structures; MOFs are highly compatible with other materials and can serve as precursors and/or templates to afford MOF composites or MOF derivatives with extraordinary physical and chemical properties. 3) Particular strengths for catalysis; MOFs combine beneficial features of homogeneous and heterogeneous catalysts, such as high catalytic efficiency, facile separation and reusability, and stability. 4) The well-defined and tailorable structures of MOFs greatly facilitate the understanding of structure-property relationships in MOF-based catalysts. All of these attributes make MOFs ideally suited for CO₂ capture and conversion.

The employment of MOFs in CO₂ capture and conversion applications has undergone three development stages. First, the CO₂ adsorption capacity and selectivity of MOFs were tuned.^{15, 47, 62, 75, 78-80} Toward this end, a variety of strategies

have been investigated in order to enhance MOF-CO₂ interactions. As many MOFs exhibiting strong interactions with CO₂ were developed, they began to garner immense attention with respect to CO₂ separation applications, mainly regarding the removal of CO₂ from CO₂/H₂ (pre-combustion carbon capture) and CO₂/CH₄ gas mixtures (natural gas purification), as well as CO₂ capture from CO₂/N₂ gas mixtures (post-combustion carbon capture).^{15, 62, 75, 77, 80} The second stage focused on development of MOF-based materials and their use for the conversion of CO₂ to organic products. Particularly, CO₂ cycloaddition with epoxides has become one of the most intensively investigated MOF-catalyzed CO₂ conversion reactions.⁶⁵⁻⁶⁸ It is important to recognize that many MOFs have a limited variety of reactive sites, with the major examples being acidic and/or basic sites on the SBU metal centers and/or the organic linkers. With this in mind, MOF composites made by combining MOFs with other materials, and MOF derivatives afforded by chemical and/or thermal conversion of MOFs with multiple active sites and high stabilities have emerged as promising materials for CO₂ capture and separation.^{74, 82-85} In the third and most recent stage, attempts have been made to explore and expand the scope of possible CO₂ transformation reactions involving MOF-based materials. Additionally, optimization of the catalytic performance of such materials for practical CO₂ capture and conversion has become the main target. On the basis of their



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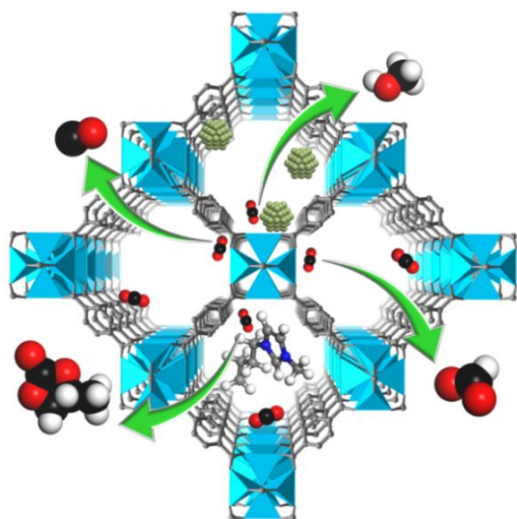
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Scheme 1 An illustration of a generic MOF, composed of tetrametallic SBUs (cyan polyhedra) linked together by terephthalate (gray), with four channels shown to capture CO₂ and convert it to either CO (left), methanol using metal nanoparticles embedded in the pore (top), formate (right), or ethylene carbonate using an ionic liquid lodged in the pore (bottom).

unique features, particularly stability and conductivity, and cooperativity between multiple active sites, MOF-based materials can serve as highly effective catalysts for numerous value-added CO₂ conversion reactions, specifically photocatalytic and electrocatalytic CO₂ reduction.^{52, 63, 70, 86-88,90, 92} With these stages in mind, current and future development promise to target optimization of the synergistic effects of CO₂ adsorption and CO₂ conversion in MOFs and MOF-based materials. Although many challenges remain, the so-called “Holy Grail” of MOF application to carbon capture and conversion technologies lies in the development of a material that can capture CO₂ from a gas mixture such as flue gas and directly, catalytically convert it to value-added compounds.

In pursuit of this lofty goal, it is crucial to have a detailed and comprehensive overview of the work that has already been reported. Thus, herein we present a summary and assessment of the development of MOF-based materials for CO₂ capture and conversion as illustrated in Scheme 1 for a generic MOF. We start by providing an overview of the CO₂ capture strategies employed in MOFs with specific focus placed on interactions between the frameworks and CO₂. Additionally, the challenges and targets intrinsic to the development of MOFs for CO₂ capture are discussed. Next, recent advances in the field of MOF-based materials for CO₂ conversion, including heterogeneous transformation into organic products, hydrogenation, photocatalytic reduction, and electrocatalytic reduction, are comprehensively described. Thirdly, we provide insight into the relationship between CO₂ capture capacity of MOF-based materials and their catalytic CO₂ conversion performance. Finally, the existing challenges and future directions in this research field are highlighted.

2. MOFs for CO₂ capture

Since their inception over 20 years ago^{93, 94}, MOFs have been targeted for CO₂ adsorption and capture applications due to their high porosity and chemical tunability.⁹⁵ To date, many reports focus on the study of CO₂ capture and increasing the capacity in MOFs as shown in Table 1. Generally, the interaction(s) between the framework and CO₂ adsorbate molecules play a critical role, as increasing the strength of such interactions augments the material’s CO₂ uptake capacity, especially at low loading pressure. The methods employed to increase these interaction strengths stem from tailoring the frameworks’ chemical and physical properties. This relies on the ability to alter the intrinsic properties of MOFs based on judicious design and synthesis of the framework via *de novo* process or by post-synthetic modification. In each case, the goal is to leverage MOFs’ chemical tunabilities and compatibilities to adjust the affinity of the framework for CO₂ molecules. Post-synthetic modification has been widely applied recently as a means of achieving this adjustment with a high degree of precision. In this section, we will explain each strategy in detail and provide examples of their employment.

2.1. CO₂ binding sites within MOFs

Traditional adsorbent materials including zeolites, silicas, polymers, activated carbons, take up CO₂ in a physisorptive manner through the use of weak interactions between CO₂ and the pore. Although MOFs also capture CO₂ by physisorption, their ultrahigh surface areas give much higher uptake capacities compared to other materials. In addition, the advantage of being able to design MOFs that possess features such as open metal sites (OMSs), Lewis basic sites (LBSs), covalently-bound polar functional groups, tunable pore sizes, framework flexibility, and hydrophobicity, provides for a better handle on their tailorability. Specifically, the interaction of CO₂ with these sites tends to result in excellent CO₂ adsorption capacity and/or preferential CO₂ adsorption over other gas molecules, such as N₂, CH₄, and H₂O. Needless to say, MOFs can employ multiple interactions in a single structure to achieve extraordinary CO₂ adsorption.

2.1.1. Open metal sites (OMSs)

Accessing OMSs on MOFs’ multimetallic secondary building units (SBUs) is one of the most widely used strategies to improve their CO₂ capture properties. In general, OMSs are generated by treating a MOF with coordinated terminal ligands such as water, *N,N*-dimethyl formamide (DMF), methanol, on the SBUs, under heat and/or vacuum to remove such ligands with retention of the overall structure. This often results in improved porosity in the activated material. These OMSs commonly serve as Lewis acid sites (LASs) that have been shown to coordinate CO₂. Such behavior at Lewis acidic OMSs endows many MOFs with high CO₂ affinities, especially at low adsorbate partial pressures.

The concept of designing OMSs and its implementation was reported in 1998 and 2000.^{96, 97} In 2005, the CO₂ uptake of HKUST-1, having OMSs, was found to be about 10 mmol g⁻¹ at 42 bar and ambient temperature.⁹⁸ In HKUST-1, the room-temperature CO₂ adsorption isotherm appears as a typical Type I isotherm in which the most gas is adsorbed at low

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Table 1 Summary of MOF-based adsorbents and the corresponding CO₂ capture capacity for each material^a

Adsorbent	Pressure (bar)	Temperature (K)	Capacity (mmol g ⁻¹)	Ref.		
MOFs with Open Metal Sites						
HKUST-1	1	298	4.1	98		
Mg ₂ (dobpdc)	0.15	298	4.9	99		
	1	298	6.4			
NU-1000	40	298	46.4	100		
PCN-61	35	298	23.5	101		
PCN-66		298	26.3			
PCN-68		298	30.4			
MIL-96	10	303	4.4	102		
SNU-5	1	195	2.6	103		
		273	0.9			
MIL-102	30	304	3.1	105		
Cu-BTtri	0.06	298	0.3	106		
	1	298	3.2			
Fe-BTT	1	298	3.1	107		
PCN-88	1	273	7.1	108		
		296	4.2			
NOTT-140	20	283	20.7	111		
		293	19.5			
[Cd ₂ L1(H ₂ O)] ₂	1	195	3.3	113		
		293	2.1			
[Zn ₄ (OH) ₂ (1,2,4-BTC) ₂ (H ₂ O) ₂]	1	295	1.9	114		
[(CH ₃)NH ₂] ₃ [(Cu ₄ Cl) ₃ (btc) ₈ ·xMeOH]	1	273	5.5	115		
[Mg(3,5-PDC)(H ₂ O)]	1	298	0.6	116		
[NH ₂ (CH ₃) ₂][Zn ₃ (BTA)(BTC) ₂ (H ₂ O)]	1	273	4.6	117		
[NH ₂ (CH ₃) ₂][Cd ₃ (BTA)(BTC) ₂ (H ₂ O)] ₂			3.8			
Mg-MOF-74	0.1	296	5.4	120		
	1		8.0			
Zn-MOF-74	0.1		1.3			
	1		5.5			
Ni-MOF-74	0.1		2.6			
	1		5.8			
Co-MOF-74	0.1		2.7			
	1		7.0			
MOFs with Both Open Metal and Lewis Basic Sites						
FJI-H14	1		195		12.5	109
		298	6.5			
MOFs with Lewis Basic Sites						
NH ₂ -MIL-53	5	303	2.3	128		
NH ₂ -MIL-125	1	273	4.0	130		
		298	2.2			
CAU-1	1	273	7.2	131		
IRMOF-74-III-(CH ₂ NH ₂) ₂	1	298	3.0	132		
IRMOF-74-III-CH ₂ NH ₂	1	298	3.3	133		
bio-MOF-11	1	298	4.1	134		
Cu-TDPAT	0.1	298	1.4	135		
	1		5.9			
MAF-25	1	195	5.2	138		

MAF-26			3.8	
IFMC-1	1	195	7.5	140
		273	4.1	
		298	2.7	
MAF-23	1	273	3.3	141
		298	2.5	
CPF-6	1	273	4.4	142
ZJNU-43	1	296	4.6	143
ZJNU-44			5.2	
ZJNU-45			4.8	
MAF-66	1	273	6.3	144
		298	4.4	
ZTF-1	1	273	5.6	145
$Zn_2(C_2O_4)(C_2N_4H_3)_2 \cdot (H_2O)_{0.5}$	1.2	273	4.4	146
[Zn(dtp)]	1	195	4.4	147
MOFs with Polar Functionalities				
TMOF-1	1	200	6.8	150
		273	2.2	
		298	1.4	
		308	1.2	
[Zn(L2)] _n	1	298	2.1	151
Zn(BPZNO ₂)	1.2	298	5.0	152
USTC-253	1	273	3.7	155
		298	2.1	
		273	6.1	
		298	2.9	
[Zn(BDC-OH)-(TED) _{0.5}]-1.5DMF _{0.3} H ₂ O	1	298	3.0	156
[Zn(BDC-NH ₂)-(TED) _{0.5}]-xDMF-yH ₂ O			2.2	
LIFM-26	1	273	5.4	159
		298	3.3	
ZJNU-40	1	273	7.6	160
		296	4.8	
Microporous MOFs				
Ni-4PyC	10	298	8.2	164
SNU-71	1	195	13.2	169
		298	1.0	
SUMOF-2	1	273	4.3	170
SUMOF-3			3.4	
SUMOF-4			3.6	
NOTT-202a	1	195	20.0	171
HPYR@ZnPC-2	0.15	298	0.7	172
HPIP@ZnPC-2			1.1	
CPM-33a	1	273	6.1	175
		298	3.3	
		273	7.8	
		298	5.6	
MOFs with Micropores and Polar Functionalities				
(choline) ₃ [In ₃ (btc) ₄] 2DMF	1	273	3.2	173
MOFs with Micropores and Open Metal Sites				
CPM-5	1	273	3.6	174
		299	2.4	
Flexible MOFs				
[Zn ₂ (2,5-BME-bdc) ₂ (dabco)] _n	1	195	4.6	179
[Zn ₂ (DB-bdc) ₂ (dabco)] _n			2.5	
SHF-61	20	298	2.4	180
PCN-123	1	295	1.0	182
{[Zn ₂ (BME-bdc) ₂ -(bipy)] _n (DMF) _{2.3} (EtOH) _{0.4} }	1	195	7.0	185
		273	2.3	
		298	1.5	

[Sm(HL)(DMA) ₂]	20	333	0.6	186
[Mn(bdc)(dpe)]	1	195	4.9	187
[Zn ₂ (L3) ₂ (dabco)] _n	1	195	6.3	188
[Zn ₂ (L4) ₂ -(dabco)] _n			8.0	
[Zn ₂ (L4) ₂ -(dabco)] _n			8.9	
SNU-M10	1	195	5.5	189
		273	3.3	
		298	2.1	
SNU-M11		195	5.5	
Post-Synthetically Modified MOFs				
mmen-Mg ₂ (dobpdc)	0.00039	298	2.0	99
	0.15	298	3.1	
	1	298	3.9	
Cu-BTtri-en	0.06	298	0.4	106
	1	298	1.3	
[Mg ₂ (dobdc)(N ₂ H ₄) _{1.8}]	0.0004	298	3.9	199
Mg ₂ (dondc)(en) _{1.5} (H ₂ O) _{0.5}	1	298	2.6	201
Mg ₂ (dondc)(mmen) _{1.2} (H ₂ O) _{0.8}			4.1	
Mg ₂ (dondc)(ppz) _{1.1} (H ₂ O) _{0.9}			3.2	
dmen-Mg ₂ (dobpdc)	1	313	4.3	202
UiO-66(Ti ₃₂)	1	273	2.3	206
UiO-66(Ti ₅₆)			4.0	
Cr-MIL-101-SO ₃ H-TAEA	0.15	313	2.3	208
	0.0004	293	1.1	
UiO-66-aminoalcohol	20	308	11.6	209
UiO-66-SO ₃ H-0.15	1	298	2.2	210
UiO-66-SO ₃ Li-0.15			3.3	
SNU-31	1	298	0.6	211
	40		2.2	
LIFM-29	1	273	2.5	212
LIFM-30			2.6	
LIFM-31			2.6	
LIFM-32			2.7	
LIFM-33			3.6	
UiO-66-AD4	1	273	3.6	213
		298	1.9	
		323	1.1	
273		3.8		
298		2.6		
323		1.7		
273		3.3		
298		1.8		
323		1.0		
273		1.3		
298		0.6		
323	0.3			
UiO-66-(COOLi) ₂ -EX	1	273	1.7	214
		298	2.4	
		273	2.9	
298		2.0		
273		2.0		
298		1.3		
273		2.3		
298		1.5		
273		3.4		
298		2.3		
273		1.9		
298		1.2		
273		0.9		

		298	0.6	
tetramethylammonium@bio-MOF-1	1	273	4.5	216
		313	1.6	
		273	4.2	
313		1.7		
tetraethylammonium@bio-MOF-1		273	3.4	
313		1.4		
tetrabutylammonium@bio-MOF-1		273	4.8	217
GND@bio-MOF-1	1	313	1.6	
		273	4.9	
AmGND@bio-MOF-1		313	1.6	
		273	5.1	
DiAmGND@bio-MOF-1		313	1.7	
SNU-100'-Li	1	298	3.5	219
SNU-100'-Mg			3.4	
SNU-100'-Ca			3.4	
SNU-100'-Co			3.8	
SNU-100'-Ni			3.8	
Li@HKUST-1			18	
MOF Composites				
PEI-MIL-101-100	0.15	298	4.2	223
A-PEI-300	0.15	298	3.6	224
B-PEI-300			4.1	
PN@MOF-5	1	273	3.5	225
MgCGr-2	0.15	298	4.9	227
	1		6.8	
MgCGr-5	0.15		4.8	
	1		8.4	
MgCGr-10	0.15		5.5	
	1		8.1	
NiCGr-2	0.15		2.6	
	1		4.5	
NiCGr-5	0.15		3.2	
	1		5.9	
NiCGr-10	0.15		3.3	
	1		5.7	
CG-3	1	273	7.9	228
CG-9			8.3	
CG-15			3.0	
HKUST-1@AC-2	1	273	8.1	229
HKUST-1/GO	1	298	3.2	231
HKUST-1/GO-U1			2.2	
HKUST-1/GO-U2			3.0	
HKUST-1/GO-U3			4.7	
MIL-53(Al)/GNP 2.5%	40	298	11.8	233
MIL-53(Al)/GNP 5%			13.0	
MIL-53(Al)/GNP 10%			9.1	
F-MOF1@AC-1	1	195	6.5	234
HCM- HKUST-1-1	1	298	2.4	235
HCM- HKUST-1-2			2.4	
HCM- HKUST-1-3			2.8	
5A@ZIF-8(I)	1	298	3.0	237
5A@ZIF-8(II)			2.6	
5A@ZIF-8(III)			2.1	
ZC-1	1	273	2.2	241
ZC-2			2.2	
ZC-3			2.0	
ZC-4			2.0	
ZC-5			1.8	

ZC-6			1.6	
CNT@HKUST-1	18	298	13.5	240

^aReports in this table include capacities in mmol g⁻¹ (some have been converted to these units from the originally reported units).

pressures, leading to a “knee” shaped behavior, indicative of high affinity of this MOF for CO₂ at low partial pressures. These conditions are interesting with respect to practical CO₂ adsorption from gas streams as the material will have large CO₂ capture working capacity. Following this work, a wide variety of MOFs bearing OMSs have been applied as CO₂ absorbents, including NU-1000, MIL-101, and M-MOF-74.⁹⁹⁻¹¹⁸ Among these, the M-MOF-74 (M = Mg²⁺, Ni²⁺, Co²⁺, Zn²⁺) isorecticular series, composed of an array of one-dimensional hexagonal channels with OMSs at the SBUs, has become one of the most well-studied sets of MOFs for CO₂ capture due to their extraordinary CO₂ uptake capacities at low pressures.^{110, 119} More importantly, the CO₂ adsorption of this series can be tuned based on the metal from which the MOF is constructed. The CO₂ uptake of Mg-MOF-74 (5.4 mmol g⁻¹ at 0.1 atm) is 2-4 times higher than those of the other isorecticular M-MOF-74 compounds at the same CO₂ loading pressures.¹²⁰ The zero-coverage isosteric heats of CO₂ adsorption (Q_{st}) of the frameworks details important information regarding the affinity of frameworks for CO₂. Applying this analysis to the M-MOF-74 isorecticular series, one concludes that Mg-MOF-74 exhibits the highest CO₂ affinity (47 kJ mol⁻¹), whereas Zn-MOF-74, Ni-MOF-74 and Co-MOF-74 exhibit initial affinities of 26, 37, and 41 kJ mol⁻¹, respectively.¹²⁰ This high affinity for CO₂ in Mg-MOF-74 stems from the increased ionic character of the Mg-O bond that imparts stronger charge-quadrupole interactions between the Mg OMSs and CO₂.

To further understand the mechanism of CO₂ adsorption on MOFs' OMSs, density function theory (DFT) calculations, neutron powder diffraction experiments, infrared and Raman spectroscopy, and *in situ* solid-state ¹³C nuclear magnetic resonance (NMR) measurements were performed.^{119,121-123} Generally, CO₂ molecules interact with OMS in an end-on fashion through lone pair electron donation.¹¹⁹ These fairly strong interactions only marginally alter the intramolecular angles of adsorbed CO₂. Additionally, DFT calculations suggest that CO₂ adsorption on the OMSs in these materials is still largely physisorptive.¹²¹ This not only reduces the energy penalty for adsorbent regeneration, a key consideration in CO₂ capture, but also accelerates the adsorptive kinetics in MOFs.

With these studies, MOFs were evaluated for potential application in selective adsorption processes. For example, temperature swing post-combustion CO₂ adsorption was studied in MOF-177 and Mg-MOF-74.¹²⁴ While MOF-177 exhibits only poor to modest selectivity, Mg-MOF-74 was marked by tremendous selectivity with an ideal adsorbed solution theory (IAST) selectivity factor of 148.1 at a typical flue gas temperature (~50 °C). In fact, the CO₂ selectivity of Mg-MOF-74 was even greater than that of the previously most studied zeolite NaX (87.4) under the same conditions. The methods in this study were applied to five different MOFs, targeting pre-combustion CO₂ capture, namely the selective capture of CO₂ in the presence of H₂.¹²⁵ Mg-MOF-74 has the

highest CO₂/H₂ selectivity (859 at 5 bar) measured from an 80:20 H₂/CO₂ mixture at 313 K because of the greater polarizability of CO₂ compared to H₂ and the high concentration of OMSs in the MOF pore.

2.1.2. Lewis basic sites (LBSs)

While the use of SBU-based OMSs for CO₂ capture lead to promising results with respect to adsorption capacity and selectivity, another important component of MOFs, the organic linkers, can also augment these properties. For instance, incorporation of organic linkers bearing LBSs into MOFs has been shown to greatly enhance their CO₂ binding affinities. This strategy was inspired by the outstanding CO₂ uptake capacities of aqueous amine solutions such as industrial solutions of monoethanolamine (MEA).¹²⁶⁻¹²⁷ As an attempt to include Lewis basic amines into a MOF, 2-aminoterephthalic acid (NH₂-H₂BDC), was utilized in the synthesis of IRMOF-3, a MOF isorecticular to MOF-5.⁹⁸ At 298 K, and over a wide pressure range (from 0 to 12.3 bar), IRMOF-3 exhibits a higher CO₂ uptake capacity (0-14.7 mmol g⁻¹) than MOF-5 (0-14.0 mmol g⁻¹). This study indicated that greater CO₂ affinities can be achieved by introducing LBSs on the organic linkers. Similar phenomena were also observed in many isorecticular MOFs, such as NH₂-MIL-53, NH₂-UiO-66, and NH₂-MIL-125.¹²⁸⁻¹³¹ It is important to note here that many aromatic amines that have been incorporated into MOFs do not necessarily capture CO₂ in the same chemisorptive manner as

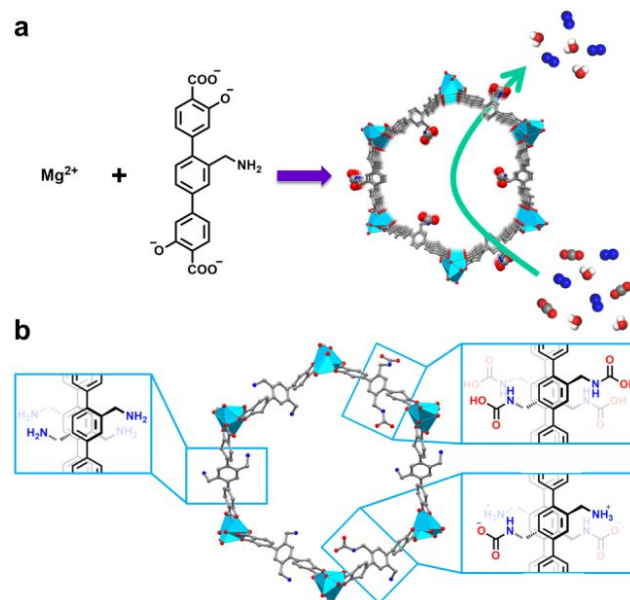


Fig. 1 (a) Synthesis of IRMOF-74-III-CH₂NH₂ from Mg²⁺ and the amine-functionalized linker (2'-(aminomethyl)-3,3''-dioxido-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate) for selective, chemisorptive CO₂ capture from a CO₂/N₂/H₂O gas mixture. (b) View of modeled IRMOF-74-III-(CH₂NH₂)₂ structure down the crystallographic *c*-axis, depicting the three pore environments before (left pore wall) and after exposure to CO₂ under dry conditions to produce carbamic acids (upper right pore wall) and 95% relative humidity (RH) to give ammonium carbamates (bottom right pore wall). Color code: C, gray; O, red; N, blue; H, white; and Mg, cyan.

aqueous amine solutions, given that aromatic amines lack the nucleophilicity of the alkylamines in solution. Recently, several functionalized IRMOF-74-III compounds were synthesized in hopes of capturing CO₂ in the presence of water (Fig. 1).^{132,133} The linker-based amine functional groups of IRMOF-74-III-CH₂NH₂ endowed the material with the highest CO₂ uptake capacity (3.2 mmol g⁻¹ at 800 torr) of the series. In contrast to the aromatic amine cases detailed above, the alkylamines in IRMOF-74-III-CH₂NH₂ chemically bind CO₂, forming new, covalent species in the MOF. Solid-state cross-polarization magic angle spinning (CP-MAS) ¹³C NMR spectra indicated that the major chemisorption product in this material was a mixture of carbamic acid (RNHCOOH) and ammonium carbamate (RNHCOO⁻ +H₃NR). More importantly, since the CO₂ capture took place at the linker-based alkylamines instead of the OMSs, the influence of water was negligible with respect to the CO₂ adsorption performance of IRMOF-74-III-CH₂NH₂. Therefore, this MOF captured CO₂ with a high capacity and selectivity even under 65% relative humidity. Recently, this strategy has been improved by doubling the linker-based alkylamines in the framework, yielding IRMOF-74-III-(CH₂NH₂)₂.¹³² With two alkylamines per organic linker, the CO₂ adsorption capacity of the framework increased by more than 100% because the arrangement of the amines in the structure allowed for the formation of only carbamic acids under dry conditions. These carbamic acids are less stable and thus more easily removed, by vacuum or lower heat, than their ammonium carbamate counterparts which are formed when CO₂ is captured under humid conditions (Fig. 1b). Clearly, the strategy of amine-incorporation onto MOF linkers can be improved to target particular chemisorption products with desirable properties for specific CO₂ capture applications.

Apart from amine-functionalized linkers, other nitrogenous linkers, including pyrimidines, triazines, and azoles, have also been utilized to synthesize MOFs bearing LBSs.¹³⁴⁻¹⁴⁸ In 2012, a new *rht*-type MOF, Cu-TDPAT, based on an LBS-rich hexacarboxylate ligand (H₆TDPAT) was reported.¹³⁵ Its CO₂ adsorption capacity (5.9 mmol g⁻¹ at 298 K and 1 atm, 10.1 mmol g⁻¹ at 273 K and 1 atm) and isosteric heat of adsorption (42 kJ mol⁻¹) were substantially higher than many previously reported *rht*-type MOFs. To investigate the interactions between Cu-TDPAT and CO₂, room-temperature IR spectroscopy was conducted after CO₂ loading showing the evolution of a distinct band at $\nu = 2335\text{ cm}^{-1}$ perhaps attributable to CO₂ adsorption at the LBSs.

While LBS incorporation strategies are effective, MOF-CO₂ interactions remain mainly single site in nature. Reliance on such interactions can result in relative weak framework affinities for CO₂ or low reversibility.¹⁴¹ As an alternative approach, MOFs can be designed such that their pores are decorated with multiple LBSs. The cooperation between these can endow the resultant MOFs with high CO₂ binding affinities, high selectivities, and reversible CO₂ adsorption. A flexible framework, MAF-23, was made from a chelating-bridging ligand (bis(5-methyl-1H-1,2,4-triazol-3-yl)methane, H₂btm)¹⁴¹, where the available triazolite N-donors of the organic linker acted as CO₂ chelation sites. At 1 atm, MAF-23 exhibited a CO₂

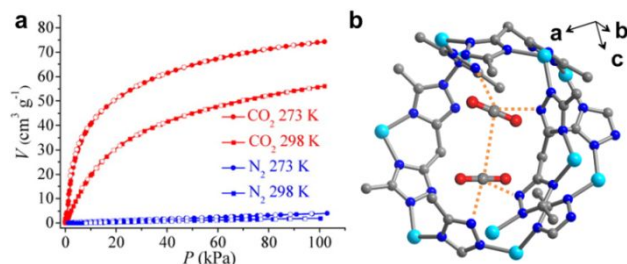


Fig. 2 (a) CO₂ (red) and N₂ (blue) adsorption (solid) and desorption (open) isotherms at 273 K (circle) and 298 K (square) of MAF-23. Reproduced from ref. 141 with permission from the American Chemical Society, copyright 2012. (b) The perspective views of two CO₂ molecules adsorbed by the N...N claws of activated MAF-23. In this structure, four independent uncoordinated N atoms come from four different triazolite rings. Orange lines depict the interactions between two CO₂ molecules and the framework. H atoms are omitted for clarity. Color code: C, gray; N, blue; Zn, cyan; and O, red.

uptake capacity of 3.3 and 2.5 mmol g⁻¹ at 273 and 298 K (Fig. 2a), with CO₂/N₂ selectivities calculated by Henry's law of 163 and 107 at 273 and 298 K, respectively. To elucidate the dynamic CO₂ adsorption behavior, the crystal structure of MAF-23 with different CO₂ loading levels was determined using single-crystal X-ray diffraction. From the data, two independent CO₂ molecules could be observed, located near the chelation sites of the organic linkers (Fig. 2b).

The quantity and accessibility of MOFs' LBSs also play vital roles in the tunability of CO₂ uptake capacities in MOFs. A series of isorecticular copper-based MOFs, ZJNU-43, ZJNU-44 and ZJNU-45, based on three rigid organic linkers, 5,5'-(quinoline-5,8-diyl)-diisophthalate, 5,5'-(isoquinoline-5,8-diyl)-diisophthalate, and 5,5'-(quinoxaline-5,8-diyl)-diisophthalate, were constructed.¹⁴³ Although these MOFs had nearly identical surface areas, distinct differences were observed in their CO₂ uptake capacities. In ZJNU-43, the linker-based nitrogen atom is located at the α -position in the spacer of the organic linkers. Upon activation, ZJNU-43 adsorbed 4.6 mmol g⁻¹ CO₂ at 1 atm and 296 K. When the LBSs were shifted to the β -position in ZJNU-44, the CO₂ uptake capacity increased significantly (to 5.2 mmol g⁻¹) under the same conditions. When the number of the LBS at the α -position was doubled, the adsorption capacity of the resulting MOF, ZJNU-45, was only 4.8 mmol g⁻¹, slightly greater than ZJNU-43. Quantum chemical calculations indicated that CO₂ in the structures of ZJNU-43 and ZJNU-45 were trapped in narrow windows, stabilized by numerous weak hydrogen bonds between CO₂ and the H, N, and O atoms of the organic linkers. In contrast, the LBSs of ZJNU-44 pointed into the pores, allowing CO₂ to bridge the organic linkers. Ultimately, the calculated binding energies of CO₂ in the series of MOFs indicated the value of ZJNU-44 (-27.6 kJ mol⁻¹) was much larger than those of other two MOFs (-18.1 and -18.7 kJ mol⁻¹), explaining the high CO₂ adsorption capacity of ZJNU-44. These examples highlight the role of LBSs' orientation in MOF pores and its impact on CO₂ capture.

2.1.3. Linkers with polar functional groups

With respect to MOFs synthesized with linkers lacking LBSs, the introduction of alternative polar functional groups such as -F, -Br, -Cl, -OH, -COOH, -NO₂, and -SO₃ on the organic linkers of MOFs can also enhance CO₂ capacity. This is based on

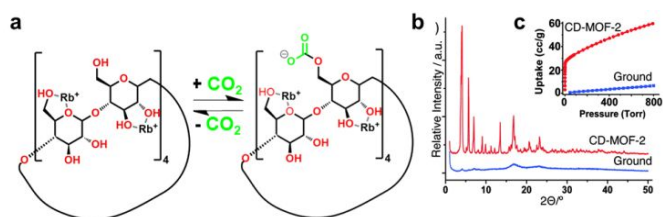


Fig. 3 (a) An illustration of the reversible carbonic acid formation during CO₂ chemisorption by free hydroxyl groups located on each individual γ -CD torus of CD-MOF-2. (b) Powder X-ray powder diffraction (PXRD) analysis of pristine CD-MOF-2 (red, top) and a sample ground in a mortar and pestle for 7 min (blue, bottom). (c) CO₂ uptake isotherms (298 K) for crystalline CD-MOF-2 (red circles) and a sample ground into an amorphous powder (blue squares). Reproduced from ref. 149 with permission from the American Chemical Society, copyright 2011.

interactions between the dipole of the polar functional group and the quadrupole of CO₂. Generally, two methods have been employed toward the synthesis of MOFs bearing such polar functional groups. The first is direct synthesis of MOFs using functionalized linkers. Numerous studies indicate that incorporation of these linkers into the frameworks results in favorable CO₂ adsorption.^{149–152} A representative example is found in the synthesis and study of CD-MOF-2, constructed from γ -cyclodextrin (γ -CD) and rubidium hydroxide.¹⁵³ Solid-state NMR experiments showed that the free hydroxyl groups located on γ -CD reacted with CO₂, forming carbonic acid groups in a chemisorptive fashion (Fig. 3a). This chemisorption led to a large CO₂ uptake capacity (~ 1.0 mmol g⁻¹) in the low-pressure region (< 1 torr) between 273–298 K.¹⁴⁹ Unfortunately, when the crystals of CD-MOF-2 were pulverized into amorphous powders, very little CO₂ was absorbed and the steep rise also disappeared from the low-pressure region of the CO₂ adsorption isotherms (Fig. 3b and c). This result highlighted the need for crystallinity and porosity in MOFs when targeting gas adsorption.

Another strategy employed to introduce polar functional groups in the pores of MOFs relies on deviating from the commonplace metal-carboxylate chemistry employed in MOF synthesis. To this end, sufficient evidence exists to suggest that organosulfonates may offer a better platform for the construction of MOFs with highly polar pore environments. A mixed-linker strategy was used to synthesize a sulfonate-based MOF (TMOF-1)¹⁵⁰ where the free oxygen atoms from the sulfonate groups were charged and highly polar. Therefore, the CO₂ uptake capacity of TMOF-1 at 200–308 K was 1.2–6.8 mmol g⁻¹ under 1 bar with a high zero-coverage isosteric heat of adsorption of 30.9 kJ mol⁻¹, much higher than many reported organosulfonate-based MOFs. The hypothesized CO₂ “encapsulation” in which adsorbed CO₂ was surrounded by four sulfonate groups facilitated the strong CO₂ binding in the framework. Polar functional groups can also be incorporated during the synthesis of the extended structure. A zinc-imidazololate-4-amide-5-imidate framework (IMOF) was synthesized by an in-situ ligand reaction and studied for CO₂ uptake.¹⁵¹ During the MOF synthesis, a new imidazololate chelate ligand was generated by partial hydrolysis of the original linker, eventually forming narrow channels with polar walls. The total CO₂ adsorption capacity of the resultant IMOF

was 2.1 mmol g⁻¹ at 298 K and 1 bar, due to the strong interactions between CO₂ and the amide and imidate functional groups.

The designability and flexibility of MOFs can also be leveraged to introduce polar functional groups into the pore structure.^{154–161} Utilizing the isorecticular approach, a given MOF’s pore surface functionality can be adjusted by utilizing different organic linkers, all while maintaining the underlying topology of the parent MOF. For example, seven zeolitic imidazololate frameworks (ZIFs), all with GME topology and variously controlled pore metrics and functionality were examined for their CO₂ uptake behavior.¹⁵⁴ The CO₂ uptake capacities of these ZIFs tracked with the expected attraction between polar functional groups in the ZIFs and CO₂. ZIF-78, bearing -NO₂ groups, adsorbed ~ 60 cm³ cm⁻³ of CO₂ at 298 K and 800 torr, a value much higher than the CO₂ uptake values of the other ZIFs in the series with -Cl, -CN, -Me, and -Br moieties. Another example is the stable Al-based MOF, USTC-253, constructed from Al³⁺ and dibenzo[*b,d*]thiophene-3,7-dicarboxylate 5,5-dioxide (Sbpdcc) whose structure is isorecticular to MOF-253.¹⁵⁵ However, in comparing the the total CO₂ uptake capacities of these two frameworks, the impact of the presence of the linker-based polar sulfone groups becomes apparent. The CO₂ uptake capacity of USTC-253 at 273 K and 1 bar is 3.7 mmol g⁻¹, 71% higher than that of MOF-253, despite the presence of bipyridine N atoms (LBSs) in the latter MOF. Moreover, when trifluoroacetic acid (TFA) was utilized as a modulator during the synthesis of USTC-253, the resultant USTC-253-TFA exhibited a higher CO₂ adsorption capacity due to the introduction of defects. Additionally, the framework adsorbed very little N₂ under the same conditions, yielding a CO₂/N₂ selectivity of 75:1. Such results highlight the importance of polar functional group incorporation in MOFs and the immense potential of application of this strategy to post-combustion CO₂ capture.

2.1.4. Pore size control

CO₂ has a relatively small kinetic diameter (3.3 Å). For this reason, micropores are typically more advantageous than mesopores and/or macropores when targeting enhanced CO₂ uptake capacity and selectivity. In the context of the application of MOFs to CO₂ capture, deliberate selection of metal salts and organic linkers can result in the formation of a variety of pore sizes. For example, by altering the length of the organic linkers in two frameworks, isorecticular series of MOF-5 and MOF-74 with pore apertures ranging from 3.8 to 28.8 Å and from 14 to 98 Å, respectively, were prepared.^{162–163} With this as a backdrop, an ultra-microporous (3.5 and 4 Å) MOF, Ni-4PyC, based on a short ligand 4-pyridylcarboxylate (4PyC) was reported.¹⁶⁴ Grand canonical Monte Carlo (GCMC) simulations predicted that Ni-4PyC could adsorb up to 8.2 mmol g⁻¹ of CO₂ at 10 bar and 298 K.¹⁶⁴ The experimental CO₂ adsorption measurement result (~ 8.2 mmol g⁻¹ at 10 bar and 298 K) was in good agreement with the simulated isotherm. In addition, simulations indicated that three main CO₂ binding locations existed in Ni-4PyC, located in the intersections of channels, 1D channels, and spherical cages. Also, cooperative

binding between CO₂ molecules was proposed to play a significant role

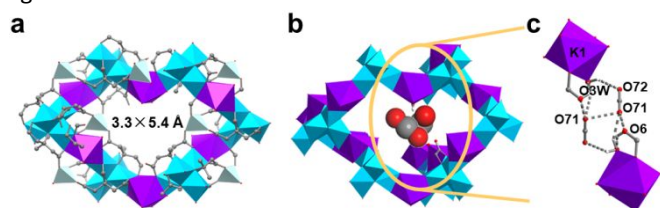


Fig. 4 (a) The diamondoid cage of UTSA-16 with a small 3.3×5.4 Å² window. All metal ions are represented as polyhedra. (b) CO₂ dimers are trapped within the cage upon gas adsorption. (c) Crystallographically observed cooperative interactions between CO₂ molecules and the framework (O₇₁(CO₂)^{···}O₇₁(CO₂) and O₇₁(CO₂)^{···}O₆ short contact; O₇₂(CO₂)^{···}H-O_{3w}, O₇₁(CO₂)^{···}H-O_{3w} and O_{3w}^{···}H-O₆ hydrogen-bonding interactions). Color code: C, gray; O, red; K, purple; Co1, light turquoise; Co2, cyan; and H, white.

in the exceptionally high CO₂ uptake of Ni-4PyC. Unexpectedly, in contrast to the excellent CO₂ adsorption performance, Ni-4PyC adsorbed almost no H₂ even at very high pressure (up to 35 bar), making it an ideal candidate for pre-combustion CO₂ capture. Using a similar strategy, a microporous MOF, UTSA-16, assembled from Co(OAc)₂·4H₂O, citric acid (H₄cit), and KOH was prepared and studied by neutron diffraction to reveal two pairs of CO₂ molecules trapped by hydrogen-bonding in the materials' micro pores (~3.3×5.4 Å²) (Fig. 4).¹⁶⁵ These small diamond cages and binding sites not only endowed UTSA-16 with a significantly large CO₂ uptake capacity (160 cm³ cm⁻³ at 296 K and 1 bar) but also enhanced the MOF's CO₂/CH₄ (29.8 at 200 kPa and 296 K) and CO₂/N₂ (314.7 at 100 kPa and 296 K) separation capabilities. As an example contributing to the fundamental understanding of precise CO₂ binding modes in a given MOF, the study on UTSA-16 demonstrates that measuring capacity alone may not be sufficient to address underlying framework chemistry.

Self-interpenetration resulting in mutually interlocking frameworks is known to occur in certain MOF topologies.¹⁶⁶ This has a couple of effects on CO₂ capture: when interpenetration reduces surface area, this in turn reduces the overall capacity; however, when more restrictive pores result from interpenetration, it has the effect of increasing the binding energy of CO₂ and therefore giving more favorable uptake.¹⁶⁶ There are cases where interpenetration as well as mixed linkers in MOFs produce what has been called pore space partition (PSP), where the original pores have been segmented in a designed fashion. This also has the effect of restricting pores and increasing CO₂ uptake.^{166, 167} A 2-fold interpenetrated microporous MOF, Cu(FMA)(4,4'-BPE)_{0.5}, with a 3.6 Å pore diameter was reported and exhibited highly selective adsorption of CO₂ over CH₄ at 195 K.¹⁶⁸ Two nearly identical frameworks, SNU-70 and SNU-71, in which the only difference between the organic linkers was the discrepancy between a C=C or a C-C bond.¹⁶⁹ SNU-71, which is interpenetrated, exhibited high CO₂ adsorption capacities at low pressures regardless of temperature, due to the decreased pore size compared to the non-interpenetrated SNU-70. In SUMOF-X (X=2-4), H₂BDC, H₂NDC, and H₂BPDC were utilized as linkers to obtain three interpenetrated MOFs.¹⁷⁰ The authors

speculated that the higher uptake of CO₂ in these interpenetrated MOFs compared with their non-interpenetrated counterparts could be attributed to the increased electric field gradients in the small pores of interpenetrated frameworks, enhancing the interactions between CO₂ molecules and the host framework. Apart from structures that commonly interpenetrate, an unusual partially interpenetrated MOF, NOTT-202a, formed from a pronounced framework phase transition during desolvation.¹⁷¹ At 195 K and 1 bar, NOTT-202a presented a high CO₂ storage capacity of 20 mmol g⁻¹, exceeding many previously reported values in In(III)-based MOFs.¹⁷¹

Pore space partition (PSP) serves to decrease MOFs' pore sizes by dividing large cages or channels into smaller segments by the insertion of additional organic linkers or other guest species.⁷⁹ PSP has gradually become a crucial tool to efficiently utilize the pore spaces of MOFs.^{79, 172} A microporous anionic framework, [In₃(btc)₄]_n³ⁿ⁻, was synthesized in seven distinct chemical environments, including a variety of organic solvents, ionic liquids, and deep eutectic solvents.¹⁷³ Some of the solvents were incorporated into the resultant MOFs as extraframework charge-balancing species. Even with the occupation of a large percentage of the pore space by charge-balancing cations like choline, the MOF, (choline)₃[In₃(btc)₄]-2DMF, exhibited a CO₂ uptake capacity of 3.2 mmol g⁻¹ at 1 atm and 273 K on account of reasonably partitioned pore spaces and hydroxyl groups on the choline cations. The same group reported an interesting cage-within-cage indium-based MOF (CPM-5) by employing In³⁺ and BTC³⁻

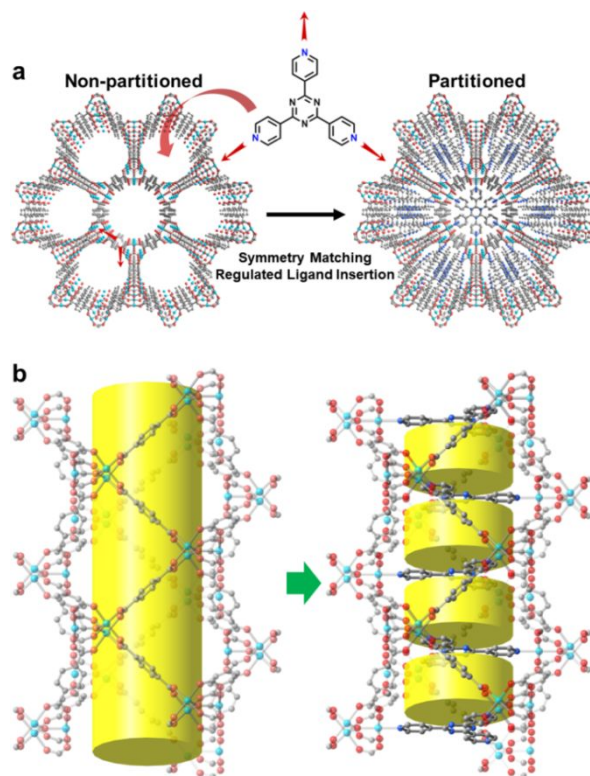


Fig. 5 Pore space partitioning through symmetry-matching regulated ligand insertion in a representative MOF (CPM-33a). (a) Viewed along *c* axis and (b) side view of the channels showing the cylindrical channel before and after partition

using 2,4,6-tri(4-pyridyl)-1,3,5-triazine. Color code: C, gray; O, red; N, blue; and Ni, cyan. H atoms are omitted for clarity. Adapted from ref. 175 with permission from the American Chemical Society, copyright 2015.

as metal ions and linkers, respectively.¹⁷⁴ In the structure of CPM-5, a small Archimedean In_{12} cage is encapsulated within a large Archimedean In_{24} cage and every two adjacent In^{3+} sites of the In_{24} cage are connected by two carboxylate groups from the BTC^{3-} linker. The remaining carboxylate group from BTC^{3-} connects the outer In_{24} cage with the inner In_{12} cage. At 273 K and 1 atm, CPM-5 adsorbed a significant amount of CO_2 (3.6 mmol g^{-1}). This was attributed to the synergy between open In^{3+} sites, charges in the framework, and the pore space partitioning effect from the cage-within-cage architecture. More recently, a symmetry-matching regulated ligand insertion strategy was developed to make crystalline porous materials with exceptional CO_2 uptake capacities.¹⁷⁵ To partition the pore space, organic linkers with C_3 symmetry such as 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) were employed to occupy the channel of MIL-88 type structures. This yielded a series of isorecticular CPM-X ($X = 33a-d$) structures by fragmenting the channels into numerous small segments (Fig. 5). By providing additional adsorptive surfaces upon incorporation of tpt, CPM-33b exhibited a very high CO_2 uptake capacity (7.8 and 5.6 mmol g^{-1} at 273 and 298 K, respectively, under 1 bar) and a moderate isosteric heat of adsorption (25.0 kJ mol^{-1}) even through the OMSs in the structure were coordinated by tpt ligands.

2.1.5. Flexible frameworks

Another property of MOFs is their propensity for structural flexibility. Upon exposure to external stimuli such as pressure and/or temperature, certain MOFs undergo structural change(s), resulting in “gated” CO_2 adsorption. In such cases, the CO_2 adsorption capacities of these MOFs suddenly and drastically increase at a definite relative pressure known as a gate pressure. It is generally accepted that the structural flexibility of MOFs is mainly related to the so-called soft porous crystals with a “breathing effect”.^{38, 176, 177} In a representative example, a flexible, doubly interpenetrated zinc(II) MOF was reported.¹⁷⁸ The CO_2 adsorption isotherm revealed a drastic adsorption step at about 10 bar and significant hysteresis during CO_2 desorption.¹⁷⁸ The calculated CO_2 uptake and Q_{st} were 7.1 mmol g^{-1} at 30 bar and 298 K and $\sim 20 \text{ kcal mol}^{-1}$, respectively. Variable temperature and pressure PXRD measurements were performed to study the effect of CO_2 adsorption on the underlying MOF structure. The results indicated that the framework contracted upon activation accompanied by considerable changes in the powder pattern. When CO_2 was loaded into the framework, the original pattern reappeared, indicating that a reversible structural transformation or “breathing” behavior was occurring. Another interesting example of the application of “breathing” MOFs to CO_2 capture can be found in a series of flexible pillared-layered MOFs. Based on a library of variably functionalized bdc-type linkers, the dangling side chains of $[\text{Zn}_2(\text{bdc})_2(\text{dabco})]_n$ acted as immobilized “guests” and interacted with other guest molecules, themselves, and the framework backbone.¹⁷⁹ This had the effect of significantly

enhancing the frameworks’ flexibility. Gas sorption measurements showed that each MOF could selectively adsorb CO_2 in a distinct stepwise fashion, while N_2 was almost never adsorbed in any appreciable quantity. More recently, SHF-61, a diamondoid continuous-breathing network, was synthesized from reactions between InCl_3 and $\text{NH}_2\text{-BDC}$.¹⁸⁰ Desolvation of the as-synthesized material led to a drastic change in not only the MOF’s morphology but also its unit-cell volume ($\Delta V \approx 2000 \text{ \AA}^3$), as monitored by a series of single-crystal X-Ray diffraction experiments. The partially solvated SHF-61-DMF exhibited the largest CO_2 uptake among those in the series (2.4 mmol g^{-1} at 20 bar and 298 K) with minor desorption hysteresis caused by a structural phase transition. An elastic layered MOF, ELM-11, displayed a gate-adsorption isotherm (195 K) with two steps at 0.2–0.4 kPa and 14–30 kPa.¹⁸¹ With the aid of *in situ* synchrotron PXRD measurements, two structural transitions and one gradual deformation of ELM-11 were observed during the CO_2 adsorption process.¹⁸¹

Structural flexibility can also stem from the incorporation of organic linkers into MOFs that are sensitive to external stimuli such as light.^{182, 183} As an example of such behavior, we turn to a photoswitchable MOF (PCN-123) made from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-(phenyldiazenyl)terephthalate which is isostructural to MOF-5.¹⁸² UV irradiation and heat treatment isomerized the organic linkers in *trans*-to-*cis* and *cis*-to-*trans* fashions, respectively. Based on this isomerization, the CO_2 uptake capacity of PCN-123 could be reversibly altered with the all *trans* configuration of the organic linkers yielding the higher CO_2 adsorption capacity (Fig. 6). An example of low-energy CO_2 capture and release in a light-responsive framework, $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$, was also reported.¹⁸³ When the AzDC and 4,4'-BPE linkers were photoisomerized between *cis* and *trans* states upon exposure to 365 nm light, an instantaneous release of about 64% (under dynamic measurements) and 42% (under static conditions) of adsorbed CO_2 was observed. It is important to note that significant structural change in $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ was not observed by synchrotron X-ray diffraction.

As has previously been discussed, gas separation and purification can be carried out by tailoring porous materials to have specific interactions with the molecule of interest. Therefore, discriminatory gate-opening can endow flexible MOFs with highly efficient CO_2 separation properties.^{184–189} For instance, one can observe conventional CO_2 uptake behavior

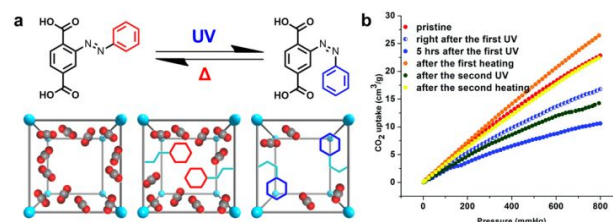


Fig. 6 (a) (Top) *Trans*-to-*cis* isomerization of the ligand (2-styrylterephthalic acid) of PCN-123 (PCN = porous coordination networks) induced by UV irradiation and the *cis*-to-*trans* isomerization induced by heat treatment. (Bottom) Suggested CO_2 uptake in MOF-5 (left), PCN-123 *trans* (middle), and PCN-123 *cis* (right). Each MOF is composed of Zn-oxo clusters (cyan balls) linked together by organic linkers (gray lines). The benzene rings in the azo functional group are highlighted

in red and blue lines in PCN-123 *trans* and PCN-123 *cis*, respectively. (b) CO₂ adsorption isotherms (at 295 K) of PCN-123 indicating altered adsorption behavior as the result of reversible linker conformational change of organic linkers. Reproduced from ref. 182 with permission from the American Chemical Society, copyright 2012.

with dynamic adsorption of other species. Such a phenomenon was reported for a flexible porous coordination polymer (PCP), [Mn(bdc)(dpe)], with zero-dimensional pores.¹⁸⁷ In addition to the Type I CO₂ adsorption isotherm (at 195 K), Mn(bdc)(dpe) displayed gate opening adsorption for acetylene (C₂H₂). Below the gate opening pressure ($P_{go} = 1.45$ kPa), negligible C₂H₂ was adsorbed by the PCP, endowing the material with highly selective adsorption of CO₂ over C₂H₂. As expected, IAST calculations indicated that the CO₂/C₂H₂ selectivity ranged from 8.8 to 13 for an equimolar CO₂/C₂H₂ gas mixture. To investigate the mechanism of selective adsorption, Mn(bdc)(dpe) was post-synthetically modified by [2 + 2] photodimerization of the dpe linkers yielding a new PCP, Mn₂(bdc)₂(rcttpcb). In the new PCP, the CO₂ and C₂H₂ uptake capacities were nearly identical (0.6 mmol g⁻¹ vs. 0.5 mmol g⁻¹), supporting the hypothesis that interactions between CO₂ and the linker-based phenylene rings played crucial roles in the gradual CO₂ adsorption in Mn(bdc)(dpe). It was also found that the chain length of alkyl ether groups (dangling on the benzene rings) and group substitution pattern of organic linkers had huge impacts on the structural flexibility and adsorption selectivity of MOFs.¹⁸⁸ Zn₂(L¹)₂(dabco) (L¹ = 2,5-bis(2-methoxyethoxy)benzene), which is isoreticular to [Zn₂(bdc)₂(dabco)]_n,¹⁹⁰ exhibits a unique two-step CO₂ uptake isotherm due to its structural flexibility. However, negligible N₂ and CH₄ adsorption was observed at 77 and 195 K, respectively. The authors speculated that the flexible and polar alkyl ether groups served as molecular gates at the MOF's pore apertures. Therefore, polar gas molecules such as CO₂ could penetrate the molecular gates more easily than their nonpolar counterparts such as N₂.

2.1.6. Hydrophobic frameworks

It is important to recognize that all practical CO₂ adsorption must occur in the presence of water. Therefore, hydrophobic frameworks are suitable for capturing CO₂ under humid conditions. Although water's large dipole moment causes it to interact more strongly than CO₂ with most frameworks, the hydrophobicity of certain MOFs allows them to suppress competitive water adsorption.

Generally, the hydrophobicity of a given MOF stems from bulky hydrophobic organic linkers or pendant hydrophobic groups on the organic linkers. For example, a series of ZIFs of chabazite (CHA) zeolite topology were made from a mixture of linkers.¹⁹¹ The entire series displayed negligible water uptake and were able to separate CO₂ from mixed gas streams without any loss of uptake capacity over three cycles under dry or humid conditions. Additionally, hydrophobic MOFs can employ the strategies we have previously outlined. For example, the CO₂ adsorption properties of a flexible and superhydrophobic MOF, FMOF-1, were modeled under humid conditions using quantum mechanical simulations.¹⁹² With many CF₃ groups lining the pores, FMOF-1 exhibited superhydrophobicity as indicated by its high contact angle with

water (158°). Simulated mixed-gas isotherms of CO₂ and water demonstrated that the CO₂ adsorption capacity of FMOF-1 was not influenced by water even at 80% relative humidity. Analogously, a family of isostructural MOFs was made by employing bi-functional organic linkers with both basic azolyl and chelating carboxylate groups.¹⁹³ The basic azolyl functional groups interacted with CO₂ and the -OCH₃ groups from acetate moieties on the pore surface provided a hydrophobic lining to the pore-walls, allowing the MOF to maintain approximately 80% of its CO₂ adsorption capacity upon exposure to 75% relative humidity.

2.2. Crafting MOFs' interiors through post-synthetic modification

The intrinsic features of MOFs provide favorable conditions for CO₂ capture and separation. Nevertheless, in the *de novo* synthesis of MOFs, the introduction of certain specific adsorption sites or functional groups can be challenging due to poor solubility of the organic linkers, competitive reactions between functional groups and the target frameworks, or the sensitivity of frameworks to the alteration of either the metal ions/ligands or their coordination environment(s). In this context, post-synthetic strategies for the incorporation of desired functionalities into MOFs have been developed. In general, post-synthetic approaches to improve MOFs' CO₂ capture capabilities can be classified into two broad categories: post-synthetic modification, and the formation of MOF composites.

2.2.1. Post-synthetic modification

Post-synthetic modification (PSM) can serve as a facile technique to introduce new CO₂ adsorptive sites into MOFs without significantly altering or damaging the underlying structure.¹⁹⁴ Specifically, PSM has been employed to accomplish the following: 1) introduction of additional functional groups, such as amine groups, or exchange of metals in the SBUs, 2) modification, insertion, or exchange of organic linkers, and 3) cation exchange in anionic MOFs.

In the case of SBU PSM, grafting alkylamine moieties onto OMSs serves as an effective means of improving the CO₂ uptake performances of MOFs based on the aforementioned strong affinities of alkylamines for Lewis acidic CO₂ molecules. As an example, the coordinatively unsaturated Cu^{II} sites in a water stable and trizolate-bridged MOF (Cu-BTT) were capped with ethylenediamine (en).¹⁰⁶ Although the pores of resultant material were occluded leading to relatively low CO₂ uptake at relatively high pressures, the CO₂ uptake at low pressures, CO₂/N₂ selectivity, and Q_{st} values dramatically increased compared to those associated with the pristine MOF. This technique was also successfully extended to other MOF systems.^{99, 195-204} Among these, Mg-MOF-74, with a high concentration of OMSs and one of the highest CO₂ adsorption capacities at low CO₂ pressures (6.1 mmol g⁻¹ at 298 K and 0.15 bar),¹²⁰ has been identified as an ideal platform for post-synthetic amine functionalization. Unfortunately, its relatively narrow, one-dimensional channels (~11 Å) hinder effective diffusion of sterically bulky amines into the pores. For this reason, extended MOF-74-type structures such as

Mg₂(dobpdc), Mg₂(dotpdc) and Mg₂(dondc) were utilized as substitutes for post-synthetic amine incorporation. All of the diamine-appended MOFs exhibited not only exceptional CO₂ adsorption capacities but also high CO₂ adsorption selectivity.^{99, 196-198, 201-204} Additionally, the thermal and chemical stabilities under humid condition of the resultant materials were markedly enhanced, despite reduction of their Brunauer-Emmett-Teller (BET) surface areas and pore volumes.^{99, 198-200} As an alternative to pore-expansion, the OMSs of Mg-MOF-74 were capped with a much smaller amine (hydrazine), yielding Mg-MOF-74(N₂H₄)_{1.8}.¹⁹⁹ The authors assumed that hydrazine would promote effective CO₂ adsorption in the MOF after PSM due to its small size, yet similar chemistry to other amines. Additionally, the distances between two adjacent amines were quite large. This inhibited the formation of weak hydrogen bonds and greatly enhanced the utility and availability of the grafted amines. Ultimately, the CO₂ uptake of Mg-MOF-74(N₂H₄)_{1.8} at 298 K and 0.4 mbar, the partial pressure of CO₂ in air, was 3.9 mmol g⁻¹ due to the high concentration (6.0 mmol g⁻¹) of surface-appended hydrazines. The Q_{st} calculated by the Clausius-Clapeyron equation and the Virial fitting method gave near zero-coverage values of 118 and 90 kJ mol⁻¹, respectively. These high heats of adsorption necessitate relatively high regeneration temperatures for such adsorbents. This interplay is an outstanding challenge in CO₂ capture; one desires strong chemical bonds between CO₂ molecules and the adsorbent to achieve selectivity, but strong bonds also typically require high adsorbent regeneration temperatures. As such, investigations into the modification of MOF SBUs with other CO₂-philic moieties were carried out. For example, a new functionalization technique, solvent assisted ligand incorporation (SALI) was developed with the goal of introducing perfluorinated chains onto the Zr₆ SBU of NU-1000. In this case, the technique relied on acid-base chemistry between the hydroxyl groups on the Zr₆ SBU and the carboxylate group of the fluoroalkyl linker (Fig. 7).²⁰⁵ All the fluoroalkane-functionalized samples had higher CO₂ adsorption capacities and zero-uptake limit (Q_{st}⁰) than those of the parent NU-1000, which can be attributed to the interactions between the C-F dipoles and the quadrupole of CO₂. More importantly, the Q_{st}⁰ value for each sample was no greater than 35 kJ mol⁻¹, implying that these adsorbents could be easily regenerated.

Post-synthetic modification for enhanced CO₂ capture in MOFs is not limited to the modification of the metals' coordination environments. Post-synthetic exchange (PSE) of metal atoms in SBUs is also a promising approach and can

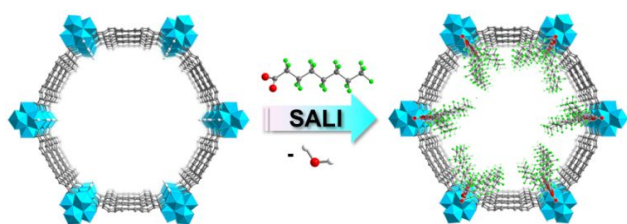


Fig. 7 Solvent-assisted ligand incorporation (SALI) on NU-1000 as a result of the reaction between the hydroxyl groups on the Zr₆ SBU (turquoise polyhedra) and the carboxylate groups bearing the perfluorinated chain (2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoate). Color code: C, gray; O, red; F, green; H, white; and Zr, cyan.

improve the CO₂ uptake capabilities and/or selectivities of MOFs. The Zr(IV) ions of UiO-66 can be exchanged with Ti(IV) ions by immersing UiO-66(Zr₁₀₀) in a DMF solution of TiCl₄(THF)₂ for various lengths of time at 368 K to give UiO-66(Zr/Ti) with progressively higher Ti loadings.²⁰⁶ The pore size distributions of the resultant frameworks as measured by N₂ adsorption experiments demonstrated that the size of the octahedral pores dramatically decreased as a result of the shorter Ti-O bonds compared to Zr-O bonds. The CO₂ adsorption capacity of UiO-66(Zr/Ti) increased from 2.2 (UiO-66(Zr₁₀₀)) to 4.0 mmol g⁻¹ (UiO-66(Ti₅₆)), which was ascribed to synergistic effects between the reduced pore size and framework density of the Ti-exchanged UiO-66. The highest Q_{st} value of the frameworks in this report was only about 38 kJ mol⁻¹, significantly lower than those of most amine-decorated MOFs. Though not mentioned in the original report, the working capacity of such materials might improve as their heats of adsorption are lower, but it comes at the cost of diminished framework CO₂ capacity. In order to stoichiometrically load new metal cations in MOFs, a new PSM strategy to exchange metal ions in a chromium-based MOF, porph@MOM-11 was devised. In porph@MOM-11, cationic porphyrin linkers serve as the pore walls.²⁰⁷ Simple immersion of porph@MOM-11 into methanol (MeOH) solutions of different metal chlorides gave four PSM derivatives with different metal site occupancies. Due to the reduced pore sizes and the introduction of Cl⁻ and metal ions, the CO₂ volumetric uptake capacities (at 273 K and 1 atm) and Q_{st} values of each of the PSM variants were improved by 3.1-14.5% and 6.6-36.0%, respectively, in comparison to those of porph@MOM-11.

Apart from modification and exchange of metal centers, modification, insertion and exchange of the organic linkers in MOFs can also enhance the interactions between frameworks and CO₂. Organic linkers can be post-synthetically modified to introduce diverse CO₂-philic moieties.²⁰⁸⁻²¹⁰ For example, alkylamines were tethered to Cr-MIL-101-SO₃H through a simple Brønsted acid-base reaction.²⁰⁸ The resultant Cr-MIL-101-SO₃H-TAEA (TAEA = tris(2-aminoethyl)amine) had a high CO₂ uptake capacity of 2.3 mmol g⁻¹ at 150 mbar and 313 K, and 1.1 mmol g⁻¹ at 0.4 mbar and 293 K. The Q_{st} value as calculated from a triple-site Langmuir model was 87 kJ mol⁻¹ at zero coverage, indicating strong chemisorption of CO₂ in Cr-MIL-101-SO₃H-TAEA. UiO-66-allyl was also subjected to a plethora of post-synthetic functionalization reactions.²⁰⁹ Amongst the modified UiO-66 analogues, the amino alcohol-decorated MOF (UiO-66-aminoalcohol) exhibited the highest CO₂ uptake capacity (11.6 mmol g⁻¹ at 308 K and 20 bar), while only a negligible amount of N₂ was adsorbed under the same conditions, suggesting that UiO-66-aminoalcohol could be a promising candidate for CO₂/N₂ gas separation.

Insertion of organic linkers emerged as the second PSM technique with a goal of incorporating new organic linkers of

similar or identical length, but bearing CO₂-philic moieties in MOFs.^{211, 212} A bridging linker was post-synthetically incorporated into a MOF by a single crystal to single crystal

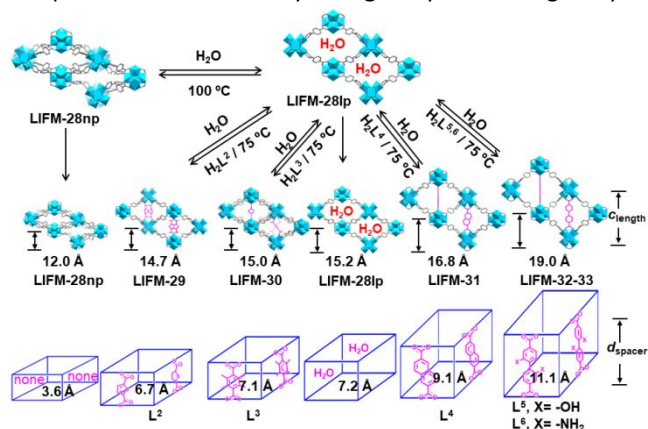


Fig. 8 (Top) Reversible breathing behavior of LIFM-28 (LIFM-28np ↔ LIFM-28lp), and (middle) stepwise installation/removal of spacers (L²-L⁶) in an increasing expansion sequence to give LIFM-29-33. Each MOF in the series is composed of Zr SBUs (cyan polyhedra) linked together by organic linkers (gray lines). The spacers are highlighted in pink lines. (Bottom) Simplified MOF structures for this series highlighting the role of organic spacers. Color code: C, gray; O, red; and Zr, cyan. H and F atoms are omitted for clarity.

(SCSC) transformation.²¹¹ By inserting 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (bpta) linker into the zinc-based MOF, SNU-30, the honeycomb-like pores were divided into smaller channels along the *ab* plane of the framework, yielding SNU-31. This PSM slightly decreased the framework's void volume from 82.1% to 76.1%. Gas adsorption isotherms showed that N₂, H₂, CH₄ and CO₂ capacity of SNU-30 could reach up to 7.04 mmol g⁻¹ (77 K, 1 bar), 16.2 mmol g⁻¹ (77 K, 61 bar), 0.23 mmol g⁻¹ (298 K, 1 bar), and 1.16 mmol g⁻¹ (298 K, 1 bar), respectively. In contrast to SNU-30, SNU-31 displayed almost no adsorption capacity for N₂, H₂, and CH₄, whereas it exhibited moderate CO₂ uptake (0.6 mmol g⁻¹ at 1 bar) at 298 K. Another interesting example was found in the incorporation of five distinct linkers into a flexible MOF using a post-synthetic variable-spacer installation strategy (Fig. 8).²¹² Unlike the effects observed in rigid frameworks, the structural flexibility of LIFM-28 enabled the material's pore size to be finely tuned by the insertion of organic linkers with various lengths and substituents.²¹² The resultant MOFs had functionalized pore environments, and improved thermal stabilities and BET surface areas. Due to these alterations, the CO₂ adsorption capacity and selectivity were greatly enhanced. The -NH₂ groups in LIFM-33 endowed it with the highest CO₂ uptake capacity (3.6 mmol g⁻¹) with a high Q_{st} of about 40 kJ mol⁻¹ based on the presence of strong NH₂-CO₂ interactions. The IAST calculation revealed that the CO₂/N₂ adsorption selectivity in LIFM-33 was about 30, demonstrably higher than that of parent MOF.

Linker exchange can also regulate MOFs' CO₂ capture performance while maintaining their crystallinity, stability, and porosity.²¹³⁻²¹⁵ A family of water-stable UiO-66-AD_n frameworks modified by diverse flexible alkanedioic acids ((HO₂C(CH₂)_{n-2}CO₂H), n = 4, 6, 8 and 10) was reported.²¹³ ¹H NMR spectra of digested MOFs demonstrated that the degree

of linker substitution increased as the hydrocarbon chain in the substituting organic linker was elongated. Each terephthalate ligand of UiO-66 was substituted by two alkanedioic acid. Among the investigated frameworks, UiO-66-AD6 had the highest CO₂ uptake capacity and CO₂ desorption free energy due to the relatively strong interactions between CO₂ and the carboxyl groups of the flexible alkanedioic acid linker which was similar in length to the BDC linker of UiO-66. In this case, the linkers could also be replaced by metalated-ligands.²¹⁴ The exchange process was carried out by incubating UiO-66 in aqueous solutions of 1,2,4,5-benzenetetracarboxylic acid (BTEC) or mellitic acid (MA) and various alkaline hydroxides, including LiOH, NaOH, and KOH. UiO-66-(COONa)₂-EX exhibited the highest CO₂/N₂ selectivity (33.3) while UiO-66-(COOLi)₄-EX had the highest CO₂ adsorption capacity (0.7 mmol g⁻¹ at 0.15 bar and 298 K). The authors attributed these effects to the mutual influence of the cations' polarizing abilities and reduced pore sizes.

With respect to ionic MOFs, CO₂ adsorption properties can be regulated by cation exchange.²¹⁶⁻²¹⁹ A series of cation-exchanged ionic MOFs were prepared by soaking Bio-MOF-1 in DMF solutions of tetramethylammonium, tetraethylammonium, or tetrabutylammonium.²¹⁶ Despite the observation of decreased BET surface areas and pore volumes in each cation-exchanged MOF, their CO₂ capacities and Q_{st} values improved compared to the parent Bio-MOF-1. This was attributed to strong interactions between CO₂ and the newly-inserted ammonium cations. The same team also exchanged the cations of Bio-MOF-1 with a series of guanidinium derivatives.²¹⁷ When a guanidinium derivative with a high population of LBSSs, diaminoguanidinium (DiAmGND⁺), was exchanged into bio-MOF-1, the MOF's CO₂ adsorption capacity and Q_{st} increased to 5.1 mmol g⁻¹ (at 273 K and 1 bar) and 29.4 kJ mol⁻¹, respectively. This was accompanied by only a slight decrease in both the pore volume and BET surface area of DiAmGND@bio-MOF-1. The authors speculated that the enhanced CO₂ uptake performance could be ascribed to the CO₂ affinity of aminated cations rather than the decreased pore size. It was demonstrated that Li⁺ exchange in an anionic MOF, [H₂N(Me)₂]₂[Zn₅(L)₃].5.5DMF.3.5H₂O (L = 3,3',5,5'-biphenyltetracarboxylic acid), can be accomplished by SCSC transformation.²¹⁸ Impressively, both the guest H₂N(Me)₂⁺ counterions located in the pores and some coordinated metal ions (Zn²⁺) of the MOF were replaced by Li⁺, resulting in a greatly increased BET surface area (from 342 to 1664 m² g⁻¹) and CO₂ adsorption capacity (from 1.7 to 6.6 mmol g⁻¹ at 273 K and 1 bar).

2.2.2. MOF composites

Although a demonstrably powerful technique, post-synthetic modification of MOFs requires OMSs, specific functional groups on the organic linkers, and/or sufficiently large pore apertures to allow for guest or reagent diffusion. The question then becomes, how can one improve the CO₂ capture performance of MOFs lacking these features? An alternative strategy, the formation of MOF composites by accommodating various guest species or combining with other materials such as polymers or ILs can enhance the CO₂ adsorption capabilities

of MOFs lacking such features. The CO₂ uptake capacities of the resultant MOF composites are typically significantly greater than those of the parent MOFs due to the generation of new pore environment(s), additional interactions at the interface between phases, and/or affinity of CO₂ to the guest(s). Moreover, the plasticity and chemical stability of certain compounds utilized in the formation of MOF composites can lead to enhanced stabilities and mechanical properties of the resultant materials, expanding the range of practical applications. To date, four classes of materials, including small molecules,²²⁰⁻²²² polymers,²²³⁻²²⁶ two-dimensional (2D) materials,²²⁷⁻²³⁴ and three-dimensional (3D) materials,²³⁵⁻²³⁷ have combined with MOFs in order to tune their CO₂ adsorption properties.

CO₂ is highly soluble in many liquid-phase small molecules, including ILs. Therefore, many experiments and computational simulations have been conducted to explore the applicability of IL-MOF composites to CO₂ capture, separation and purification.^{220-222, 238-239} For example, the theoretical CO₂ separation performance of several room temperature ionic liquid (RTIL)-MOF composites was evaluated. In the study, 1-ethyl-3-methylimidazolium [EMIM⁺] salts were incorporated in HKUST-1.²³⁹ At low pressures, the CO₂ uptake capacities, CO₂/CH₄ and CO₂/N₂ selectivities were significantly enhanced upon incorporation of RTILs due to the strong chemisorption of "dissolution" of CO₂ in such compounds. The successful incorporation of 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) into a zeolitic imidazolate framework, ZIF-8, led to a [BMIM][PF₆]/ZIF-8 composite.²²⁰ The researchers then investigated the composite's gas adsorption performance using a wide array of experiments, atomically detailed simulations, and DFT calculations. Although the gas adsorption capacity of [BMIM][PF₆]/ZIF-8 was attenuated compared to the pristine ZIF-8, the selectivities (CO₂/CH₄ and CO₂/N₂, in 50/50 v/v mixtures) of the composite were more than twice as high than those of the parent ZIF-8 at low pressures. Such work indicated that incorporation of ILs in MOFs can yield materials that exhibit strong, preferential interactions with CO₂.

In the context of MOF composite formation, polymers possess various unique attributes such as softness and high stability. These properties facilitate integration with MOFs. Among them, polyethyleneimine (PEI), a polymer with repeating amine groups and two aliphatic carbon (CH₂CH₂) spacers, has been incorporated in MOFs to augment both the strength and number of adsorbent-CO₂ interactions. The numerous amine sites, commercial availability, and low volatility relative to low-molecular weight amines such as monoethanolamine of PEI make it an ideal candidate for MOF composite formation. A series of PEI-decorated MOFs were prepared with various amounts of PEI using a wet impregnation method.²²³ In the resultant composites, low molecular-weight linear PEI was tethered onto the exposed Cr³⁺ centers of MIL-101. This left other amine groups available to interact with CO₂. As expected, the BET surface areas and pore volumes of the MOF composites dramatically decreased compared to the parent MIL-101 due to pore occlusion.

However, the CO₂ adsorption capacities of the PEI-MIL-101 samples were significantly enhanced between 0-2 bar. When the PEI loading was increased to 100 wt%, the CO₂ uptake

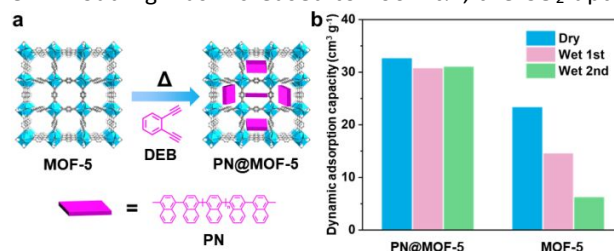


Fig. 9 (a) Polymerization of 1,2-diethynylbenzene (DEB) in the pores of MOF-5 to give PN@MOF-5 (PN = polynaphthylene, pink plate). Color code: C, gray; O, red; and Zn, cyan. H atoms are omitted for clarity. (b) Dynamic CO₂ adsorption capacities of PN@MOF-5 and MOF-5 under dry conditions and in the presence of water (RH = 65%).

capacity of the resultant composite (PEI-MIL-101-100) was over 12 times greater (4.2 mmol g⁻¹ at 298 K and 0.15 bar) than that of pristine MIL-101. Additionally, the CO₂/N₂ selectivities (in a 15/75 v/v mixture) of PEI-MIL-101-100 and PEI-MIL-101-125, with 100 and 125 wt% PEI loading, respectively, at 25 °C were as high as 120 and 150, respectively. Given the ease with which small MOF particles can be loaded with PEI and the fact that branched PEI possesses more-nucleophilic primary amines (-NH₂) as opposed to the secondary amine groups (-NH-) present in linear PEI, the former was impregnated into MIL-101 crystals about 150 and 300 nm in size.²²⁴ Each composite exhibited an exceptionally high CO₂ uptake capacity at 0.15 bar and 298 K. However, the performances of the small MOF composites (with higher PEI loadings) were slightly worse than those of the large one, likely due to inner pore inaccessibility.

Polymers trapped within the channels of MOFs can also serve to partition the pore spaces. Recently, a hydrophobic MOF-polymer composite, PN@MOF-5 (PN = polynaphthylene), was fabricated (Fig. 9a).²²⁵ As the PN loading increased, the number of 0.6 nm diameter pores drastically increased with a simultaneous decrease in the amount of 1.2 nm pores (the pore size of MOF-5). This indicated that the channels of MOF-5 were partitioned by incorporation of the PN polymer. As expected, the CO₂ uptake increased from 1.7 mmol g⁻¹ (MOF-5) to 3.5 mmol g⁻¹ (PN@MO-5) at 273 K and 760 torr. Most importantly, the stability of PN@MOF-5 under humid conditions was significantly greater than that of MOF-5, which is typically instable in water or humid air. The dynamic CO₂ adsorption capacity of the hydrophobic composite under humid conditions was nearly identical to that of the composite under dry conditions (Fig. 9b).

MOF composites can also be prepared by growing MOFs on the surface or within the pores of other materials. Some 2D materials such as graphene, graphene oxide, layered double hydroxides and aminoclays can be used as substrates for the growth of MOF composites because their surfaces can be functionalized and/or they frequently possess diverse, reactive functional groups. Several benzoic acid-functionalized graphene/M-MOF-74 composites, MCGr-X (M = Mg²⁺, Ni²⁺ or Co²⁺, X = 0, 2, 5, and 10 wt%), were synthesized in which the graphene basal planes acted as supports to reinforce the MOF

matrices (Fig. 10).²²⁷ Interestingly, the CO₂ adsorption capacity of each MCGr-X composite was enhanced relative to that of the corresponding pristine MOF. As the most striking example,

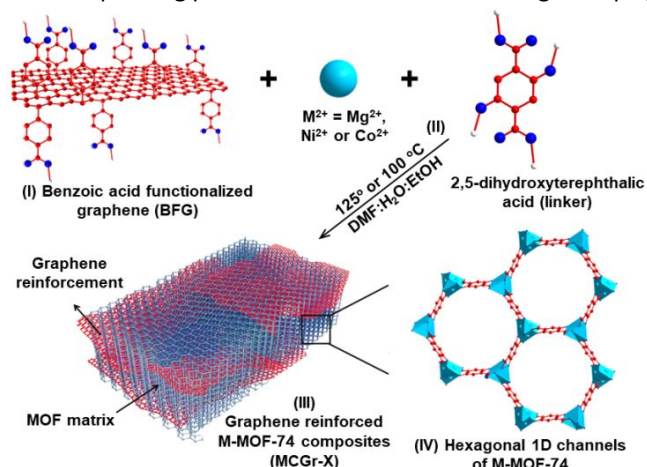


Fig. 10 Synthesis of covalently-linked MCGr-X composites (M = Mg²⁺, Ni²⁺ or Co²⁺, X = 0, 2, 5, and 10 wt%). (I) Benzoic acid functionalized graphene (BFG). (II) In situ growth of M-MOF-74 (M = Mg²⁺, Ni²⁺ or Co²⁺) crystals on the graphene basal plane. (III) Graphene reinforced MCGr-X composites. (IV) Hexagonal (*ca.* 1.1 × 1.1 nm²) 1D channels of M-MOF-74. Color code: C, red; O, blue; H, white; and M (Mg²⁺, Ni²⁺ or Co²⁺), cyan. Adapted from ref. 227 with permission from Wiley-VCH, copyright 2016.

MgCGr-10 adsorbed 8.1 mmol g⁻¹ CO₂ at 1 atm and 298 K. Since the composite exhibited similar BET surface areas and pore volumes to the pristine MOF, the increased CO₂ uptake capacity and selectivity of the composite were attributed to dispersive forces between the π electron cloud of graphene and quadrupole moment of CO₂. Moreover, mechanical property measurements such as nanoindentation revealed that both the hardness and elastic modulus of each MOF increased upon graphene introduction, which undoubtedly be favorable with respect to practical technological application of MOFs and MOF-based materials. Two-dimensional (2D) materials can also act as substrates or templates during the construction of MOF composites. For example, an HKUST-1-graphene oxide composite in which the oxygen-containing functional groups from the graphene oxide (GO) acted as seed sites for crystallization and dispersion of HKUST-1 nanocrystals.²²⁸ Interestingly, the defects in the GO layers inhibited the growth of the MOF nanoparticles (NPs). As such, the HKUST-1 crystallites were relatively small (10-40 nm). Although GO is not intrinsically porous, the composite exhibited both an augmented porosity (BET surface area, 1532 m² g⁻¹) and CO₂ uptake (8.3 mmol g⁻¹ at 273 K and 1 atm) compared to the original HKUST-1 (BET surface area of 1305 m² g⁻¹, CO₂ uptake of 6.4 mmol g⁻¹ at 273 K and 1 atm). The authors attributed this to the improved gas accessibility of the well-dispersed nano-MOF crystallites. Another example of 2D material MOF composite templation was reported in the application of highly water-dispersible aminoclay (AC) sheets to the synthesis of HKUST-1-AC composites.²²⁹ The amine functional groups in the AC served as metal binding sites for the stabilization of Cu²⁺ ions, which lead to decreased aggregation of HKUST-1 crystallites during the growth process. Therefore, the resultant MOF composites were decorated with

ultra-small (2-3 nm) HKUST-1 NPs. The BET surface area and CO₂ uptake capacity values for the HKUST-1-AC composite were 1381 m² g⁻¹ and 8.1 mmol g⁻¹ (at 273 K and 1 bar), respectively, representing increases of 70% and 39%, respectively, over the reported values for HKUST-1. These enhancements could potentially stem from the formation of new voids at the interface of HKUST-1 NPs and the AC layers. This strategy was adapted to other systems, including aminated graphite oxide,^{230, 231} suggesting its potential universality.

It is important to note, however, that many 2D materials do not exhibit high surface areas. As an alternative, many three dimensional (3D) materials (and even some one dimensional [1D] materials) have moderate to high porosities and can be beneficial for MOF composite formation based on their potential miscibility with MOFs. A representative example is found in the incorporation of carbon nanotubes (CNTs) into HKUST-1 to give a CNT hybrid composite CNT@HKUST-1.²⁴⁰ The carboxylate groups of the CNTs acted as nucleation sites to support continuous growth of HKUST-1. This crystal growth was beneficial for thorough removal of guest molecules during activation, leading to an enhanced composite pore volume (from 0.73 to 0.87 cm³ g⁻¹). The CO₂ isotherm revealed that the adsorption capacity of CNT@HKUST-1 was 13.5 mmol g⁻¹ at 298 K and 18 bar, about twice as high as that of HKUST-1 under the same conditions. Additionally, crystal growth confinement in the mesopores or macropores of templates can lead to smaller MOF particle sizes than those of MOFs synthesized via the *de novo* process.^{235, 236} Typically, smaller MOF crystals can be more easily and efficiently activated, which is naturally beneficial with respect to gas adsorption as active sites and pore volumes are more easily accessible in properly evacuated materials. Finally, due to the discrepancies between the pore diameters of MOFs and other materials, the pore size distributions of composite materials can fall within a wide range, thus potentially improving CO₂ adsorption and selectivity.²⁴¹

2.3. Challenges and opportunities in developing MOFs for CO₂ capture

Remarkable advances have been made toward CO₂ capture and separation in MOFs and MOF-based materials. In contrast to many other porous materials, MOFs have both high CO₂ capacities and outstanding CO₂ selectivities for capture in the presence of other gasses. This largely stems from MOFs' unique properties such as structural flexibility, the potential for framework post-synthetic modification, and relatively facile composite formation. Many of these strategies have only recently been developed and further optimization promises to improve MOFs' CO₂ capture properties as more work is performed. However, many challenges regarding the preparation and application of MOFs with high CO₂ capture capacities remain unaddressed. For example, many MOFs still have low CO₂ selectivities in the presence of moisture/water/acidic gasses, even if their overall adsorption capacities are high. Additionally, under these conditions many MOFs chosen for studies lack the requisite stability for

practical application. In the future, it would be necessary to choose MOFs which are known to have high chemical and thermal stability, as found for MOF-808.^{242, 243} In this context, it is important to recall that CO₂ capture from large stationary sources such as the flue gas of power plants is regarded as one of the most promising avenues to mitigate rising atmospheric CO₂ concentrations. Generally, flue gas from power plants (CO₂ point sources) is composed of 15-16% carbon dioxide, 5-7% water vapor, 73-77% nitrogen, 3-4% oxygen and traces of acidic gasses such as H₂S, NO_x, SO_x.¹⁰⁹ Consequently, during adsorption, gasses with higher polarities and/or binding energies such as H₂O or acidic gasses are preferentially adsorbed over CO₂ on the OMSs of MOFs. This has to be considered when selecting a MOF for CO₂ capture in the presence of water. Many pre- and post-synthetic strategies have been developed for improving the water and acid stabilities of those MOFs already under consideration.^{34, 225, 243-246} Nevertheless, there are suites of MOFs as yet uninvestigated which may well be more appropriate for this application. Additionally, certain strategies can be accompanied by new issues such as dramatic reduction of the materials' specific surface areas and/or pore volumes. These issues are beginning to be addressed as we learn how to

balance functionalization with maintaining crystallinity and porosity. Finally, for many MOFs, direct capture of CO₂ at low partial pressures remains a challenge due to relatively weak CO₂-framework interactions. Although CO₂ adsorption capacities at low partial pressures can be improved by introducing CO₂-philic moieties on MOFs' organic linkers, adsorbent regeneration energies also typically sharply increase.^{199, 208} This can, of course be overcome by precisely tuning the chemistry between the frameworks and CO₂. In the future, it is likely that high stability and high CO₂ adsorption capacity will be targeted in order to position MOFs as the next-generation of materials for practical CO₂ capture.

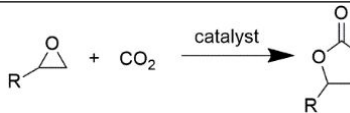
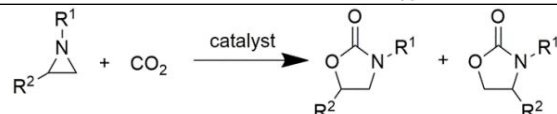
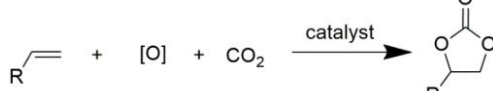
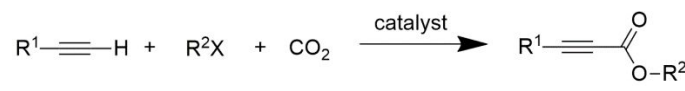
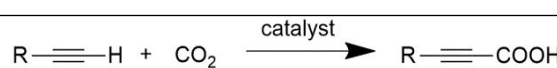
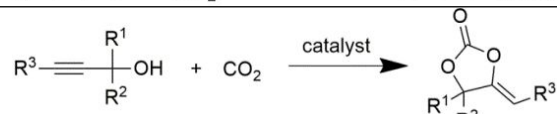
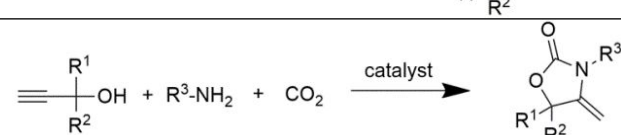
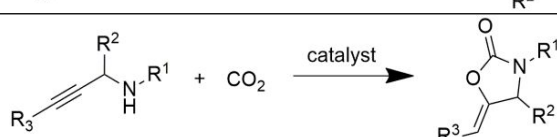
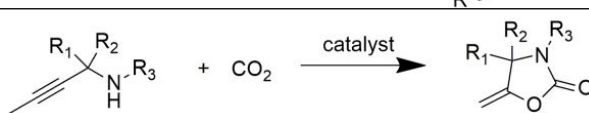
3. MOFs for catalytic CO₂ conversion

The modular, tunable, and porous nature of MOFs make them ideal candidates for heterogeneous catalysis. In particular, catalytic CO₂ conversion has been a target. In addition to MOFs, many MOF composites and MOF derivatives have been reported as efficient CO₂ conversion catalysts. In MOF composites, additional components are hypothesized to serve as new active sites and/or cooperative agents. This chemically

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Table 2 Summary of CO₂ organic transformation in MOF-based materials

Reaction	Equation	Active Site(s)	Ref.
Cycloaddition		Lewis acid, Lewis base, Brønsted acid, organic salt, organic base, etc	109, 150, 155, 247-293, 311-322
			272, 294-295
Olefin Oxidative Carboxylation		oxidant, Lewis acid, Lewis base, halide	291-293, 296
Terminal Alkyne Carboxylation		Cu(I)	297
		Ag, Pd-Cu NPs	306-310
Propargylic Alcohol Carboxylic Cyclization		Ag(I), Cu(I)	298-300
Three-Component Carboxylic Cyclization of Propargyl Alcohols, CO ₂ , and Primary Amines		Ag(I)	299
Propargyl Amine Carboxylic Cyclization		Ag(I)	299
Terminal Propargylamine Oxidative Cyclization		amidogen	323

emphasizes the respective functional advantages of both MOFs and the added components. MOF composites are typically more stable than the parent MOF(s), leading to improved recyclability and turnover. This area of CO₂ conversion using MOFs is nascent and requires more fundamental studies dealing with reactivity, optimization of performance, study of the long-term properties of the materials, and cyclability. When utilized as templates or precursors, stable MOF derivatives can be obtained. To a large degree, MOF-derived porous materials are able to inherit the salient properties of pristine MOFs, such as high surface area, tailorable porosity, adjustable morphology, and compositional diversity. Additionally, the process of pyrolyzing MOF composites has the potential to create additional active sites,

improved conductivity and other important structural and chemical features which are not present in the parent frameworks. Therefore, many MOF-derived porous materials have the potential to affect enhanced CO₂ transformation in comparison to their parent MOF analogues. In this section, we describe CO₂ conversion reactions performed using MOF-based catalysts, mainly focusing on CO₂ organic transformation into organic products, CO₂ hydrogenation, photocatalytic CO₂ reduction, and electrocatalytic CO₂ reduction.

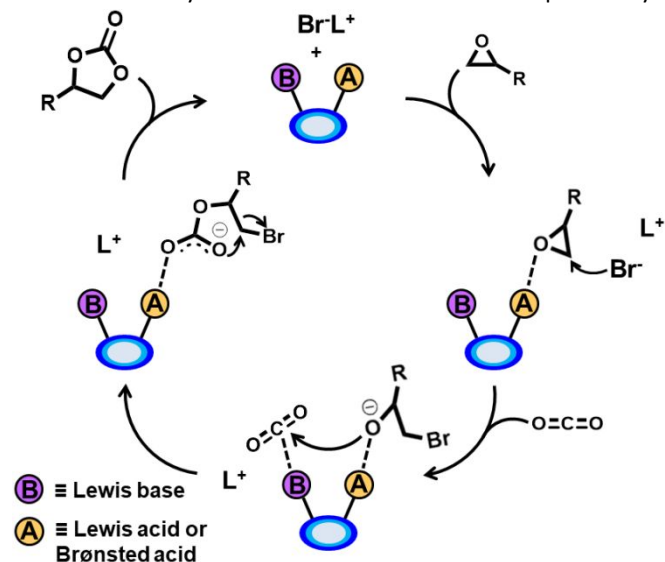
3.1. Heterogeneous CO₂ organic transformation

A variety of MOF-based materials have been reported for CO₂ organic transformation. The scope of catalytic CO₂ conversions to organic products has been summarized in Table 2.

3.1.1. Conversion of CO₂ into organic products using MOFs

MOFs have high CO₂ adsorption capacities and adjustable pore apertures and cavities. Many of the same active sites applied to CO₂ capture, including OMSs or LASs, Brønsted acid sites (BASs) and LBSs, can convert CO₂ into chemical products by organic transformation. This is frequently analogous to the transformations performed by numerous conventional homogeneous and heterogeneous catalysts. The utilization of MOFs' intrinsic functionalities for CO₂-epoxide cycloaddition reactions has been widely explored. This class of reactions can yield products with a variety of applications. Specifically, cyclic carbonates, the major product of many CO₂ cycloaddition reactions, have been widely applied as intermediates for the production of engineering plastics, electrolyte solvents for lithium-ion batteries, polar aprotic solvents, degreasers, and fuel additives.^{301, 302}

Generally, the mechanism of MOF-based CO₂ epoxide cycloaddition involves coordination of an epoxide oxygen atom with a LAS and/or a BAS in a MOF-based material (Scheme 2). This coordination polarizes the C-O bond which is then heterolytically cleaved with concurrent nucleophilic attack of the less sterically hindered carbon atom of the epoxide by a



Scheme 2 Proposed mechanism for CO₂-epoxide cycloaddition in MOFs and related materials involving Lewis acidic, Brønsted acidic, and/or Lewis basic sites, in the presence of cocatalytic TBAH (Br⁻L⁺).

co-catalyst-based halide anion (a typical co-catalyst is tetrabutylammonium bromide, TBAB) to form a halo-alkoxide intermediate. Subsequently, the CO₂ carbon atom, which is frequently activated by LBSs through dipolar interactions, is nucleophilically attacked by the ring-opened alkoxide intermediate and the cyclic carbonate is obtained by intramolecular ring-closure, regenerating the catalyst and co-catalyst. Interestingly, some MOFs can exhibit excellent catalytic activities in the absence of co-catalyst.²⁴⁷⁻²⁵⁵ Unfortunately, on account of the limited types and relatively low activities of active sites in the MOFs studied for this application, as well as the intrinsic inertness of CO₂, high temperatures and/or pressures must inevitably be applied in these cases. In this context, several strategies for improving the catalytic activities of MOFs towards CO₂ cycloaddition

reactions have been developed. Above all, it is inferred that the natures, quantities and locations of the active sites have enormous impacts on the catalytic efficiencies of the materials.

To support this inference, numerous reports exist. In one case, a porous 3D framework, [(Zn₄O)₂(Zn₂)_{1.5}(L)₆(H₂O)₃] (H₃L = 10-(4-carboxy-phenyl)-10H-phenoxazine-3,6-dicarboxylic acid) in which the parent Zn(II) ions could be partially exchanged by Cu(II) and Co(II) ions was reported (Fig. 11a).²⁵⁶ Upon post synthetic exchange, no obvious enhancement was observed in any of the frameworks' BET surface areas, pore volumes, or CO₂ adsorption capacities. However, the yield of the propylene oxide-CO₂ cycloaddition product, propylene carbonate, was dramatically reduced from 99% in the zinc MOF to 50% in the

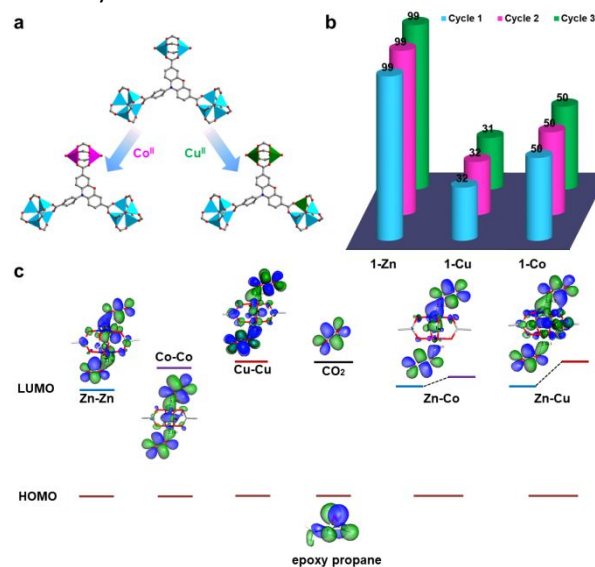


Fig. 11 (a) Illustration of fragmental cluster change via metal cation exchange in the Zn clusters (cyan polyhedra) of [(Zn₄O)₂(Zn₂)_{1.5}(L)₆(H₂O)₃] (H₃L = 10-(4-carboxy-phenyl)-10H-phenoxazine-3,6-dicarboxylic acid). Color code: C, gray; O, red; N, blue; Zn, cyan; Cu, green; and Co, pink. H atoms are omitted for clarity. (b) Comparison of propylene carbonate yields using different MOF catalysts for up to three cycles. (c) LUMO orbital of CO₂ adsorbed on MOFs with different metal centers during the catalytic process. Adapted from ref. 256 with permission from Wiley-VCH, copyright 2016.

cobalt analogue and 32% in the copper MOF (Fig. 11b). Since the post-synthetic metal exchange process mainly occurred at the dimeric paddlewheel (Zn₂(COO)₄) SBUs, the tremendous difference between the catalytic activities of these MOFs was mainly attributed to the presence or absence of various metal species. Molecular dynamics (MD) simulations indicated that CO₂ cycloaddition reactions are limited by the energy gap between the highest occupied molecular orbital (HOMO) of the epoxides and the lowest unoccupied molecular orbital (LUMO) of CO₂. Upon CO₂ binding to an OMS, a decrease of LUMO energy is observed, reducing the energy gap and accelerating the reaction. The simulations ultimately demonstrated that the energy gap between the LUMO of CO₂ and the epoxide's HOMO increases in the order of Zn-Zn < Zn-Co < Zn-Cu < Co-Co < Cu-Cu (Fig. 11c), which was in accordance with experimental results and reflected the effect of the nature of the active sites on the catalytic capabilities of MOFs. As further evidence, it was discovered that the catalytic efficiency of a Hf-based MOF (Hf-NU-1000) for the

cycloaddition reaction of CO₂ with styrene oxide (SO) was superior to that of the Zr-based NU-1000 under the same reaction conditions.²⁵⁷ The typical dissociation enthalpy of typical Zr-O bonds in NU-1000 is 776 kJ mol⁻¹. In contrast, the dissociation enthalpy of Hf-O bonds of Hf-NU-1000 is relatively high (802 kJ mol⁻¹), leading to the higher oxophilicity of Hf in NU-1000's SBUs, enhancing the Brønsted acidity and thus the catalytic activity of Hf-NU-1000.

With respect to the quantity and position of active sites, an interesting example is found in the *nbo* framework MMCF-2. This compound, which is isoreticular to MOF-505, was synthesized from 1,4,7,10-tetrazacyclododecane-N,N',N'',N'''-tetra-*p*-methylbenzoic acid (H₄tactmb), yielding a framework containing a high density of well-oriented LASs.²⁵⁸ In contrast to MOF-505's [1,1'-biphenyl]-3,3',5,5'-tetracarboxylic acid (H₄bptc) linker, the azo macrocycles of H₄tactmb acted as copper chelating agents. Therefore, six center-oriented copper sites were added within the cuboctahedral cage of MMCF-2, resulting in a 50% increase of the amount of LASs in MMCF-2. Based on this increase in the quantity of active sites, MMCF-2 displayed a remarkably increased catalytic activity (95.4% yield) for the cycloaddition of propylene oxide (PO) and CO₂ in the presence of a co-catalyst under mild reaction conditions (room temperature and 1 atm CO₂ pressure). This activity surpassed both MOF-505 (48.0%) and HKUST-1 (49.2%) and was mainly attributed to the higher density of preferentially-oriented active sites (LASs) in the framework that promoted interactions with substrates (PO). To improve MOFs' reactivities for CO₂ cycloaddition reactions, salen-, porphyrin- and 2,2'-bipyridine-containing organic linkers can also serve as metal chelating agents to diversify and increase the quantities of metal active sites in MOFs.^{259-261, 286} As an example, a multi-component MOF, PCN-900(Eu), fabricated from a combination of Eu₆ clusters, tetrapropyl porphyrinic linkers, and linear linkers can be modified by post-synthetic exchange of the latter and/or metalation of the former linkers to form three isoreticular compounds, PCN-900(Eu)-BPYDC, PCN-900(Eu)-CoTCPP, and PCN-900(Eu)-CoTCPP-CoBPYDC.²⁶¹ With the highest density of LASs (Eu³⁺ and Co²⁺ ions), PCN-900(Eu)-CoTCPP-CoBPYDC exhibited the highest catalytic activity for the CO₂-PO cycloaddition reaction under mild conditions, surpassing that of the non-metalated counterpart (PCN-900(Eu)-BPYDC) or the partially metalated framework (PCN-900(Eu)-CoTCPP).

Taking advantage of synergetic effects between multiple active sites can also boost the catalytic efficiencies of MOF catalysts for CO₂ cycloaddition reactions. Specifically, Lewis acid-Lewis basic synergy,^{109, 249, 253, 255, 272, 279-280} Lewis acid-Brønsted acid synergy,^{155, 264-268, 291} Lewis acid-Lewis acid synergy,^{256, 261, 286} and Lewis acid-Brønsted acid-Lewis base synergy²⁷⁰ have been studied for this series of reactions. Employing 2, 4-bis(3, 5-dicarboxyphenylamino)-6-ol triazine (H₄BDPO) as an organic linker has led to the synthesis of a stable Cu(II)-based MOF, JUC-1000, in which the phenol, amino, and triazine groups serve as weak acids and/or bases. This combination of acidic and basic moieties in one material improved the MOF's chemical stability due to the presence of -

O⁻/-OH, -NH-/NH⁺- and -N=/NH⁺= pairs facilitating a so-called "buffering effect".²⁷⁰ The synergy between multiple catalytic sites in JUC-1000, including open Cu(II) metal sites (LASs), phenol hydroxyl groups (BASs), and the LBSs from both the -NH- and triazine groups, allowed the system to produce propylene carbonate in 96% yield under ambient conditions with the aid of a co-catalyst. The authors speculated that the epoxides were synergistically activated by the open Cu(II) Lewis site, and the -OH and -NH- functional groups from the organic linkers by dipolar interactions and/or hydrogen bonding. Additionally, the CO₂ molecules were activated upon adsorption, as facilitated by the LBSs located in the pores.

Nevertheless, high-densities of active sites and synergetic behavior between them doesn't always translate to excellent catalytic performance in MOFs. Interactions between the substrates and active sites as well as the facile transport of reactants and products also play crucial roles in epoxide conversion reactions. A combination of Ni(NO₃)₂·6H₂O, tetrakis(4-carboxyphenyl)ethylene (H₄TCPE), and L-proline (L-Pro) was used to form two new (4,4)-network, Ni(II)-based MOFs, Ni-TCPE1 and Ni-TCPE2, that were hypothesized to catalyze CO₂-epoxide cycloaddition.²⁷¹ In contrast to the 1D quadrilateral channels (17.9 × 17.9 Å²) present in Ni-TCPE2, Ni-TCPE1 possesses large single-walled nanotubes (exterior wall diameter: 3.6 nm; interior channel diameter: 2.1 nm), liberating active sites within the framework and facilitating the transfer of both substrates and products. In this context, although both MOFs possessed an identical amount of OMSs, a total turnover number (TON) of 17500 per mole of catalyst after 10 repetitions of the reaction (32.5 h) was obtained when using Ni-TCPE1, whereas it took over 70 h for Ni-TCPE2 to achieve the same value. As an unfortunate drawback, the utilization of a homogeneous halide co-catalyst cannot be avoided in most of the approaches detailed above. This serves to complicate the implementation, and increase the costs of these catalytic systems.²⁵⁴ As an alternative approach, such co-catalysts can be immobilized onto MOFs' backbones using pre- or post-synthetic modification, opening new pathways toward the realization of truly heterogeneous catalytic systems. As a very early example of such tethering, a co-catalyst-functionalized MOF (F-IRMOF-3) was made by nucleophilic substitution of the amine groups of IRMOF-3 using methyl iodide.²⁴⁹ The yield of propylene carbonate (PC) produced by F-IRMOF-3 quickly increased to 98% in 1.5 h from 2% in unfunctionalized IRMOF-3 (5 h). Also, a similar process was used to synthesize a bifunctional imidazolium decorated UiO-66 variant, (I⁻)Meim-UiO-66, (Fig. 12).²⁵⁴ Taking advantage of the coexistence of BASs (Zr-OH/Zr-OH₂) and LBSs (I⁻), (I⁻)Meim-UiO-66 exhibited fantastic catalytic activity for the cycloaddition of epichlorohydrin (ECH) and CO₂ under relatively mild conditions (120 °C and 1 atm CO₂), with a yield of 93%. Furthermore, due to the heterogeneous nature of the catalyst, no significant loss of catalytic activity was observed during six sequential reaction trials. Most significantly, each subsequent trial could be conducted without the addition of any halide co-catalyst. Therefore, one can conclude that in order to achieve efficient catalytic CO₂ cycloaddition under

mild conditions, it is desirable to construct MOFs possessing a large number of accessible active sites, large pores, synergistic

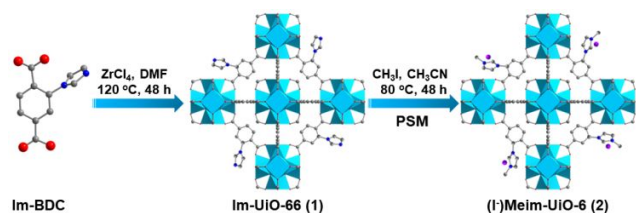


Fig. 12 Solvothermal synthesis of Im-UiO-66 (1, middle) composed of Zr_6 clusters (turquoise polyhedra) and Im-BDC linkers (left) followed by subsequent PSM using CH_3I to give (I)Meim-UiO-66 (2, right). Color code: C, gray; O, red; N, blue; Zr, cyan; and I, purple. H atoms are omitted for clarity.

effects between multiple active sites, and organic linker-tethered halide ions.

As analogues to epoxides, aziridines, a class of three-membered heterocyclic compounds with one amine group, can be converted to oxazolidinones, a versatile class of compounds commonly applied as antimicrobial agents. Such a reaction was reported in a 3D Zn(II)-MOF (ZnGlu) synthesized from glutamate and zinc sulfate heptahydrate.²⁷² Utilizing LASs (Zn^{2+}), LBSs ($-NH_2$), and a TBAB co-catalyst, about 90% of 2-methylaziridine was converted to 4-methyloxazolidin-2-one at room temperature under 1 MPa of CO_2 , with a high selectivity of 99%. As an additional example, tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine (H_{10} TBCPPP) was used as an organic linker to synthesize a copper porphyrin-based MOF.²⁹⁴ At room temperature, under 1 bar of CO_2 pressure, the MOF converted 1-methyl-2-phenylaziridine to 3-methyl-5-phenyl-2-oxazolidinone with a moderate yield of 63%, higher than that of HKUST-1 (47%) under similar reaction conditions. The amplified catalytic performance of the copper porphyrin based MOF in this study was attributed to the increased accessibility of Lewis-acidic Cu(II) sites.

An alternative CO_2 conversion route is found in the oxidative carboxylation of olefins following a two-step process involving the epoxidation of olefins and subsequent epoxide- CO_2 cycloaddition. The development of such tandem reactivity in one material is highly desirable and economical due to the availability and potential complexity of the olefin substrates. Unfortunately, oxidative carboxylation of olefins generally requires high CO_2 pressures and yields numerous byproducts with low carbonate yields.²⁹² A zirconium-based MOF, MOF-892, with dual acidic sites (LASs from Zr(IV) and BASs from uncoordinated carboxylates) was utilized as a catalyst for the one-pot synthesis of styrene carbonate (SC) from styrene and CO_2 .²⁹¹ Remarkably, in the presence of *tert*-butyl hydroperoxide (TBHP) and TBAB, styrene was completely converted in MOF-892 at 80 °C and 1 atm CO_2 in only 9 h. Furthermore, the reaction was 80% selective for SC with *t*-butanol and benzaldehyde as the major byproducts. Targeting synergistic effects between multiple components, Keggin-type $[ZnW_{12}O_{40}]^{6-}$ anions (oxidant), zinc(II) ions (LASs), NH_2 -BPY (LBSs) and pyrrolidine-2-yl-imidazole (PYI, asymmetric organocatalytic groups) were incorporated within a single MOF (Fig. 13).²⁹³ The resultant polyoxometalate-based MOFs

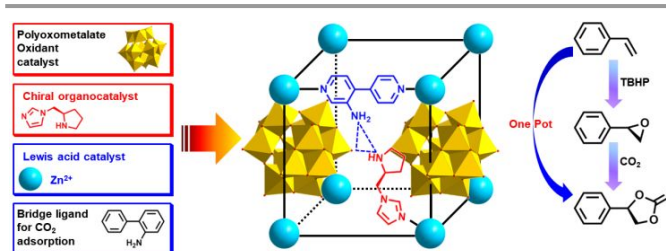


Fig. 13 (Left) Synthetic procedure used to form a polyoxometalate-based MOF highlighting the materials' constituents, including the polyoxometalate oxidant catalyst (gold polyhedra), chiral organocatalyst, Lewis acid catalyst (Zn^{2+} , cyan ball), and bridging ligand used to adsorb CO_2 . The organic linkers (NH_2 -bipyridine) in the MOF are represented as black lines. (Right) One pot asymmetric cyclic carbonate formation from the olefin and CO_2 achieved by tandem catalysis.

exhibited not only excellent CO_2 cycloaddition catalytic efficiency (>99% yield) and high enantioselectivity (90-96% ee) with (R) or (S)-styrene oxide (SO) but could also convert SO into phenyl(ethylene carbonate) in ~4 days with high yield (90-92%) and ee (77-80%) at 50 °C and 0.5 Mpa CO_2 .

Carboxylation of terminal alkynes, yielding alkynyl carboxylic acids or esters, is also a sought-after CO_2 conversion reaction to which MOF-based materials have been applied. These products are highly significant to pharmaceutical and fine chemical applications.³⁰³⁻³⁰⁴ Indeed, many catalytic systems have been developed for these reactions.³⁰⁵ However, most of these systems feature nonporous materials, dramatically hindering mass transport and active site accessibility. Under the assumption that they can more competently affect these terminal alkyne carboxylations, MOFs have been investigated for such reactions. For instance, inspired by the excellent terminal alkyne carboxylation catalytic performance of CuI and the facile conversion of CuI to $[Cu_xI_y]$ under solvothermal conditions, a pair of two cluster-based MOFs assembled from multinuclear Gd-clusters and Cu-clusters ($[Cu_{12}I_{12}]$ or $[Cu_3I_2]$) were made.²⁹⁷ Both MOFs afforded encouraging yields of *n*-butyl 2-alkynoate (74-80%) as the product of phenylacetylene carboxylation at 80 °C and 1 atm CO_2 pressure in the presence of Cs_2CO_3 and *n*-Bul.

More recently, based on the specific alkynophilicity of silver complexes, a porous silver coordination polymer was synthesized, in which the decentralized silver(I) chains were shown to activate the $C\equiv C$ bonds of propargylic alcohols and subsequently cyclize them with CO_2 .²⁹⁸ In the presence of this Ag(I)-based MOF and triphenylphosphine (Ph_3P), propargylic alcohols were converted to the target products ((*Z*)-5-benzylidene-4,4-dimethyl-1,3-dioxolan-2-one) with excellent yields (>89%) under 0.5 Mpa CO_2 and 50 °C within 36 h. Another exciting example is found in the application of an organosulfonate-based MOF, TMOF-3, with a defective *pcu* topology.²⁹⁹ In this MOF, the missing linker defects were ordered, providing an array of linker-pendant sulfonate groups for post-synthetic Ag(I) metalation (Fig. 14). In the post-synthetically modified material, the sulfonate groups on the organic linkers had a high CO_2 affinity and the Ag(I) ions could activate alkynes. Therefore, the synergy in the resultant

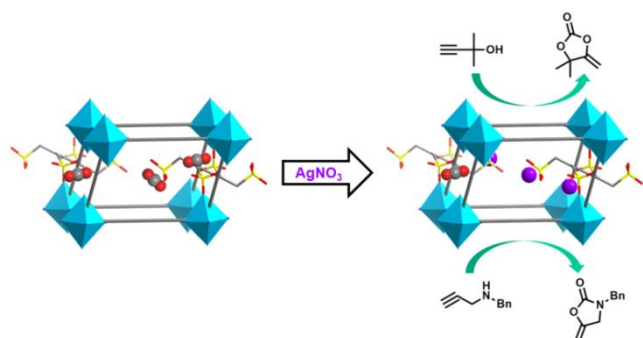


Fig. 14 The Ag(I) metalation of TMOF-3 composed of Zn clusters (cyan polyhedra) and organic linkers (grey lines). (Right, top and bottom) Carboxylic cyclization of propargylic alcohols and propargyl amine using CO₂. The reactions are catalyzed by the Ag(I)-decorated sulfonate-MOF. Color code: C, gray; O, red; N, blue; Zn, cyan S, yellow; and Ag, purple. H atoms are omitted for clarity.

framework allowed it to catalyze the carboxylic cyclization of propargylic alcohols in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) under 0.1 MPa CO₂ pressure at room temperature, with satisfying yields (>86%) for most substrates. Encouraged by the high catalytic performance of the Ag(I) ions towards propargylic alcohol cyclization, the Ag(I)-decorated sulfonate-MOF was also employed to catalyze two CO₂ conversion reaction, including three-component reactions between propargyl alcohols, CO₂ and primary amines, as well as carboxylic cyclization of propargyl amines with CO₂, yielding oxazolidinones which are significant components of antibiotics. After 15 hours, the Ag(I)-decorated sulfonate-MOF converted propargyl alcohols into oxazolidinone derivatives with high yields (>97%) in the present of Ph₃P under mild reaction conditions. Additionally, upon DBU addition, carboxylic propargyl amine cyclization was achieved under extremely mild conditions (1 atm CO₂ and room temperature) after 6 h, with high yield (>89%). Notably, all these catalytic results were determined by ¹H NMR, as an average value of three runs, indicating their reliability and repeatability.

As previously mentioned, copper based MOFs also show great potential for alkyne activation.²⁹⁷ By employing 5-aminonicotinic acid (L5) as the organic linker, a unique, three dimensional, anionic framework, {(NH₂C₂H₆)_{0.75}[Cu₄L₅]₃-(In)_{0.75}·DMF·H₂O}, was constructed and applied to the catalysis of carboxylic cyclization of various propargylic alcohols.³⁰⁰ With the addition of trace triethylamine (TEA), various propargylic alcohols were smoothly converted to the corresponding products in this MOF without any solvents based on the synergistic effect between Cu(I) and In(III) in this heterometallic framework. Not limited to these metal centers, the Lewis basic sites on the organic linkers can also affect chemical transformation of CO₂. As an example, the reaction of an amino tripodal imidazole ligand (N¹-(4-(1H-imidazol-1-yl)benzyl)-N¹-(2-aminoethyl) ethane-1,2-diamine) with Cd(II) ions gave a flexible MOF decorated with -NH₂ groups, which exhibited decent catalytic performance for the carboxylative cyclization of propargylamines with CO₂ with desirable TON (9300).³²³ The authors speculated that the amidogen ligand played an important role in facilitating ring closure to yield the oxazolidinone derivatives, which was fairly stable under the reaction conditions.

3.1.2. Conversion of CO₂ to organic products using MOF composites

MOFs impregnated with metal oxides, noble metal NPs, and other catalytically active species, also known as MOF composites, have been studied as CO₂ conversion catalysts. As a representative example, ~1.4 nm Ag NPs were incorporated into the cavities of MIL-101 using a liquid impregnation-reduction method to obtain a series of Ag@MIL-101 composites.³⁰⁶ The resultant materials had excellent CO₂ adsorption capacities and were decorated with unsaturated Cr(III) sites and highly active Ag NPs that were stabilized by MIL-101. The resultant Ag@MIL-101 (4.16 wt% Ag) exhibited remarkable catalytic activity (96.5 % yield) and excellent stability over 5 runs of terminal alkyne carboxylation reactions utilizing CO₂ under extremely mild conditions (1 atm CO₂, 50 °C). By employing similar processes, Ag NPs were encapsulated in the pores of MIL-100(Fe) and UiO-66 to give Ag@MIL-100(Fe) and Ag@UiO-66.³⁰⁷ In the presence of Cs₂CO₃ (base) and DMF (solvent), each MOF composite carboxylated terminal alkynes in good yield (>94%) at 50 °C after 15 h.

MOFs' surfaces can also serve as supports for pre-synthesized metal nanoparticles (MNPs).⁶⁹ As examples of this application, monometallic Ag NPs and bimetallic Pd-Cu NPs were separately loaded on the surface of two different MOFs (Co-MOF and MIL-101) for carbon dioxide fixation via terminal alkyne carboxylation.^{308, 309} Using Cs₂CO₃ as a base, both resultant MOF composites (Ag/Co-MOF and Pd-Cu/MIL-101) displayed high catalytic activities (yield > 96%) at room temperature. More recently, Sun et al. employed an electrostatic attraction strategy to incorporate atomically precise nanoclusters (APNCs) into MOFs.³¹⁰ The resultant composite, Au₁₂Ag₃₂(SR)₃₀@ZIF-8, not only adsorbed CO₂ but also activated terminal alkynes. Therefore, outstanding catalytic performance in the synthesis of phenylpropionic acid from CO₂ and phenylacetylene under mild conditions (1 atm CO₂ pressure, 50 °C) with a high TON of 18164 and good recyclability was observed.

MOF composites also play unique roles in CO₂-epoxide cycloaddition reactions.³¹¹⁻³¹⁵ Recently, a new strategy to imprison chiral salen(Co(III)) complexes within the pores of IRMOF-3 was developed.³¹¹ The (R,R)-salen(Co(III)) complexes were adsorbed in the pores of IRMOF-3, followed by decoration of the organic linkers with acetic anhydride by PSM. The chiral composite ((R,R)-Salen(Co)@IRMOF-3-AM) gave an acceptable PO conversion of 25% and a PC ee of 21%. Following this, two Salen-Cu(II) complexes (Salen-*t*Bu-Cu(II) and Salen-H₂-Cu(II)) were encapsulated inside the pores of MIL-101 using a "ship in a bottle" approach to obtain bifunctional catalysts for CO₂ epoxide cycloaddition.³¹² Salen-*t*Bu-Cu(II)@MIL-101 with 0.3 g/g Salen-*t*Bu-Cu(II) loading gave the highest catalytic conversion (87.8 %) of PO in the presence of TBAB under extremely mild conditions (25 °C, 1 atm CO₂ pressure).

As with MOFs, a goal of heterogeneous catalysis in MOF composites is to avoid the use of a co-catalyst. Toward this end, imidazolium-based poly(ionic liquid)s (polyILs) were confined in the cavities of MIL-101 using an *in situ* polymerization

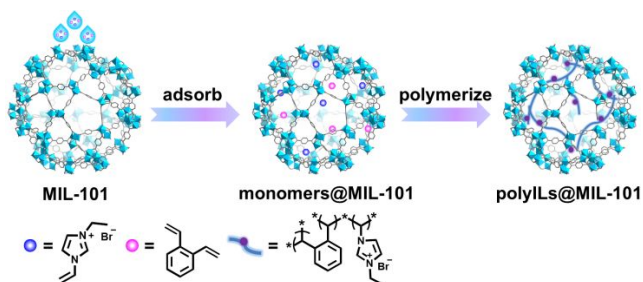


Fig. 15 Preparation of polyILs@MIL-101 involving the adsorption of monomers (3-ethyl-1-vinyl-1H-imidazol-3-ium bromide [blue balls] and 1,2-divinylbenzene [pink balls]) within the cavity of MIL-101 (middle) followed by the *in situ* polymerization of imidazolium-based poly(ionic liquid)s (dark blue lines with purple balls). Color code: C, gray; O, red; and Cr, cyan. H atoms are omitted for clarity. Adapted from ref. 313 with permission from the American Chemical Society, copyright 2018.

strategy (Fig. 15).³¹³ In the absence of co-catalyst, 94% of ECH was converted into the targeted product with high selectivity (>99%) in polyILs@MIL-101 at 70 °C and 1 bar of CO₂ after 24 h, with no significant decrease in catalytic performance after ten reactions. Similarly, a linear ionic polymer was inserted into the pores of MIL-101 to give a composite (MIL-101-IP).³¹⁴ With respect to CO₂-ECH cycloaddition, the authors found that MIL-101-IP (99% yield) outperformed the ionic polymer (3% yield), MIL-101 (32% yield), and the physical mixture of the two individual components (80% yield) under the same conditions. Kinetic studies indicated that the reaction's rate constant doubled in MIL-101-IP compared to that of the physical mixture at room temperature. Such work demonstrates a depleted energy requirement to obtain the similar conversion results in MIL-101-IP.

New components can also endow the corresponding composites with emergent functions/properties.³¹⁵ For example, templated growth and anchoring of ZIF-8 crystals on carbon nitrides (CNs), which possess micrometer-sized pores and high nitrogen contents, gave ZIF-8/CN foams with hierarchical porosities.³¹⁵ The composites were highly hydrophobic as evidenced by their water contact angles in excess of 135°. The 24 h conversion of ECH under 1 Mpa of CO₂ and 80 °C was greatly improved in the ZIF-8/CN foam (100% with 100% selectivity to chloropropene carbonate) compared to that of the pristine ZIF-8 (conversion: 84.1%; selectivity: 52%). The significantly increased catalytic performance was mainly ascribed to the hydrophobicity and hierarchical porosity of the ZIF-8/CN foam which effectively improved the transport of reactants to the catalytically active sites.

3.1.3. Conversion of CO₂ into organic products using MOF derivatives

Pyrolysis of MOFs containing transition metals and organic linkers especially those with O, N, and S produces a class of very interesting materials known as MOF derivatives. In such derivatives, a diverse array of active sites can be observed that are not typically found in MOFs.⁸⁸

As an example of the use of MOF derivatives for these reactions, several zeolitic imidazolate frameworks (ZIFs; ZIF-7, -8, -9, and -67) were used as precursors to develop a series of N-doped, metal-containing nanoporous carbons, which were applied as catalysts for cyclic carbonate synthesis from

epoxides and CO₂.³¹⁷ Among the obtained carbons, a bifunctional acid-base porous carbon synthesized by pyrolysis of ZIF-9 at 600 °C under an Ar stream exhibited the best catalytic activity (90% yield) under 0.6 Mpa of CO₂ and 80 °C. The authors attributed the high activity to uniformly distributed, partly oxidized cobalt NPs and nitrogenous species, which acted as acidic and basic sites, respectively. Recently, employing ZIF-8 as a template and sodium hypochlorite (NaClO) as an oxidant, an oxidized porous carbon was synthesized.³¹⁸ Upon moderate oxidation, several oxygen-containing functional groups, including carboxyl, lactone and alkoxy, were introduced onto the surface of the N-doped porous carbon without any loss of the original active sites including ZnO and pyridinic nitrogen atoms. On the basis of the porosity inherited from ZIF-8, the synergistic effects between the multiple catalytic sites and the aid of TBAB, the optimized catalyst, ZnO@NPC-Ox-700 (NPC: N-doped porous carbon), exhibited high catalytic conversion, selectivity and recyclability for CO₂ cycloaddition with diverse epoxides under mild conditions (25–60 °C, 1 atm of CO₂).

These two reports demonstrate the potential for high activity and stability in MOF derivative-catalyzed CO₂ conversion. It is likely that the approach can be extended to other MOFs, opening new avenues to catalysts with enhanced activities, stabilities, and selectivities for CO₂ organic transformation.

3.2. Heterogeneous hydrogenation of CO₂

CO₂ hydrogenation produces feedstock chemicals such as methane, methanol, alkyl formates and formic acid. Such reactions have been extensively studied in recent years.^{324, 325} Homogeneous catalysts frequently show satisfactory activity but need to be utilized under very high total pressures (20–200 bar) and are difficult to separate from catalytic systems.³²⁵ As an alternative, heterogeneous catalysts such as the industrially-applied ternary Cu/ZnO/Al₂O₃ are desirable in terms of catalyst separability, stability, and applicability. Unfortunately, reactions utilizing such systems always employ high temperatures (200–300 °C) and pressures (50–100 bar) as heterogeneous catalytic reactions have higher activation barriers than their homogeneous counterparts.³²⁶ In contrast, regarding heterogeneous CO₂ hydrogenation, MOFs possess the following advantages: 1) structural designability; MOFs can incorporate highly reactive frustrated Lewis pairs (LASs and LBSs) in a single material.^{327–329} 2) porosity and availability of organic coordinating groups; classical catalysts such as metals, metal oxides, metal complexes, and metal clusters can be confined and/or stabilized in MOFs, and can cooperate with MOFs to augment their respective strengths and offset their respective drawbacks.^{330–340} 3) certain MOFs can be thermally decomposed; a thermally converted MOF yields metal/metal oxide nanoparticles in a porous carbon matrix with uniform dispersion of active sites and enhanced thermal and chemical stability, resulting in highly efficient conversion of CO₂ under a variety of reaction conditions.^{341–348} As summarized in Table 3, some MOF-based materials have been reported to catalyze CO₂ hydrogenation reactions under various conditions.

As an example of heterogeneous CO₂ hydrogenation achieved by a MOF, DFT calculations were used to study the catalytic behavior of UiO-66 functionalized with frustrated Lewis pairs (FLPs).³²⁷ The calculated reaction mechanism involved first heterolytic dissociation of H₂ by the FLPs, then, in the second step a hydride and a proton were added to CO₂ in a concerted fashion, producing formic acid (HCOOH).^{327, 328} Through the studies, it was determined that H₂ heterolysis was the critical step in the catalytic reaction. The drawback in such a mechanism, however, was that the MOF must preferentially bind H₂ over CO₂. To this end, the same researchers developed a new catalyst for CO₂ reduction based on the expanded,

isorecticular framework, UiO-67.³²⁹ In UiO-67, more FLPs could be introduced without being quenched by adjacent FLP moieties. Furthermore, in the material, UiO-67(NbF₂)₄, heterolytic dissociation of H₂ was found to be much easier than CO₂ chemisorption due to the stronger binding of H₂ over CO₂ with adsorption energies of -0.22 and -0.50 eV for CO₂ and H₂, respectively. This dramatically reduced each activation energy for carbon dioxide methanolization. These calculated results suggested that MOFs could be adept CO₂ hydrogenation catalysts. Recently, molecular iridium catalysts were incorporated into two UiO-type MOFs by anchoring Ir³⁺ to the N atoms of bpydc linkers.³³⁰ The resultant catalysts were

Table 3 Summary of CO₂ hydrogenation reactions in MOF-based materials^a

Catalyst	Product	Temp. (°C)	Pressure (bar)	TOF (h ⁻¹)	Ref.
mbpyOH-IrCl ₃ -UiO	HCOOH	85	1 (H ₂ /CO ₂ =1)	36±2	330
mbpy-IrCl ₃ -UiO				1.5±0.2	
mbpyOH-[Ir ^{III}]-UiO				410±3	
mbpy-[Ir ^{III}]-UiO				28±2	
Cu@UiO-66	CH ₃ OH	175	10 (H ₂ /CO ₂ =3)	13.3	331
20Ni@MIL-101(DSM)	CH ₄	300	H ₂ /CO ₂ =4 (GHSV ^b =3000 h ⁻¹)	5.9	332
20Ni@MIL-101(IM)		320		5.1	
Ni@UiO-66	CH ₄	320	10 (H ₂ /CO ₂ =3)	154.8	333
Au&Pt@ZIF	CH ₃ OH+HCOOH	150	32 (H ₂ /CO ₂ =3)	1522	335
(Pt ⁰) _{0.5} -(Pt ^{II} Cl ₂)@{Ca ^{II} Cu ^{II} ₆ [(S,S)-methox] ₃ (OH) ₂ (H ₂ O)}·15H ₂ O	CH ₄	140	6 (H ₂ /CO ₂ /N ₂ = 4:1:1)	1.1	339
PZ8-400	CH ₃ OH	270	45 (H ₂ /CO ₂ =3)	972	342

^aThe reports in this table include TOF values in h⁻¹ (some have been converted to these units from the originally reported units). ^bGas hourly space velocity.

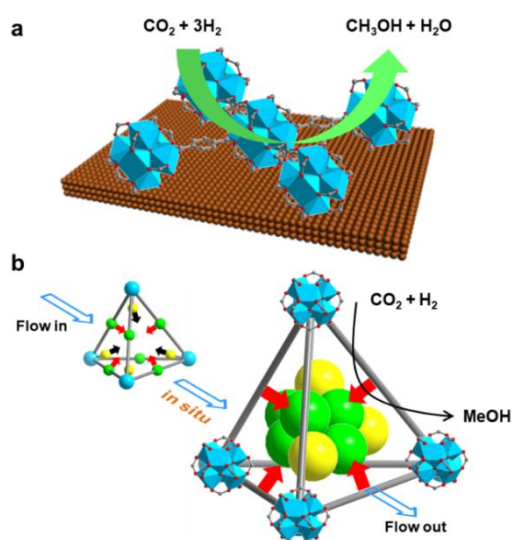


Fig. 16 (a) CO₂ hydrogenation using Cu@UiO-66 to give CH₃OH. (b) Preparation of Cu/ZnO_x@UiO-bpy (Cu/ZnO_x nanoparticles are represented as green and yellow balls) by *in situ* reduction of post-synthetically metalated UiO-bpy (left) for selective MeOH synthesis as the product of catalytic CO₂ hydrogenation. All MOFs are composed by Zr SBUs (cyan balls or polyhedra) and BDC and bpydc

linkers (gray lines). Color code: C, gray; O, red; Zr, cyan. H atoms are omitted for clarity.

placed in the condensing chamber of a Soxhlet extractor for hydrogenation of CO₂ to formate. This special reaction device maximized contact between the two reaction gases (CO₂ and H₂) and solvent (H₂O), and neutralized the solution using sodium bicarbonate (Na₂HCO₃) efficiently shifting the reaction H₂(g) + CO₂(g) ⇌ HCO₂H(aq) toward formic acid formation. Moreover, the ligand's hydroxyl group acted as an electron-donating group and a hydrogen-bonding site, further facilitating the conversion of CO₂, resulting in a high TOF of 410 ± 3 h⁻¹ under 1 MPa H₂/CO₂ (H₂:CO₂ = 1:1) and 85 °C.

Various metal catalysts can be combined with MOFs, yielding hybrid materials designed to catalyze CO₂ hydrogenation reactions. As an example of such material, Cu nanocrystals (~18 nm) were encapsulated within UiO-66 to yield a composite catalyst (Cu@UiO-66) for highly selective CO₂ hydrogenation to methanol (Fig. 16a).³³¹ The catalytic performance of Cu@UiO-66 was investigated under a 10-bar gas mixture (CO₂:H₂ = 1:3) at 175 °C. The initial turnover frequency (TOF) of MeOH formation was 3.7 × 10⁻³ s⁻¹, more

than 8 times greater than that of the conventional Cu/ZnO/Al₂O₃ catalyst. More importantly, no byproducts were detected at any reaction temperature in the range of 175–250 °C. X-ray photoelectron spectroscopy (XPS) suggested that the Zr(IV) atoms in UiO-66 were reduced upon coming into contact with the Cu nanocrystals. This indicated that the improved TOF and selectivity of Cu@UiO-66 over Cu/ZnO/Al₂O₃ were caused by the increased contact area between the SBUs and the Cu nanocrystals. Different sized Ni NPs incorporated in MOFs also resulted in varied catalysts for CO₂ hydrogenation to methane.^{332–334}

Integrating MOFs with two or more metal components may lead to unexpected CO₂ hydrogenation catalytic activity.^{335, 336} In order to hydrogenate CO₂ to MeOH, both Pt nanocubes (~6 nm) and Au nanocages (~31 nm) were embedded within ZIF-8 to form a composite, Au&Pt@ZIF.³³⁵ Under irradiation by a Xe lamp, the heat generated by the photothermal effects of Au nanocages was insulated by ZIF-8. This improved the catalytic activity of the Pt nanocubes. The resultant catalytic CO₂ hydrogenation reaction had a high TOF number of 1522 h⁻¹. In fact, even at 60 °C, the Au&Pt@ZIF CO₂ hydrogenation catalyst was still active.

Although the noble MNPs in the abovementioned materials exhibit desirable CO₂ hydrogenation catalytic efficiencies, non-noble metal oxide catalysts are more economical and thus may be a better option for such conversions. Toward this end, a series of α-Fe₂O₃/ZIF-8 catalysts were assembled in which ~30 nm α-Fe₂O₃ NPs were dispersed on the ZIF-8 supports.³³⁷ Under a 3 Mpa (CO₂:H₂ = 1:3) pressure at 573 K, α-Fe₂O₃/ZIF-8 supported on 150 nm ZIF-8 crystals displayed considerable CO₂ conversion and light olefin (C1–C4) selectivity. More recently, a novel composite catalyst, Cu/ZnO_x@UiO-bpy with <1 nm Cu/ZnO_x NPs, was made by two post-synthetic metalations of UiO-bpy with Cu²⁺ and Zn²⁺, respectively, and subsequent *in situ* reduction at 250 °C using a binary H₂/CO₂ mixture (total pressure: 4 Mpa; H₂:CO₂ = 3:1) (Fig. 16b).³³⁸ In comparison with the industrial ternary Cu/ZnO/Al₂O₃ catalyst, the strong metal-support interactions (SMSIs) and confinement effects from UiO-bpy effectively prevented Cu NP aggregation. The phase separation between Cu and ZnO_x preserved the number of active interfaces. At 250 °C and under a constant flow of H₂/CO₂ (3/1) at 4 Mpa, Cu/ZnO_x@MOF presented a high space-time yield of 2.59 g_{MeOH} kg_{Cu}⁻¹ h⁻¹ with 100% MeOH selectivity, as well as high stability over 100 h. However, for the Cu/ZnO/Al₂O₃ catalyst, only 0.83 g_{MeOH} kg_{Cu}⁻¹ h⁻¹ was obtained with low MeOH selectivity of 54.8% under the same conditions, possibly caused by competing catalytic reactions such as reverse water gas shift (RWGS).

In addition to metal/metal oxide NPs, other highly active metal species can also be incorporated within MOFs in order to hydrogenate CO₂. For example, dinuclear Pt₂ clusters were homogeneously incorporated into a bimetallic MOF ({Ca^{II}Cu^{II}}_6[(S,S)-methox]_3(OH)_2(H₂O)}·16H₂O).³³⁹ Under a gas mixture (CO₂:N₂:H₂ = 1:1:4) at 4 bar and 140 °C, the composite had a CO₂ methanation TOF of 3.1×10⁻⁴ s⁻¹, outperforming several industrial catalysts such as Ru-Al₂O₃. Recently, a facile

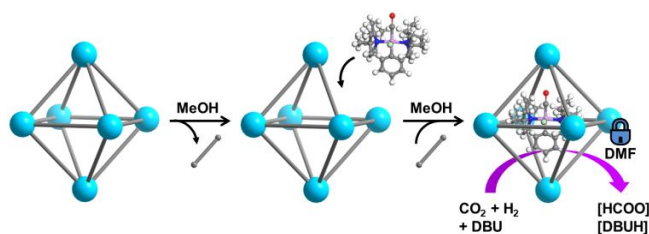


Fig. 17 Encapsulation of the transition metal catalyst, (t^{bu}PNP)Ru(CO)HCl, in UiO-66 by terephthalate linker-SBU dissociation and catalyst incorporation in protic solvent (MeOH). This compound was applied to the hydrogenation of CO₂ to formate. UiO-66 is composed of Zr clusters (cyan balls) and BDC linkers (gray lines). Color code: C, gray; O, red; N, blue; Ru, pink; Cl, yellow-green; and H, white.

method to immobilize a homogenous CO₂ hydrogenation catalyst, (t^{bu}PNP)Ru(CO)HCl, in the pores of UiO-66 was developed.³⁴⁰ The process was based on the relative size of the catalyst with respect to the MOF's pore metrics as the catalyst is larger than the pore apertures of UiO-66 but smaller than the pore size (Fig. 17). In the hybrid material, catalytic hydrogenation of CO₂ to formate was investigated in a DMF solution under 3 bar CO₂ and 12 bar H₂ at 300 K. The TON of the hybrid catalyst was comparable to that of the molecular catalyst and the catalytic activity was retained after 5 runs of reaction. The authors attributed the prolonged activity of the catalyst to impediment of bimolecular catalyst deactivation as is common in heterogeneous catalysis.

Although many MOFs display excellent catalytic CO₂ hydrogenation performance, some are unstable at high temperature, preventing practical application. To remedy this drawback, MOF-derived materials were studied and applied.^{341–348} A highly-active CO₂ methanation catalyst was generated by *in situ* pyrolysis of ruthenium (Ru)-impregnated UiO-66 during the catalytic methanation reaction.³⁴¹ The resultant catalysts were composed of a mixture of Ru⁰ NPs (2–5 nm) supported by ZrO₂ NPs (10–20 nm) with two crystal forms (tetragonal and monoclinic). In the composites, the Ru⁰ NPs served as active sites and the oxygen vacancies of the ZrO₂ NPs served as CO₂ adsorption sites. The composites with different Ru loadings (0.75–2 wt%) exhibited high CO₂ conversion efficiencies (>90%) with exceptional methane selectivities (nearly 100%) at 350 °C and under a 5 bar gas mixture (H₂:CO₂ = 4:1). More importantly, the remarkable catalytic performance of 1Ru/UiO-66-derived catalyst (1 wt% of Ru loading) was maintained in excess of 160 h, demonstrating the catalyst's high stability.

It should be noted that reports of *in situ* catalyst preparation are very rare. Instead, most MOF-derived materials are formed by calcination at high temperatures, and only after this calcination can each catalyst's performance be evaluated.^{342–346} For example, in a two-step process, presynthesized Pd@ZIF-8 was pyrolyzed in air and the products were then reduced by H₂ to afford a PdZn alloy catalyst supported on ZnO.³⁴² The catalyst was applied to CO₂ hydrogenation reactions targeting methanol as the product. After the two-step process, nearly 50% of the surface Pd atoms in the Pd NPs were substituted by Zn atoms, forming 3.7–5.8 nm PdZn alloy NPs. The highest methanol yield over the PdZn alloy catalysts was 0.65 g_{cat}⁻¹

h^{-1} at 270 °C and a total pressure of 4.5 MPa ($\text{H}_2:\text{CO}_2 = 3:1$). The excellent catalytic activity was attributed to the small size of the PdZn alloy NPs and abundant oxygen defects on the surface of the ZnO. Also, Cu/Zn nanoparticles in a carbon matrix can be prepared as exemplified by the calcination of Zn-doped HKUST-1 at 500 °C under an argon atmosphere.³⁴³ In this case, the metals did not sinter, nor did the bimetallic catalyst phase separate, leaving pyrolyzed 15–25 nm Cu/Zn NPs. The authors attributed this to protection of the metals by the carbon matrix. The Cu/Zn@C catalysts were subsequently applied to the RWGS reaction. A submillimeter-sized Cu/Zn@C sample exhibited the highest CO_2 conversion (5.0%) and CO selectivity (100%) at 500 °C and 1 bar ($\text{H}_2:\text{CO}_2 = 3:1$). Additionally, the catalyst remained active for over 20 hours. When using MIL-101(Fe) as both the template and self-sacrificing precursor, a core-shell Fe@C photocatalyst was formed by a two-step calcination approach. The material was then applied to solar-powered CO_2 conversion using H_2 (Fig. 18).³⁴⁴ The pyrolysis process effectively prevented the generation of large Fe NPs at higher temperatures, resulting in the formation of ultrafine Fe NPs (~9.7 nm). Upon irradiation with UV-light, the Fe NP excitation was amplified by the plasmon-photon coupling effect on the surface of the Fe@C. This facilitated the formation of energetic hot electrons that activated CO_2 . Accordingly, Fe@C produced 2196.17 μmol of CO after light irradiation for 2 h, outperforming both Fe/ SiO_2 (1963.3 μmol) and Fe/CNT (1453.2 μmol) under the same reaction conditions. More importantly, the ultrathin carbon layers (1–3 layers) on the Fe NPs significantly facilitated the desorption of CO from the catalyst's surface of catalyst, leading to high CO selectivity (>99.9%).

Though MOF-derived materials' sizes clearly play important roles in their catalytic activities, it was also determined that this activity could be regulated by tailoring a MOF's

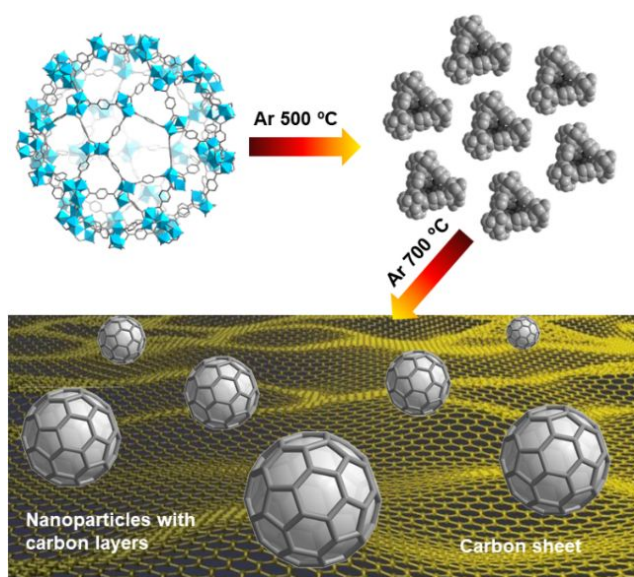


Fig. 18 The two-step preparation of core-shell Fe@C hybrids (bottom) from MIL-101(Fe) (upper left) with intermediate formation of Fe_3C and Fe_3O_4 (upper right) at 500 °C in Ar gas, and subsequent conversion to the final nanoparticles. Color code: C, gray; O, red; and Fe, cyan. H atoms are omitted for clarity.

morphology.³⁴⁵ By utilizing an ionic surfactant, cetyltrimethylammonium bromide (CTAB), the morphology of ZIF-67 crystals was transitioned from cubic to rhombic dodecahedron while the particle size increased from 150 nm to 1 μm . Upon pyrolysis in a N_2 atmosphere, Co-based porous carbon catalysts with Co NPs (7–20 nm in size) were obtained while the original morphology of the MOF was preserved. Additionally, these Co NPs were well separated by the graphite-like carbon of the resultant catalyst, which effectively prevented metal sintering. When 0.01 wt% of CTAB was added, the resultant Co-based porous carbon catalyst exhibited a high BET surface area (346 $\text{m}^2 \text{g}^{-1}$), CO_2 adsorption capacity, CO_2 conversion efficiency (52.5%) and CH_4 selectivity (>99.2%) under 3 Mpa of gas ($\text{H}_2:\text{CO}_2 = 4:1$) at 270 °C. Additionally, the catalytic performance of MOF derivatives for the hydrogenation of CO_2 can be promoted by loading a MOF (Basolite F300) with metals (0.75 wt%) using a well-established catalyst preparation method, namely incipient wetness impregnation.³⁴⁶ Specifically, upon potassium loading, the catalyst exhibited improved olefin selectivity with $\text{C}_2\text{-C}_4$ olefin space time yields of 33.6 $\text{mmol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, on account of the increased CO_2 and CO affinity, while decreasing H_2 uptake and the balance between different active phases in the resultant K-doped catalysts.

As an alternative strategy, MOF derivatives for catalytic CO_2 conversion can be synthesized without thermal treatment.

Table 4 Summary of photocatalytic CO₂ reduction reactions in a selection of MOF-based materials^a

Catalyst	Electron donor	Light irradiation	Product	Photocatalytic efficiency ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Ref.
(Y[Ir(ppy) ₂ (dcbpy)] ₂ [OH])	TEOA	visible-light	HCOO ⁻	158.3	349
ZrPP-1-Co	TEOA	visible-light	CO+CH ₄	14.5	351
NH ₂ -MIL-125	TEOA	visible-light	HCOO ⁻	16.3	352
PCN-222	TEOA	visible-light	HCOO ⁻	60.0	353
Eu-Ru(phen) ₃ -MOF	TEOA	visible-light	HCOO ⁻	94.0	354
NH ₂ -UiO-66	TEOA	visible-light	HCOO ⁻	26.4	355
mixed NH ₂ -UiO-66				41.4	
MOF-253-Ru(CO) ₂ Cl ₂	TEOA	visible-light	CO+HCOO ⁻ +H ₂	65.5	357
NH ₂ -MIL-101(Fe)	TEOA	visible-light	HCOO ⁻	445.0	358
MIL-101(Fe)				147.5	
NH ₂ -MIL-53(Fe)				116.3	
MIL-53(Fe)				74.3	
NH ₂ -MIL-88(Fe)				75.0	
MIL-88(Fe)				22.5	
NUU-28	TEOA	visible-light	HCOO ⁻	52.8	359
MOF-525-Co	TEOA	visible-light	CO+CH ₄	237.4	360
UiO-66-CrCAT	BNAH+TEOA	visible-light	HCOOH	1724.3±88	361
UiO-66-GaCAT				959.3±84	
HKUST-1@TiO ₂	-	UV	CH ₄	2.6	376
UiO-66/CNNS	TEOA	visible-light	CO	9.9	377
BIF-20@g-C ₃ N ₄ (20 wt%)	TEOA	visible-light	CH ₄ +CO	69.4	378
CdS/UiO-bpy/Co	TEOA	visible-light	CO+H ₂	276.0	379
CZS@UN20	-	visible-light	CH ₃ OH	6.8	380
Au/NH ₂ -MIL-125(Ti)	TEOA	visible-light	H ₂ +HCOO ⁻	123.2	383
Pt/NH ₂ -MIL-125(Ti)				619.9	
ZIF0.03/T	-	UV-visible	CO+CH ₄ +H ₂	22.2	387
TiMOF-2	-	UV	CO+CH ₄	0.71	388
Mg-MOF-74/TiO ₂	-	365 nm UV	CO+CH ₄ +O ₂	12.7	390
TCNZ8	-	UV-visible	CH ₃ OH	0.75	394
Au@NENU-10	H ₂ O	visible-light	CO+H ₂ +CH ₄	17.5	397
NH ₂ -rGO (5 wt%)/Al-PMOF	TEOA	visible-light	HCOO ⁻	685.6	398
C-Cu _{2-x} S@g-C ₃ N ₄ -2	-	visible-light	CO+H ₂	90.75	403

^aThe reports in this table include photocatalytic efficiencies in $\mu\text{mol g}^{-1} \text{h}^{-1}$ (some have been converted to these units from the originally reported units).

Recently, a water-soaking process created a ZIF-67-derived (ZIF-67 is unstable in water) nanoreactor taking advantage of the phase transitions of ZIF-67@Pt@mSiO₂ (mSiO₂ = mesoporous silica) nanocubes.³⁴⁷ During this phase transition, ZIF-67 acted as both a morphological template and a sacrificial

cobalt source to react with the silicic acid from SiO₂ hydrolysis, yielding a cobalt silicate. The CO₂ methanation was catalyzed by the final catalyst, Pt@CSN (cobalt silicate nanocubes). The two-step reaction mechanism involves (i) CO intermediate formation as the result of RWGS reaction on Pt sites, and (ii)

CO methanation over Co sites. The shell structure of the Pt@CSN nanoreactor not only immobilized the Pt NPs but also offered additional diffusion pathways for reaction gasses and intermediates, prolonging their retention times and eventually boosting the CO₂ conversion and the selectivity toward CH₄ (41.8 and 94%, respectively at 30 bar [CO₂:H₂:N₂ = 6:18:1] and 320 °C).

3.3. Photocatalytic CO₂ reduction

One envisions a carbon-neutral energy cycle where any produced CO₂ can be converted to useful fuels and/or commodity chemicals with minimal energy input. To accomplish this, the importance of the application of solar energy to CO₂ conversion is paramount. Although semiconductor materials represent the state-of-the-art with respect to photocatalysis, they are plagued by rapid hole-electron recombination and poor CO₂ adsorption capacity, restricting their photocatalytic CO₂ reduction efficiencies. On the other hand, MOF-based materials have been identified as a new class of CO₂ reduction photocatalysts.^{45, 63, 86, 90} Their CO₂ capture performances are summarized in Table 1. The photocatalytic performances for CO₂ reduction in MOF-based materials are summarized in Table 4.

3.3.1. MOFs for photocatalytic CO₂ reduction

The unique properties of MOFs position them as ideal platforms for the integration of photosensitizers, catalytic centers and CO₂ adsorption sites in a single material to target photocatalytic CO₂ reduction.^{52, 63, 86, 90}

As an example of photosensitizer and photocatalyst incorporation in a MOF, BPDC and [Re(CO)₃(bpydc)Cl] were used as the organic linkers in the synthesis of a UiO-67 variant.⁴⁶ In the resultant framework, [Re(CO)₃(bpydc)Cl] served as both the photoactive and catalytically active unit, leading to high catalytic activity. With TEA as a sacrificial reducing agent, the resulting mixed-linker UiO-67 exhibited a total CO-TON of 10.9 after a 20 h reaction, three times higher than that of the homogeneous [Re(CO)₃(bpydc)Cl] catalyst. Such work demonstrates the utility of MOFs' porous natures. Photocatalysts do not have to be incorporated using a mixed-linker approach, however. In fact, Ir(ppy)₂(Hdcbpy) was used as the organic linker to directly incorporate a photoactive catalyst into a MOF (Ir-CP) to achieve visible-light mediated CO₂ reduction.³⁴⁹ The Ir-CP exhibited remarkable catalytic performance in the conversion of CO₂ to formate using triethanolamine (TEOA) as a sacrificial electron donating agent. Transition metal porphyrins can also be similarly useful in MOFs.^{350, 351} A metalloporphyrinic MOF (ZrPP-1-Co) was applied to CO₂-to-CO photoreduction.³⁵¹ The uniformly distributed porphyrinic Co²⁺ ions not only adsorbed CO₂, enhancing the MOF's uptake capacity (~4.0 mmol g⁻¹ at 1 atm and 273 K), but also functioned as mediators, promoting electron transfer from linker-based benzene rings to the porphyrin cores to afford Co⁰ in the presence of TEOA. The Co⁰ species then activated and converted CO₂ to CO and hydrogenated CO to CH₄ with the aid of protonated TEOA.

The photocatalytic CO₂ reduction activities of MOFs can also be improved by combining photosensitizers and catalytically

active sites within a single framework.³⁵²⁻³⁵⁷ A titanium-based MOF, NH₂-MIL-125, was applied to CO₂ capture and subsequent photocatalytic reduction to formate under visible-light irradiation.³⁵² In this compound, the light was absorbed by the NH₂-BDC linkers, generating photoelectrons that were then transferred to the Ti centers in the SBUs by a ligand-to-metal charge transfer (LMCT) process. The metals then acted as active sites for CO₂ reduction and the Ti⁴⁺ ions were reduced to Ti³⁺ in the presence of TEOA. After 10 h, the material produced 8.14 mmol of HCOO⁻ without significant degradation of the MOF's crystalline structure. Using a similar strategy, the photocatalytic activity of a porphyrin-based MOF (PCN-222), greatly extended the light harvesting capability of NH₂-MIL-125 such that it could absorb light from the entire visible spectrum (Fig. 19).³⁵³ PCN-222 adsorbed CO₂ adeptly (2.6 mmol g⁻¹ at 273 K and 1 atm) and electron-hole recombination in the

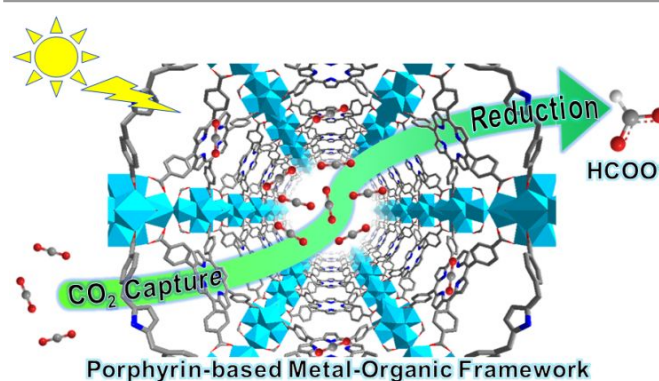


Fig. 19 Idealized scheme representing CO₂ capture and photocatalytic reduction to formate in PCN-222 which is composed of Zr₆ clusters and porphyrin linkers. Color code: C, gray; O, red; N, blue; H, white; and Zr, cyan. Adapted from ref. 353 with permission from the American Chemical Society, copyright 2015.

material was dramatically suppressed as the photoelectrons were generated by electron transfer from the organic linkers to the Zr-oxo clusters. Such suppression of electron-hole recombination clearly demonstrates a potential advantage of MOF application to photocatalytic redox reactions. All of these advantages led to a considerable yield of formate (30 μmol in 10 h) as the product of photocatalytic CO₂ reduction. Time-resolved photoluminescence (PL) spectroscopy and ultrafast transient absorption spectroscopy confirmed that an extremely long-lived electron trap state existed in PCN-222. A photosensitizing MOF featuring dinuclear Eu(III)₂ clusters and Ru(phen)₃-derived organic linkers for visible-light-driven CO₂ reduction was also reported.³⁵⁴ Calculations and characterization by ultrafast transient absorption, and EPR spectroscopy indicated that, upon visible light irradiation, the Ru(phen)₃ linkers were excited to triplet MLCT excited states, initiating electron injection into the Eu SBUs, which then became catalytically active. In this catalytic system, CO₂ was converted to formate with a fantastic rate of 321.9 μmol h⁻¹ mmol MOF⁻¹, far exceeding many previous MOF catalysts under similar conditions.

In some cases, both the SBUs and organic linkers of MOFs can be simultaneously photoexcited, leading to dual photocatalytic excitation pathways in a single material.^{358, 359} This phenomenon was reported in some amine-functionalized

MOFs including NH₂-MIL-101(Fe), NH₂-MIL-53(Fe), and NH₂-MIL-88B(Fe).³⁵⁸ Upon exposure to visible light, the NH₂-BDC linkers were excited followed by electron transfer to the Fe-oxo clusters in a process analogous to the one detailed above. In addition, the Fe-oxo SBUs were directly excited, greatly enhancing the MOFs' photocatalytic activities (Fig. 20). Without amine functionalities, a zirconium-based MOF was synthesized using an anthracene-based organic linker.³⁵⁹ The linker was an effective visible light harvester, transferring photogenerated electrons to the Zr-oxo SBU by LMCT. Meanwhile, photoinduced charges were generated on the linker by radical formation. The dual excitation routes simultaneously contributed to the photocatalytic CO₂ reduction activity, yielding formate and boosting the CO₂ conversion efficiency.

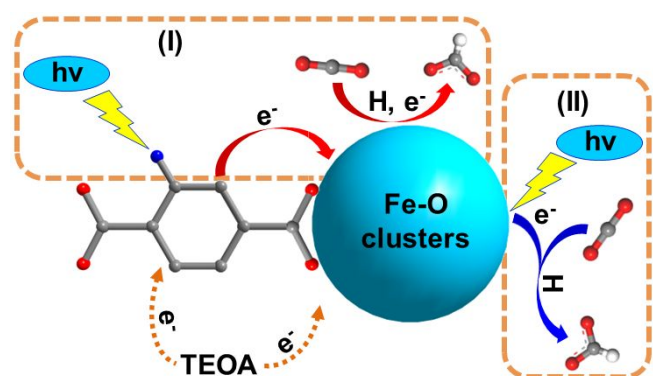


Fig. 20 Dual excitation pathways in a series of amine-functionalized Fe-Based MOFs allowing for the conversion of CO₂ to formate. (I) The NH₂-BDC linkers were excited followed by electron transfer to the Fe-oxo clusters (turquoise polyhedra). (II) Direct excitation of Fe-oxo SBUs. Color code: C, gray; O, red; N, blue; Fe, cyan; and H, white.

It should be noted that each photocatalytic MOF system detailed above was synthesized in a traditional, one-pot, solvothermal manner. As an alternative, post-synthetic modification (PSM) can expand the scope of available materials to achieve effective photocatalytic CO₂ reduction.^{356-357, 360-364} For instance, a metalloporphyrin zirconium-based MOF, MOF-525-Co, was synthesized by post-synthetic metalation of the porphyrin rings in MOF-525.³⁶⁰ Upon irradiation with visible light, MOF-525-Co exhibited a drastically enhanced activity compared to that of pristine MOF-525. Photoluminescent (PL) quenching measurements of MOF-525-Co demonstrated that photogenerated excitons could directionally migrate from the organic porphyrin backbone to the core (i.e. the catalytic Co center). This extended the lifetime of the photoelectrons, allowing them to react with CO₂ in a reductive fashion. In another report, two Ru complexes, Ru(CO)₂Cl₂ and Ru(bpy)₂Cl₂, were tethered to the open N,N'-chelating sites in MOF-253.³⁵⁷ In this case, Ru(CO)₂Cl₂ and Ru(bpy)₂Cl₂ served as the active site and photosensitizer, respectively and the total TON of the resultant catalyst was 55 after 8 h of visible light irradiation, about ten times higher than that of the homogenous Ru(CO)₂Cl₂ catalyst.

These strategies are clearly powerful, but they are marred by the fact that many organic linkers are difficult to be functionalized using PSM. To address this, postsynthetic linker

exchange was employed to synthesize a photoactive UiO-66 variant.³⁶¹ In the report, the BDC linkers of UiO-66 were exchanged with their catechol-functionalized counterparts (catbdc). The catechol groups were subsequently metalated with Cr³⁺ and Ga³⁺, leading to the formation of metal-monocatecholato species within UiO-66. With the aid of 1-benzyl-1,4-dihydronicotinamide (BNAH) and TEOA, both functionalized UiO-66 frameworks displayed decent catalytic activity (6.14-11.22 TON after 13 h) for photocatalytic CO₂ reduction to formic acid. The Hf₁₂ SBU surface of a two-dimensional MOF, Hf₁₂-Ru, with M(bpy)(CO)₃X (M = Re and X = Cl or M = Mn and X = Br) was modified by carboxylate

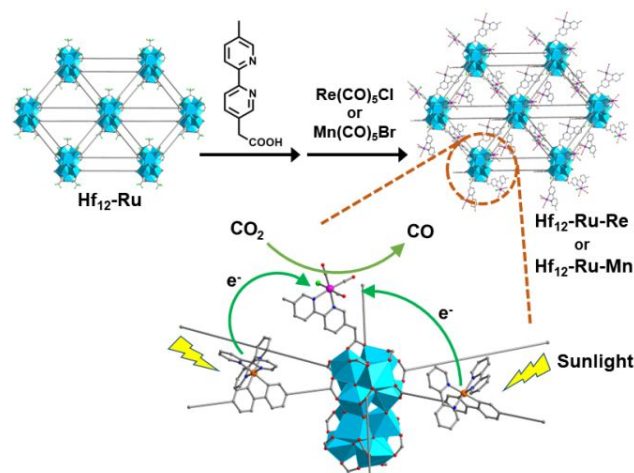


Fig. 21 Preparation of Hf₁₂-Ru-M (M = Re or Mn) (upper right) via monocarboxylic acid exchange of Hf₁₂-Ru (upper left) and sunlight-driven CO₂ reduction using Hf₁₂-Ru-Re (bottom). Color code: C, gray; O, red; N, blue; Hf, cyan; Ru, pink; Re, orange; and Cl, green. H atoms are omitted for clarity.

exchange to afford two photosensitizing metal-organic layers (MOLs, Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn) for photocatalytic CO₂ reduction (Fig. 21).³⁶² The MOL combined [Ru(bpy)₃]²⁺ photosensitizers and M(bpy)(CO)₃X catalysts, in order to target synergistic effects between the two species. In particular, the proximity of the MOL skeleton to the capping molecules (1-2 nm) facilitated electron transfer from the reduced photosensitizer ([Ru(bpy)₃]⁺) to the catalytic centers (M'(bpy)(CO)₃X (M = Re, X = Cl or M = Mn, X = Br)), leading to high CO₂ reduction TONs of 3849 and 1347, respectively, after 12 h of visible light irradiation. Remarkably, when irradiated with natural sunlight, Hf₁₂-Ru-Re catalyzed CO₂ reduction with extraordinary efficiency, achieving a TON of 670 in 6 h. All of these catalytic performances were evaluated by several runs with low standard deviation, indicating the reliability of catalytic activities. In addition to the organic linkers, metal atoms in MOF SBUs can also be substituted. For example, a Ti-substituted NH₂-UiO-66(Zr/Ti) was synthesized and used as a visible-light-responsive photocatalyst for CO₂ reduction.³⁶³ After metal substitution, the CO₂ uptake capacity and the photocatalytic formate yield were improved compared to NH₂-UiO-66. In contrast to the simple LMCT mechanism postulated to occur in NH₂-UiO-66, the authors speculated that the excited NH₂-BDC linkers of NH₂-UiO-66(Zr/Ti) would be inclined to transfer electrons to the Ti ions in the SBUs of

(Ti³⁺/Zr⁴⁺)₆O₄(OH)₄ and the reduced Ti³⁺ functioned as electron mediators donating electrons to Zr⁴⁺.

In addition, MOFs can behave solely as CO₂ photoreduction cocatalysts, achieving high photocatalytic activities in the resultant systems.³⁶⁵⁻³⁷⁴ For instance, a visible-light-driven catalytic system employing ZIF-9, [Ru(bpy)₃]Cl₂·6H₂O and TEOA as cocatalyst, photosensitizer and electron donor, respectively, was applied to the photosplitting of CO₂.³⁶⁵ Upon visible-light irradiation for 30 min, the catalyst produced 71.7 μmol of CO and H₂ based on the synergetic effects between cobalt and benzimidazolone moieties in ZIF-9. This activity surpassed those of many other MOFs such as Co-MOF-74 (23.8 μmol), Mn-MOF-74 (5.5 μmol), ZIF-8 (5.6 μmol) and NH₂-UiO-66 (4.3 μmol), indicating the unique ability of Co-ZIF-9 to photoreduce CO₂.

3.3.2. MOF composites for photocatalytic CO₂ reduction

Despite the fact that MOFs are appealing for photocatalysis, numerous MOFs have sufficiently large bandgaps such that they only absorb UV light and cannot be directly used for photocatalytic CO₂ reduction when irradiated with visible or longer-wavelength light. To address this challenge, metal complexes such as [Ru(bpy)₃]Cl₂·6H₂O can be added to the catalytic systems to serve as photosensitizers.³⁶⁵⁻³⁷⁴ Nevertheless, given the high cost and homogeneous nature of these noble metal complexes, a myriad of solid materials including inorganic semiconductors and metal NPs have been employed to replace them in conventional systems.³⁷⁵⁻³⁹⁶ Inorganic semiconductor materials incorporated in MOFs act as photosensitizers and excite the frameworks upon exposure to light.^{376-378, 385-389} In turn, certain MOFs can effectively suppress the recombination of electron-hole pairs by transferring photoexcited electrons from the semiconductor materials to the MOFs and/or adsorbing the dissolved CO₂ in the reaction system, significantly improving the catalytic efficiencies of the given semiconductor.^{375-378, 385-398}

A semiconductor-MOF composite was designed for photocatalytic CO₂ reduction by growing ZIF-8 nanoparticles on Zn₂GeO₄ nanorods.³⁷⁵ The photocatalytic activity of the resultant Zn₂GeO₄/ZIF-8 for CO₂ reduction was investigated in aqueous solution. Under light irradiation for 10 h, evolution of the product (MeOH) was enhanced by 62% in comparison to the pure Zn₂GeO₄. The authors speculated that this was caused by the increased CO₂ capture capacity and light response of the catalyst after the introduction of ZIF-8. By coating of TiO₂ onto the HKUST-1 microcrystals, a core-shell structured hybrid photocatalyst, HKUST-1@TiO₂, was made.³⁷⁶ Given that TiO₂ is not able to harvest visible light HKUST-1@TiO₂ was illuminated with UV light and exhibited a catalytic efficiency over five times greater than that of TiO₂, with high CH₄ selectivity. Ultrafast spectroscopy demonstrated that the photogenerated electrons were transferred from the TiO₂ shell to the HKUST-1 core. This enhanced the charge-separation efficiency of the semiconductor and supplied adequate electrons to the adsorbed CO₂ molecules. All these factors facilitated highly selective conversion of CO₂ to CH₄ by an eight-electron process. Nanosheets were also incorporated with MOFs in an electrostatic self-assembly approach that integrated positively-

charged UiO-66 crystals with negatively-charged nanosized carbon nitride nanosheets (CNNS).³⁷⁷ The resultant material was a UiO-66/CNNS heterogeneous photocatalyst. The CO evolution rate afforded by UiO-66/CNNS was 9.9 μmol g_{CN}⁻¹ h⁻¹ under light irradiation for 6 h, over three times greater than that of CNNS (2.9 μmol g_{CN}⁻¹ h⁻¹). The authors ascribed the improvement of photocatalytic performance to the electron transfer from the photoexcited CNNS to UiO-66 and effective inhibition of the electron-hole pair recombination in the CNNS, ultimately offering long-lived electrons for CO₂ reduction. More recently, this self-assembly method was applied to the combination of BIF-20 with graphitic carbon nitride (g-C₃N₄) to prepare a BIF-20@g-C₃N₄ nanosheet photocatalyst.³⁷⁸ When the surface of BIF-20 was loaded with 20% g-C₃N₄, the resultant composite exhibited the highest catalytic performance (CH₄ evolution rate of 15.524 μmol g⁻¹ h⁻¹ and CO evolution rate of 53.869 μmol g⁻¹ h⁻¹), outperforming the g-C₃N₄ nanosheet, bulk g-C₃N₄, and ZIF-8@g-C₃N₄ nanosheet. First-principles simulations indicated that the B-H bonds in BIF-20 functioned not only as electron capture centers to prevent the recombination of electron-hole pairs but also activated the adsorbed CO₂ molecules in BIF-20, greatly facilitating the photoreduction process. More recently, a ternary CdS/UiO-bpy/Co composite was synthesized by combining inorganic semiconductors (CdS) and molecular redox catalysts (Co complex) in a MOF.³⁷⁹ Under visible light irradiation, the Co complex accepted electrons from the CdS photosensitizer and subsequently photochemically reduced CO₂ to CO. Additionally, in the composites, CdS NPs (~10 nm) were obtained due to the coordination of bpydc with Cd²⁺, eventually affording a high CO evolution rate of 235 mmol g⁻¹ h⁻¹ with a desirable selectivity (>85%). The authors attributed the high catalytic performance to the promoted separation and migration of photo-induced charge carriers, enhanced CO₂ uptake capacity (compared with pure CdS) as well as the abundant active sites for CO₂ reduction.

As a matter of fact, MOFs can also serve as photosensitizers in some semiconductor-MOF composites.³⁸⁰⁻³⁸² A prime example is found in a series of Cd_{0.2}Zn_{0.8}S@NH₂-UiO-66 composites.³⁸⁰ Under visible-light irradiation, both Cd_{0.2}Zn_{0.8}S and NH₂-UiO-66 were excited, generating electron-hole pairs. Since the LUMO potential of NH₂-UiO-66 (-0.60 eV vs. NHE) is more negative than the conduction band (CB) potential of Cd_{0.2}Zn_{0.8}S (-0.56 eV vs. NHE), the photogenerated electrons can transfer from the LUMO of NH₂-UiO-66 to the CB of Cd_{0.2}Zn_{0.8}S, suppressing the recombination of electron-hole pairs and prolonging the lifetime of photoinduced charge carriers. This ultimately accelerated the photocatalytic conversion of CO₂ up to 6.8 mol h⁻¹ g⁻¹ under visible-light irradiation, over 3 times higher than that of pure Cd_{0.2}Zn_{0.8}S. Since the LUMO potential of NH₂-UiO-66 is more negative than the CB potential of anatase TiO₂ (-0.28 eV vs. NHE), a Type II heterojunction was formed in a TiO₂/NH₂-UiO-66 composite.³⁸¹ By transferring photogenerated electrons from NH₂-UiO-66 to TiO₂, the electron-hole separation in NH₂-UiO-66 was promoted and CO₂ was reduced to CO by TiO₂, with a superior CO evolution rate as compared to the pure TiO₂.

Enhanced photocatalytic performance can be realized in MNP-MOF composites along two pathways: visible-light harvesting and electron transfer.^{383, 384} As an example, Pt nanoparticles were encapsulated in NH₂-MIL-125 using the wetness impregnation method.³⁸³ Although the absorption spectrum of the resultant composite (Pt/NH₂-MIL-125) was not affected by the incorporation of Pt NPs, a 21% increase in the photocatalytic activity (CO₂ to formate) was observed. Electron spin resonance (ESR) studies and DFT calculations demonstrated that the hydrogen spilled over from the doped Pt to Ti-O oxo-clusters, generating the active sites (Ti³⁺) in the material. Recently, Re₃-MOF layers were coated onto pre-synthesized Ag nanocubes (98 nm), resulting in a core-shell photocatalyst (Ag@Re₃-MOF) for CO₂-to-CO conversion (Fig. 22).³⁸⁴ In this system, the strong Ag localized surface plasmon resonance (LSPR) ($\lambda_{\text{max}} = 480 \text{ nm}$) overlapped with the

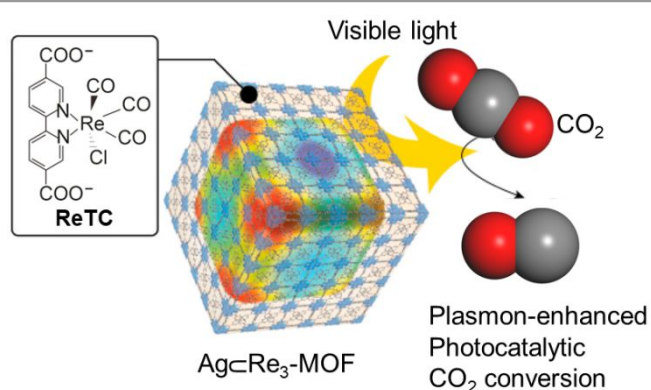


Fig. 22 Plasmon-enhanced photocatalytic CO₂ reduction to CO using Ag@Re₃-MOF under visible light irradiation. Adapted from ref. 384 with permission from the American Chemical Society, copyright 2017.

absorption range of the Re₃-MOF (400 nm < λ < 550 nm). Therefore, the Ag@Re₃-MOF composite inherited the characteristic LSPR properties of the Ag nanocubes and the photoactive Re centers of Re₃-MOF were spatially confined to the intensified near-surface electric fields created at the surface of the Ag core. All of these effects lead to a 7-fold increase in the (visible light) photocatalytic conversion of CO₂ to CO compared to pristine Re₃-MOF, with long-term catalytic stability maintained up to 48 h.

To summarize, conventional strategies applied to make MOF composite photocatalysts include: 1) Combination of MOFs with semiconductors such as g-C₃N₄ or TiO₂. The intimate interfacial contact between semiconductors and MOFs results in the formation of heterojunctions, while the MOFs act as cocatalysts. This synergy induces efficient, persistent electron-hole separation and thus improves photocatalytic efficiency. 2) Stabilization of cocatalysts such as Cd_{0.2}Zn_{0.8}S by MOFs. The conjugated organic linkers in MOFs can behave as molecular antennae to be photoexcited. The photoelectrons then transfer to the cocatalyst for CO₂ reduction. 3) Immobilization of photoactive metal nanoparticles into MOFs. Such components harvest solar energy, exciting and then transferring electrons to active sites in the MOF(s) for subsequent CO₂ reduction.

3.3.3. MOF derivatives for photocatalytic CO₂ reduction

In an analogous fashion to CO₂ capture, MOF pyrolysis can be applied to the synthesis of materials for photocatalytic CO₂ reduction.³⁹⁹⁻⁴⁰³ To various extents, these catalysts inherit the pore characteristics of their MOF templates. This not only benefits the adsorption and subsequent concentration of CO₂, but can also create new catalytically active sites.

A MOF-derived TiO₂ material was made by directly pyrolyzing NH₂-MIL-125 in an oxygen atmosphere and applied to CO₂ photoreduction.³⁹⁹ When the precursor (NH₂-MIL-125) was replaced by (GNPs) gold NPs-doped NH₂-MIL-125, a dramatic increase in CH₄ yield was observed due to the visible light absorption of gold surface plasmon and/or the electron storage capacities of GNPs, and the minimal GNP/TiO₂ lattice defects, which effectively inhibited electron-hole recombination. Wang et al. employed core-shell ZIF-8@ZIF-67 crystals as precursors for the synthesis of a porous ZnO@Co₃O₄ composite.⁴⁰⁰ Interestingly, unlike the unstable CH₄ evolution observed in ZIF-8-derived ZnO, the CH₄ evolution increased steadily during the entire reaction involving ZnO@Co₃O₄. This was attributed to suppressed ZnO photocorrosion after embedding the Co₃O₄ co-catalyst on the surface.

Some structural features of MOF-derived materials (e.g. hollowness) can reduce bulk-to-surface diffusion length (accelerating electron-hole separation) and provide high surface area in order to boost CO₂ adsorption and substrate/product transfer.⁴⁰¹⁻⁴⁰⁴ These features play significant roles in enhancing a given MOF derivative's photocatalytic CO₂ reduction activity. Using MIL-68(In) as precursor, a series of sandwich-like ZnIn₂S₄-In₂O₃ photocatalysts with hierarchical tubular heterostructures were generated by growing ZnIn₂S₄ on both surfaces of the In₂O₃ microtubes (Fig. 23).⁴⁰¹ The highest CO evolution rate of

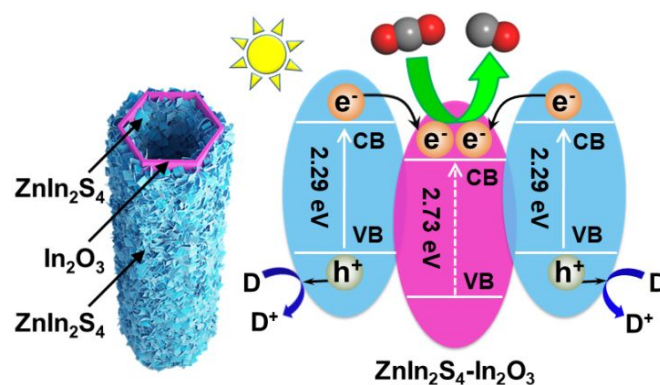


Fig. 23 (Left) Sandwich-like ZnIn₂S₄-In₂O₃ hierarchical tubular heterostructures and (right) Catalytic CO₂ photoreduction using the ZnIn₂S₄-In₂O₃ with double-heterojunction shells under visible light irradiation. Adapted from ref. 401 with permission from the American Chemical Society, copyright 2018.

ZnIn₂S₄-In₂O₃ was 3075 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which was further confirmed by repeated experiments. The authors attributed this to the promoted transport of photoinduced charges and accelerated electron-hole separation from the double-heterojunction formed by the sandwich-like structure.

Again, MOF derivatives do not have to be synthesized by high-temperature pyrolysis. Indeed, the same team

demonstrated the construction of hierarchical $\text{In}_2\text{S}_3\text{-CdIn}_2\text{S}_4$ nanotubes by converting MIL-68(In) to hierarchical In_2S_3 nanotubes through a liquid phase sulfidation process with subsequent cation exchange.⁴⁰⁴ The hierarchical heterostructured tubes were capable of separating and migrating photoinduced charge carriers, improving the material's CO_2 adsorption capacity, and providing abundant catalytically active sites. The resultant material exhibited a decent CO production rate ($825 \mu\text{mol h}^{-1} \text{g}^{-1}$) in the presence of $\text{Co}(\text{bpy})_3^{2+}$ and TEOA, approximately 12 times higher than that of pure In_2S_3 .

3.4. Electrocatalytic CO_2 reduction

Electrochemical carbon dioxide reduction reactions (CO_2RR) can be accomplished under mild conditions, putting them in stark contrast with many other transformations. Furthermore, the energy utilized to carry out these reactions can be obtained from renewable energy sources. Generally, electrochemical CO_2 reduction occurs by proton abstraction from solvent molecule(s), yielding various fuels and value-added chemicals.

3.4.1. MOFs for electrocatalytic CO_2 reduction

Extensive efforts have been devoted to the development of homogeneous and heterogeneous catalysts for CO_2RR . Outstanding challenges remain, such as low catalytic efficiency, undesirable selectivity, and poor long-term stability. Fortunately, MOFs can incorporate redox-active sites, concentrate CO_2 , and even facilitate uniform proton transport to catalytic sites. In this section we give examples of how these properties allow MOFs to improve upon previous attempts to affect CO_2RR reactions.

Inspired by the unique catalytic properties of metallic Cu for

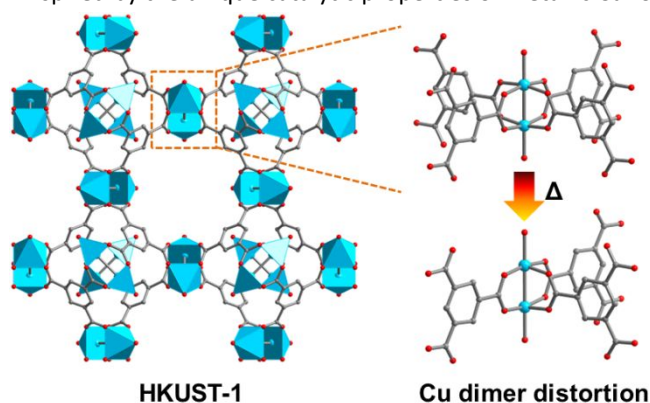


Fig. 24 Desymmetrization of the Cu dimers in HKUST-1 during calcination at 250 °C. Color code: C, gray; O, red; and Cu, cyan. H atoms are omitted for clarity.

electrochemical CO_2 reduction, select proton-conductive, Cu-based, MOFs have been applied as electrochemical CO_2RR catalysts.⁴⁰⁵⁻⁴¹⁰ As an example, a copper rubeanate MOF was used for highly selective conversion of CO_2 to HCOOH .⁴⁰⁵ Since HCOOH is easily produced at relatively weak CO_2 adsorption, the final selectivity of HCOOH using this MOF was 98%, significantly greater than that of metallic Cu (~38%), with a current efficiency of 30% from -1.6 to -1.2 V vs. SHE, due to its weak CO_2 adsorption behavior. Current efficiency (also called faradaic efficiency) which refers to the percentage of charge

from an electrochemical process that is used to generate a specific product is a critical parameter used to evaluate the applicability of a given electrode. As a typical copper-based MOF, HKUST-1 has been deposited on different electrodes to serve as an electrocatalyst.⁴⁰⁶⁻⁴⁰⁹ In these reports, oxalic acid, alcohols, and hydrocarbons have been produced. More recently, the paddle-wheel Cu dimer SBUs of HKUST-1 were desymmetrized to target multiple-carbon product generation (Fig. 24).⁴⁰⁹ By simply heating the material to 250 °C, adjacent benzene-1,3,5-tricarboxylate (BTC) moieties were separated from the Cu dimer, decreasing the Cu-Cu coordination number (CN) in HKUST-1 as confirmed by extended X-ray absorption fine structure (EXAFS) spectroscopy. When the calcination time was increased to 3 h, the Cu-Cu CN reduced to 9.5 ± 0.9 while the framework maintained its structural integrity and crystallinity. The C_2H_4 faradaic efficiency (FE) in this distorted HKUST-1 variant was 45% with a current density of 262 mA cm^{-2} at -1.07 V vs. RHE, whereas the best C_2H_4 FE was only ~10% in pristine HKUST-1, yielding a range of products. The experiment were reproducible with small data deviation, indicating the reliability.

To produce another MOF-based electrocatalyst, Zn-MOFs were deposited on carbon paper (CP), yielding Zn-MOF/CP electrodes by an electrophoretic deposition (EPD) method. These electrodes were used to convert CO_2 to CH_4 using ionic liquid (IL) electrolytes.⁴¹¹ Fluorine-containing, imidazolium-based ILs can not only absorb and activate CO_2 molecules but also promote the transformation of CO_2 to a $\text{CO}_2^{\cdot-}$ intermediate. The highest electrochemical activity ($80.1 \pm 6.6\%$ of CH_4 FE) was obtained with a current density of $3.1 \pm 0.5 \text{ mA cm}^{-2}$ at an applied potential of -2.2 V vs. Ag/Ag^+ over 2 h based

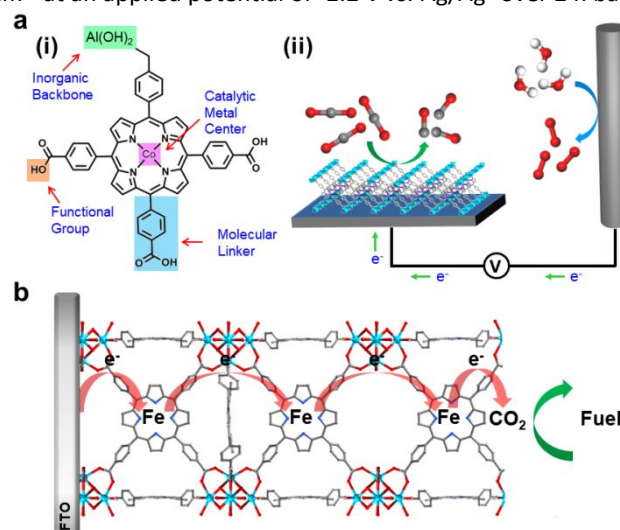


Fig. 25 (a) $\text{Al}_2(\text{OH})_2\text{TCPP-Co}$ serves as an electrocatalytic CO_2 reduction catalyst (i: molecular-level view of $\text{Al}_2(\text{OH})_2\text{TCPP-Co}$ catalyst highlighting the modular nature of the metal centers, organic linkers, and additional functional groups; ii: The MOF is integrated with a conductive substrate yielding the functional CO_2 electrochemical reduction system. (b) CO_2 photoreduction in Fe-porphyrin-based MOF-525/FTO thin films. In the system, the functionalized Fe-porphyrins act as catalytically competent, redox-conductive linkers. Color code: C, gray; O, red; N, blue; and Al/Zr, cyan. H atoms are omitted for clarity.

on the combination of Zn-MOF/CP cathode and the IL (BmimBF_4). Four zinc-based ZIFs, including ZIF-7, ZIF-8, ZIF-108,

and SIM-1 were studied for CO₂RR activity in an aqueous electrolyte.⁴¹² In a CO₂-saturated 0.25 M K₂SO₄ solution (pH = 4.2), the best CO faradaic efficiency was 81.0% at -1.1 V vs. RHE over ZIF-8, and ZIF-108 manifested the highest CO current density (12.8 mA cm⁻² at -1.3 V vs. RHE). Imidazolate ligands coordinated with the Zn(II) center was proved to be the active sites in ZIFs for CO₂RR by *in situ* X-ray absorption near edge structure (XANES) spectra and DFT calculations.

Incorporating redox-active organic linkers into MOFs can also yield materials with enhanced catalytic CO₂RR performance.⁴¹³⁻⁴¹⁶ A thin film MOF electrode was made by depositing alumina (5 nm thickness) onto conductive carbon disk electrodes using atomic-layer deposition (ALD) and subsequently converting the alumina films to Al-TCPP-Co (Fig. 25a).⁴¹³ A CO selectivity over 76% was achieved by the resultant electrode with a per-site TON of 1400 and extremely small deviations were found upon repetitions of the experiment. The catalyst remained stable for up to 7 h. *In situ* spectroelectrochemical measurements demonstrated that the porphyrinic Co(II) were reduced to Co(I) during electrocatalysis. Liquid-phase epitaxy has also been demonstrated to be a valid approach for fabricating homogeneous and highly orientated MOF thin films of controllable thicknesses. For example, highly oriented surface grafted MOF (SURMOF) thin films were grown on fluorine doped tin oxide (FTO) glass electrodes using a liquid-phase epitaxy process.⁴¹⁴ The Re(CO)₃(bpydc)Cl linkers in the SURMOF electrocatalytically reduced CO₂ to CO with a FE up to 93 ± 5% at a -1.6 V vs. NHE potential, far exceeding that of the homogeneous Re(CO)₃(bpydc)Cl catalyst. Using a post-synthetically metalated Fe-porphyrin-based MOF-525 thin film electrode on FTO glass, CO₂ was reduced to CO (Fig. 25b).⁴¹⁵ Controlled potential electrolysis (CPE) experiments (at -1.3 V vs. NHE) showed that the current density increased to 5.9 mA cm⁻² and the FEs of CO and H₂ were 41 ± 8 and 60 ± 4 %, respectively, after ~4 h of electrolysis, which implied that the total faradaic efficiency (CO + H₂) of this catalytic system was ~100%.

All of the abovementioned cases demonstrate that MOFs are a superb platform to immobilize redox-active moieties, yielding heterogeneous catalysts for effective and selective CO₂RR. However, due to the poor electrical conductivities of most MOFs, at this stage, working electrodes for CO₂RR must be fabricated by the deposition of MOF nanocrystals on various conductive substrates such as CP, FTO glass, gas diffusion electrodes, etc.⁴⁰⁵⁻⁴¹⁹

3.4.2. Carbon materials derived from MOFs for electrocatalytic CO₂ reduction

MOFs can also be used to form carbon-based MOF derivatives for CO₂RR. These compounds usually possess excellent stabilities and high electrical conductivities, making them powerful electrocatalysts. Moreover, the well-dispersed active sites are confined in the resultant carbon matrix. This can dramatically improve the catalytic activities and selectivities of the associated reactions. Additionally, the resultant porous structures provide a means of CO₂ enrichment, greatly affecting CO₂ chemical transformations by increasing local concentrations.

As an example, the CO₂ electrochemical conversion capabilities of oxide-derived Cu/carbons (OD Cu/C) fabricated by carbonization of HKUST-1 were evaluated.⁴²⁰ The highest methanol yield was obtained using the catalyst OD Cu/C-1000, which produced 12.4 mg L⁻¹ h⁻¹ at -0.3 V vs. RHE. Additionally, and the maximum ethanol production rate (13.4 mg L⁻¹ h⁻¹) was observed at -0.7 V vs. RHE. This was attributed to synergistic effects between the highly dispersed Cu and porous carbon matrix. Recently, ZIF-8 was also utilized as a precursor in the preparation of nitrogen-doped porous carbons.⁴²¹ The resultant materials exhibited excellent electrocatalytic CO₂ to CO reduction with a CO FE of ~78% at -0.93 V vs. RHE on

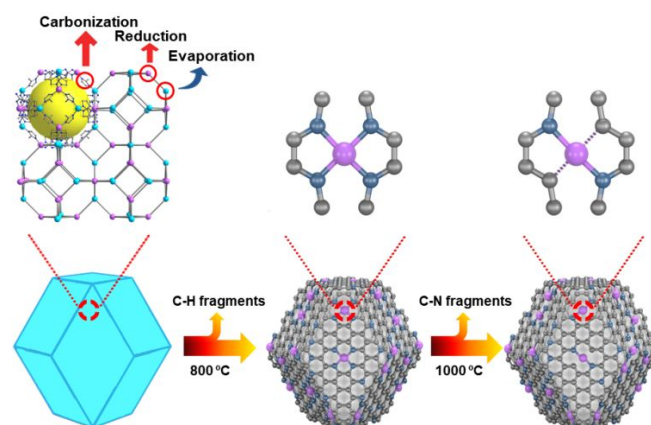


Fig. 26 The formation of Co-N₄ (upper middle) and Co-N₂ (upper right) via pyrolysis of bimetallic Co/Zn zeolitic imidazolate frameworks (upper left and bottom left) at 800°C and 1000 °C, respectively. Color code: C, gray; N, gray-blue; Zn, cyan; and Co, purple. Adapted from ref. 422 with permission from Wiley-VCH, copyright 2018.

account of the presence of abundant pyridinic-N and quaternary-N species. Both the pyridinic-N and quaternary-N species in the carbon matrix can promote the transfer of proton-electron pairs to CO₂, lowering the energy barrier for the production of the intermediate (COOH*) for CO formation. A series of nitrogen-doped carbons containing atomically dispersed Co sites was synthesized by annealing bimetallic Co/Zn ZIFs at different temperatures (Fig. 26).⁴²² Interestingly, the N coordination number of Co sites could be controlled by varying the temperature at which the pyrolysis was performed. The catalyst containing Co-N₂ active sites was more capable of activating CO₂, leading to the generation of the CO₂* intermediate. Therefore, this catalyst exhibited the highest electrocatalytic performance with a CO FE and current density of 94% and 18.1 mA cm⁻², respectively, at an overpotential of 520 mV, among the investigated samples. Notably, the CO TOF over this Co catalyst with the lowest N coordination number was up to 182000 h⁻¹, outperforming most reported metal-based catalysts under comparable conditions. Two atomically dispersed Fe and Co catalysts (Fe-N-C and Co-N-C), were synthesized using bimetallic Fe/Zn and Co/Zn ZIFs, separately, as precursors.⁴²³ In comparison to the optimized catalytic activity of Co-C-N (CO FE of 45% at an overpotential of 0.48 V), Fe-N-C displayed a higher CO FE of >93% with a current density of -2.8 mA cm⁻² at a low overpotential of 0.47 V. The first principle calculations indicated that the edge-hosted M-N₂₊₂-C₈

moieties bridged by two adjacent armchair-like graphitic layers were more active than the bulk-hosted M-N₄-C₁₀ moieties embedded in the graphitic layers with respect to CO₂RR. Particularly, CO₂RR is more favorable than hydrogen evolution on the Fe-N₂₊₂-C₈ sites of the Fe-N-C catalyst, leading to the reported remarkable CO FE.

In contrast to the direct thermal decomposition of MOFs, a ZIF-assisted strategy was employed to synthesize Ni single atoms distributed in a nitrogen-doped porous carbon (Ni SAs/N-C) matrix. This was accomplished by exchanging ions between the Zn SBUs and the adsorbed Ni salts in the pores of ZIF-8.⁴²⁴ Compared with Ni NPs and Ni foam, the obtained Ni SAs/N-C catalyst was able to selectively reduce CO₂ with an excellent current density and CO FE of 10.48 mA cm⁻² and 71.9%, respectively, at an overpotential of 0.89 V, indicative of the superiority of single atom catalysts for CO₂RR. Furthermore, no obvious decline of CO FE and current density was observed during 60 h of CO₂ electroreduction at a potential of -1.0 V vs. RHE, demonstrating the high electrocatalytic stability of this single-atom catalyst. The surface of ZIF-8 was functionalized by taking advantage of the coordination interactions between Zn nodes and ammonium ferric citrate (AFC).⁴²⁵ Upon pyrolysis, isolated iron-nitrogen (Fe-N) sites were formed on the surface of the resulting carbon matrix. These highly exposed Fe-N sites endowed the resultant catalyst (C-AFC@ZIF-8) with an optimal faradaic efficiency for CO production of 93.0% at an overpotential of -0.43 V.

In order to further improve the electrocatalytic performance of carbon materials derived from MOFs for CO₂RR, a hybrid material, composed of ZIFs and multi-walled carbon nanotubes (MWCNTs) loaded with furfuryl alcohol (FA) was used as a precursor, to fabricate a pyrolyzed ZIFs supported on carbon nanotube networks.⁴²⁶ The MWCNT support was capable of enhancing the CO₂ mass transport and electron transport in the resultant hybrid catalyst, resulting in a fantastic CO faradaic efficiency (~100%) and a high current density of 7.7 mA cm⁻² at a low overpotential of 740 mV. When the hybrid catalyst was doped with Fe, the overpotential was as low as 440 mV with a desirable CO FE and current density of 97% and 2 mA cm⁻², respectively. Given the decent electrocatalytic activities of transition-metal phosphides, MoP NPs supported on In-doped porous carbon (In-PC) were made using MIL-68(In) as a carbon precursor.⁴²⁷ The hybrid structure, strong interactions, and cooperative effects between the nano-MoP (4 nm) and In-PC support of the resultant catalyst (MoP@In-PC) ensured more active sites and space for efficient CO₂ adsorption and electrolyte diffusion to the electrode. Additionally, these features allowed for faster electron transfer to the adsorbed CO₂ to form CO₂^{-•} intermediates than which in the bulk MoP. Accordingly, MoP@In-PC exhibited excellent catalytic performance for CO₂RR to formic acid with an outstanding faradaic efficiency and current density of 96.5% and 43.8 mA cm⁻², respectively, by choosing ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate as the electrolyte.

4. The relationship between CO₂ capture capacity of MOF-based materials and their catalytic performance for CO₂ conversion

After over two decades of investigation, MOFs that outperform other porous materials with respect to CO₂ adsorption capacity have been developed. Additionally, catalytic CO₂ conversion in MOF-based materials has also been well studied. In this context, an understanding of how the CO₂ capture capabilities of MOF-based materials affect their catalytic conversion efficiencies is paramount. Such an understanding will guide the development of efficient catalysts for CO₂ conversion.

The relationship between the CO₂ capacity of a given MOF-based material and its catalytic CO₂ conversion efficiency is clear. This relationship is governed by the following phenomena: 1) MOF-based materials can increase the local CO₂ concentration around materials' catalytically active sites by CO₂ adsorption. In this context, MOF pores serve as "microreactors", providing favorable environments for reactions between CO₂ and substrates. This has led to the observation of high reaction yields and selectivities in MOF-based materials; 2) Some functional groups in MOFs enhance their CO₂ uptake and activate CO₂ molecules and/or other reactants, further improving MOFs' catalytic efficiencies;⁴²⁸ 3) The high CO₂ adsorption selectivities of MOF-based materials can guarantee high catalytic performance even in mixed-gas environments with low CO₂ concentrations.^{109, 286, 313, 367, 369, 374}

To demonstrate the culmination of these phenomena, we will present a couple of examples. One is found in a UiO-67-Ru^{II} composite (UiO-67/RuCO). This material was prepared by

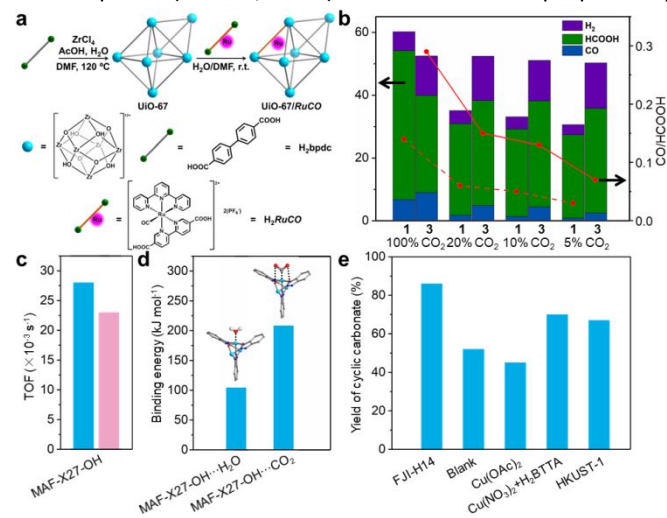


Fig. 27 (a) Synthesis of UiO-67 from ZrCl₄ and H₂bpdc, and UiO-67/RuCO by post-synthetic exchange of H₂RuCO with H₂bpdc. Both UiO-67 and UiO-67/RuCO are composed of Zr clusters (cyan balls) and organic linkers (gray and/or orange lines). (b) Photochemical reduction of CO₂ with Ru^{II}-CO complex and UiO-67/RuCO: left y-axis, catalytic activity (bar graph); right y-axis, product selectivity (line graph). (c) Comparison of the TOF values for the photocatalytic reduction of CO₂ to CO under 1.0 atm (blue) and 0.1 atm (pink); (d) Comparison of the CO₂ and H₂O binding structures and energies of reduced MAF-X27-OH. Color code: C, gray; O, red; N, blue; Co, cyan; and H, white. (e) Catalytic conversion of CO₂ cycloaddition with styrene oxide over different catalysts.¹⁰⁹

incorporating a photoactive Ru^{II}-CO complex ([Ru^{II}(bpy)(terpy)(CO)](PF₆)₂) into UiO-67 using a facile PSE method (Fig. 27a).³⁶⁹ Although the total TON produced by the homogeneous Ru^{II}-CO complex catalyst was slightly higher than that of the composite, the photocatalytic activity of the molecular catalyst was drastically reduced as the partial pressure of CO₂ decreased (Fig. 27b). This indicated that catalysis was heavily dependent on the concentration of CO₂ in the reaction mixture. In stark contrast, UiO-67/RuCO displayed almost the same catalytic performance even under a 5 % CO₂ atmosphere. This surpassed both the homogeneous catalyst and a physical mixture of UiO-67 and the Ru^{II}-CO complex, and the results demonstrated that the UiO-67/RuCO composite could enrich gas mixtures containing CO₂ and take advantage of synergy between the adsorptive sites and the catalysts' active sites. Similarly, the catalytic performance of an IL-MOF composite (polyILs@MIL-101) for cycloaddition of CO₂ with ECH was maintained in a wide CO₂ pressure range from 0.5-1.5 bar, whereas the catalytic activity of the pure IL significantly declined once the CO₂ pressure was reduced to 0.5 bar.³¹³ More recently, three isostructural MOFs (MAF-X27-Cl, MAF-X27-OH and MOF-74-Co) were used for photocatalytic CO₂ reduction.³⁶⁷ Interestingly, when the CO₂ partial pressure was reduced to 0.1 atm, only MAF-X27-OH exhibited a high CO TOF of $23 \times 10^{-3} \text{ s}^{-1}$ with an unaltered CO selectivity (97.2%) compared to the TOF at 1 atm CO₂ ($28 \times 10^{-3} \text{ s}^{-1}$) (Fig. 27c). Periodic density functional theory (PDFT) simulations revealed that the μ -OH coordinated on the open Co sites of MAF-X27-OH stabilized the Co-CO₂ adduct by strong hydrogen bonding and promoted CO₂ reduction. Furthermore, it was observed that MAF-X27-OH bound CO₂ more strongly than H₂O (Fig. 27d). This suppressed H₂ (the byproduct) production and ensured high CO selectivity. A similar phenomenon was observed in monolayers of a Ni metal-organic framework (Ni MOLs).³⁷⁴ In simulated flue-gas (10% CO₂), the photocatalytic activity and selectivity of Ni MOLs was nearly equivalent to those obtained in pure CO₂ due to the stronger adsorption energy of CO₂ (-200.11 kJ mol⁻¹) on Ni MOLs than H₂O (-62.47 kJ mol⁻¹). As a final example, a Cu(II)-MOF with high density of LASs and LBSs exhibited remarkable CO₂ volumetric uptake (171 cm³ cm⁻³ at 298 K and 1 atm) and excellent CO₂/N₂ selectivity (51 for the 15/85 v/v mixture at 1 atm) due to the cooperation of multiple active sites.¹⁰⁹ The MOF, FJI-H14, was then employed to catalyze CO₂ cycloaddition reactions using 1 atm simulated post-combustion flue gas (CO₂:N₂ = 15:85) as a feedstock. The material exhibited a desirable product yield (86%), outperforming the copper salt (Cu(OAc)₂), the physical mixture of the copper salt (Cu(NO₃)₂) and the H₂BTTa linker, as well as a typical Cu(II)-based MOF (HKUST-1) (Fig. 27e), again providing evidence for the synergistic effects between LASs and LBSs.

5. Conclusions and perspectives

The development of MOF-based materials has opened a door leading to a new set of promising adsorbents and catalysts for CO₂ capture and conversion. Keys to the successful

implementation of MOFs as CO₂ adsorbents lie in their chemical tunabilities that improve interactions with the gaseous molecule and even other substrates. These interactions are mostly between CO₂ and open metal sites, Lewis basic sites, polar functional groups, and/or micropores. Exploration of these interactions has precipitated magnificent adsorption capacities and selective CO₂ capture in the presence of N₂, CH₄, and H₂O, among other gases. Furthermore, given the challenges involved with the introduction of certain functional groups into MOFs by *de novo* syntheses, various post-synthetic strategies, such as post-synthetic modification and the construction of MOF composites, have been developed. Large-scale application of MOFs to CO₂ capture remains subject to research to address further improvements of selectivity in the presence of water or acidic gases. It is incumbent upon researchers to choose the appropriate MOFs for the desired performance.

Many classes of reactions for CO₂ conversion have been explored over MOFs, mainly including CO₂ organic transformation, CO₂ hydrogenation, photocatalytic CO₂ reduction, and electrocatalytic CO₂ reduction. Beyond that, MOFs can be combined with other materials or used as precursors to synthesize MOF composites and MOF derivatives, respectively. Generally, the catalytic efficiencies of MOF-based materials are favorable. This can be attributed to the following factors: (a) The relatively high surface areas and porous structures stabilize the catalytically active moieties and prevent deactivation while guaranteeing mass transfer and electron migration; (b) The synergetic effects from multiple functionalities can activate CO₂ and/or substrate molecules, facilitating CO₂ conversion; (c) Based on their specific compositions, MOF composites and derivatives exhibit enhanced electrical conductivities, visible-light absorbance, and/or stabilities further expanding potential applications of catalysts.

These MOF-based materials would not be efficient catalysts, however, if it were not for their high CO₂ capture capacities. Thus, the relationship between the CO₂ capture capacity of MOF-based materials and their catalytic CO₂ conversion performance is critical. In this review, we have highlighted this importance in three manners: (a) In contrast to homogeneous catalysts, the local CO₂ concentration at catalytically active sites can be vastly increased by the CO₂ capture capabilities of MOF-based materials, boosting reaction yields and selectivities; (b) Certain functional groups in MOFs not only improve the CO₂ uptake capacities but also activate CO₂ molecules and/or other reactants, further enhancing the catalytic efficiencies of MOF-based materials; (c) The high CO₂ adsorption selectivities of MOF-based materials can endow them with high catalytic activities and selectivities even in mixed gas environments with low CO₂ concentrations or partial pressures. Therefore, in the future, the synthesis of MOF-based materials with outstanding CO₂ uptake capacities and selectivities must be tied in with the development of catalytic CO₂ conversion.

Although dramatic advances have been made in the last ten years, this field is still in its infancy. This is especially true in

regards to CO₂ hydrogenation, photocatalytic CO₂ reduction, and electrocatalytic CO₂ reduction. Many open issues remain that should be addressed as MOF-based CO₂ conversion catalysts undergo further development. First, a plethora of reported catalytic CO₂ conversion reactions are carried out under harsh conditions. For example, some organic transformations and CO₂ photoreduction reactions are performed in alkaline environments,³ and CO₂ hydrogenation is mainly carried out at high temperatures. Fortunately, great progress on this topic has been achieved in recent years. Also, as we have demonstrated, most MOF-based catalytic systems still require the presence of co-catalysts or electron sacrificial agents. Although these compounds significantly boost the performance of MOF-based catalysts, they can also serve to pollute the environment or consume/sacrifice active sites, making the materials less efficient. Therefore, it is important that future studies focus on integrating these active species into the frameworks or mitigating the need for additional reagents whatsoever. Unfortunately, the catalytic efficiencies of many MOF-based materials featuring mainly micropores are restricted by mass transfer. To address this issue, 2D MOFs and hierarchically porous MOFs might be worthy of further investigation. As for the stability of materials, cycling performance tests might not be sufficient to prove that the catalysts are permanently stable. As the field moves toward the industrial application phase, the reproducibility of reported catalytic activities and long-term stability of MOF-based catalysts should be evaluated more thoroughly. Finally, while MOFs with well-defined structures are beneficial when it comes to mechanistic understanding, advanced characterization and multi-dimensional in-operando reactions are still important. Therefore, in order to understand the reaction mechanisms involved with CO₂ conversion in MOF-based catalysts and further push to practical application in the future, it is likely that this ongoing research will require collaboration between scientists from different disciplines including theoretical, synthetic, and physical chemistry, chemical engineering, and physics.

MOF-based materials are already showing great promise as the next-generation of CO₂ capture and conversion systems. That is evidenced not only by the examples we detailed in this review, but also in the speed with which the field is advancing. We foresee additional rapid growth as there are numerous opportunities to design, synthesize, characterize, and utilize MOF-based materials for this set of critical applications.

List of acronyms and abbreviations

abtc: (E)-5,5'-(diazene-1,2-diyl)diisophthalate
 ad: adenine
 atz: (1H-1,2,4-triazol-3-yl)amide
 AzDC: 4,4'-azobenzenedicarboxylate
 bbta: 1H,5H-benzo-(1,2-d:4,5-d')bistriazole
 BDC: 1,4-benzenedicarboxylate
 BDC-allyl: 2-allylterephthalate
 BDPO: 5,5'-((1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(4-hydroxyisophthalate)

bIM: benzimidazole
 BPDC: biphenyl-1,4-dicarboxylate
 4,4'-BPE: *trans*-bis(4-pyridyl)ethylene
 BPT: biphenyl-3,4',5-tricarboxylate
 bpta: 3,6-di(4-pyridyl)-1,2,4,5-tetrazine
 bpy: 2,2'-bipyridine
 4,4'-bpy: 4,4'-bipyridine
 bpydc: (2,2'-bipyridine)-5,5'-dicarboxylate
 BPZNO₂: 5-nitro-[4,4'-bipyrazole]-1,1'-diide
 BTB: 1,3,5-benzenetribenzoate
 btc: benzene-1,3,5-tricarboxylate
 btei: 4,4',4''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzoate
 btm: bis(5-methyl-1H-1,2,4-triazol-3-yl)methane
 1,2,4,5-BTMS: 1,2,4,5-benzenetetramethanesulfonate
 btpc: 3,3',5,5'-biphenyltetracarboxylate
 BTT: 1,3,5-benzenetristetrazolate
 BTTA: 2,5-di(1H-1,2,4-triazol-1-yl)terephthalate
 catbdc: 2,3-dihydroxyterephthalate
 γ-CD: γ-cyclodextrin
 CEB: 4-(2-carboxylatoethyl)benzoate
 CVB: (E)-4-(2-carboxylatovinyl)benzoate
 dabco: 1,4-diazabicyclo[2.2.2]octane
 dcbpy: 2,2'-bipyridine-4,4'-dicarboxylate
 DCDPS: 4,4'-dicarboxydiphenyl sulfone
 dhbdc: 2,5-dihydroxybenzene-1,4-dicarboxylate
 DH₃PhDC: 3,3''-dihydroxy-2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate
 dobdc: 2,5-dihydroxyterephthalate
 dobpdc: 4,4'-dioxido-3,3'-biphenyldicarboxylate
 dondc: 1,5-dioxido-2,6-naphthalenedicarboxylate
 dotpdc: 4,4''-dioxido-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate
 dpe: 1,2-di(4-pyridyl)ethylene
 dpt24: 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazolate
 dtp: 2,3-di-1H-tetrazol-5-ylpyrazine
 EDS: 1,2-ethanedisulfonate
 FMA: fumarate
 H₄cit: citric acid
 H₆CPB: 1',2',3',4',5',6'-hexakis(4-carboxyphenyl)benzene
 H₁₀TBCPPP: tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine
 Im-BDC: 2-(1H-imidazol-1-yl)terephthalate
 L1: 3,3'-(perfluoropropane-2,2-diyl)dibenzoate
 L2: 5-carbamoyl-4-(iminooxidomethyl)-2-methylimidazol-1-ide
 L3: 2,5-bis(2-methoxyethoxy)isophthalate
 L4: 2-(2-methoxyethoxy)isophthalate
 L-Pro: L-proline
 L-Ru: bis(2,2'-bipyridine)[5,5'-di(4-carboxyl-phenyl)-2,2'-bipyridine]ruthenium(II) dichloride
 mdpt24: 3-(3-methyl-2-pyridyl)-5-(4-pyridyl)-1,2,4-triazolate
 MeIm: 2-methylimidazole
 nbIm: 5-nitro benzimidazole
 NDC: 2,6-naphthalenedicarboxylate
 1,4-ndc: naphthalene-1,4-dicarboxylate
 NH₂-BDC: 2-amino-1,4-benzene dicarboxylate
 NH₂-BPY: NH₂-bipyridine
 nIm: 2-nitroimidazole

- ntei: 4,4',4''-(nitriлотris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))tribenzoate
- OBB: 4,4'-oxybis(benzoate)
- pbdc: 5-phosphonatoisophthalate
- PHIM: benzimidazole
- ppy: 2-phenylpyridine
- ptei: 4,4'-(5'-(4-((4-carboxylatophenyl)ethynyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(ethyne-2,1-diyl)dibenzoate
- 4Pyc: 4-pyridylcarboxylate
- rctt*-tpcb: *region-cis, trans, trans*-tetrakis(4-pyridyl)cyclobutane
- Sbpd: dibenzo[*b,d*]thiophene-3,7-dicarboxylate 5,5-dioxide (S,S)-methox: bis((S)-methionine)oxalyl diamide
- tactmb: 1,4,7,10-tetrazacyclododecane-N,N',N'',N'''-tetra-*p*-methylbenzoate
- TBAPy: 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoate
- ^{tBu}NP: 2,6-bis((di-tert-butylphosphino)methyl)pyridine
- TCDC: 2,3,5,6-tetrachloroterephthalate
- TCPBDA: 4,4',4'',4'''-([1,1'-biphenyl]-4,4'-diylbis(azanetriyl))tetrabenzoate
- TCPE: 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrabenzoate
- TCPP: tetrakis(4-carboxyphenyl)porphyrin
- TCPP-Co: tetrakis(4-carboxyphenyl)porphyrin-Co
- TDPAT: 5,5',5''-((1,3,5-triazine-2,4,6-triyl)tris(azanediy))trisiophthalate
- terpy: 2,2':6',2''-terpyridine
- THPP-Co: 5,10,15,20-tetrakis(3,4,5-trihydroxyphenyl)porphyrin-Co
- THPP-Fe: 5,10,15,20-tetrakis(3,4,5-trihydroxyphenyl)porphyrin-Fe
- TMPyP: *meso*-tetra(N-methyl-4-pyridyl) porphine tetratosylate
- tpt: 2,4,6-tri(4-pyridyl)-1,3,5-triazine
- Tz: 3,5-bis(trifluoromethyl)-1,2,4-triazolate
- Tz-Bz: 4-(1H-1,2,4-triazol-1-yl)benzoic acid
- Al-TCPP-Co: [Al₂(OH)₂TCPP-Co]
- BIF-20: Zn₂(BH(MeIm)₃)₂(OBB)
- BiO-MOF-1: (Zn₈(ad)₄(BPDC)₆O·2Me₂NH₂)
- bio-MOF-11: Co₂(ad)₂(CO₂CH₃)₂·2DMF·0.5H₂O
- CAU-1: Al₄(OH)₂(OCH₃)₄(NH₂-BDC)₃
- CD-MOF-2: [(C₄₈H₈₀O₄₀)(RbOH)₂]
- CPF: Zn(HBTT)
- CPM-5: [(CH₃)₂NH₂][In₃O(BTC)₂(H₂O)₃]₂-[In₃(BTC)₄]-7DMF·23H₂O
- CPM-33a: Ni₃OH(bdc)₃tpt
- CPM-33b: Ni₃OH(dhbdc)₃tpt
- CPM-33c: Ni₃OH(NH₂-BDC)₃tpt
- CPM-33d: Ni₃OH(1,4-ndc)₃tpt
- Cu-TDPAT: [Cu₃(TDPAT)(H₂O)₃]-10H₂O·5DMA
- ELM-11: [Cu(4,4'-bpy)₂(BF₄)₂]
- Fe-BTT: Fe₃[(Fe₄Cl)₃(BTT)₈]₂
- FJI-H14: [Cu(BTTA)]_n
- FMOF-1: {Ag₂[Ag₄Tz₆]}
- Hf-NU-1000: [Hf₆(μ₃-O)₄(μ₃-OH)₄]₂(TBAPy)₆
- Hf₁₂-Ru: Hf₁₂(μ₃-O)₈(μ₃-OH)₈(μ₂-OH)₆(TFA)₆(L-Ru)₆
- HKUST-1: [Cu₃(btc)₂(H₂O)₃]
- IFMC-1: [Zn(HL)] (H₃L = 4,5-di(1H-tetrazol-5-yl)-2H-1,2,3-triazole)
- IISERP-MOF4: (Mg(Tz-Bz)(CH₃COO))
- Im-UiO-66: [Zr₆O₄(OH)₄(Im-BDC)₆]
- Ir-CP: Y[Ir(ppy)₂(dcbpy)]₂[OH]
- IRMOF-3: [Zn₄O(NH₂-BDC)₃]
- IRMOF-74-III: [Mg₂((DH₃PhDC))]
- JUC-1000: [Cu₂₄(BDPO)₁₂(H₂O)₁₂]-30DMF·14H₂O
- LIFM-26: Fe₃(TCDC)₃(H₂O)₃
- LIFM-28: [(Zr₆(μ₃-O)₈(H₂O)₈(L¹)₄] (L¹ = 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarboxylate)
- MAF-23: [Zn₂(btm)₂]
- MAF-25: [Co(dpt24)₂]
- MAF-26: [Co(mdpt24)₂]
- MAF-66: [Zn(atz)₂]
- MAF-X27-Cl: [Co₂(μ-Cl)₂(bbta)]
- MAF-X27-OH: [Co₂(μ-OH)₂(bbta)]
- MIL-68(In): In(OH)(BDC)
- MIL-100(Fe): Fe₃O(H₂O)₂F·{C₆H₃(CO₂)₃}₂·nH₂O (n ≈ 14.5)
- MIL-101: Cr₃F(H₂O)₂O(BDC)₃·nH₂O (n ≈ 25)
- MIL-101(Fe): Fe₃F(H₂O)₂O(BDC)₃
- MIL-102: Cr^{III}₆O₂(H₂O)₄F₂{C₁₀H₄(CO₂)₄}₃
- MMCF-2: [Cu₂(Cu-tactmb)(H₂O)₃(NO₃)₂]
- M-MOF-74: [M₂(dobdc)(H₂O)₂] (M = M = Mg²⁺, Ni²⁺, Co²⁺, Zn²⁺)
- MOF-5: [Zn₄O(BDC)₃]
- MOF-74-Co: [Co₂(dobdc)]
- MOF-177: [Zn₄O(BTB)₂]
- MOF-253: [Al(OH)(bpydc)]
- MOF-505: [Cu₂(bptc)(H₂O)₂(DMF)₃(H₂O)]
- MOF-525: Zr₆O₄(OH)₈(TCPP)₂
- MOF-525-Co: Zr₆O₄(OH)₈(TCPP-Co)₂
- MOF-525(Fe): Zr₆O₄(OH)₈(TCPP-Fe)₂
- MOF-892: [Zr₆O₄(OH)₄(H₂CPB)_{1.5}(CH₃CO₂)₆]
- NH₂-MIL-53: [Al(OH)(NH₂-BDC)]_n
- NH₂-MIL-53(Fe): Fe(OH)(NH₂-BDC)
- NH₂-MIL-88B(Fe): Fe₃O(solvent)₃Cl(NH₂-BDC)₃(solvent)_m
- NH₂-MIL-101(Fe): Fe₃F(H₂O)₂O(NH₂-BDC)₃
- NH₂-MIL-125: [Ti₈O₈(OH)₄(NH₂-BDC)₆]
- NH₂-UiO-66: [Zr₆O₄(OH)₄(NH₂-BDC)₆]
- Ni-4Pyc: Ni₉(m-H₂O)₄(H₂O)₂(C₆NH₄O₂)₁₈
- NOT-140: [Cu₄L(H₂O)₄]-10DMF·C₄H₈O₂·8H₂O (L = 4',4''',4''''',4''''''-methanetetrayltetrakis([1,1'-biphenyl]-4-carboxylate))
- NOTT-202: (Me₂NH₂)_{1.75}[In(L)]_{1.75}(DMF)₁₂(H₂O)₁₀ (H₄L = biphenyl-3,3',5,5'-tetra-(phenyl-4-carboxylic acid))
- NU-1000: [Zr₆(μ₃-O)₄(μ₃-OH)₄]₂(TBAPy)₆
- PCN-61: Cu₃(H₂O)₃(btei)
- PCN-66: Cu₃(H₂O)₃(ntei)
- PCN-68: Cu₃(H₂O)₃(ptei)
- PCN-123: [Zn₄O(L)₃] (L = 2-(phenyldiazanyl)terephthalate)
- PCN-222: Zr₆(μ₃-OH)₈(OH)₈(TCPP)₂
- PCN-900(Eu): [(CH₃)₂NH₂]₂[Eu₆(μ₃-OH)₈(TCPP)_{1.5}-(DCDPS)₃](solvent)_x
- PCN-900(Eu)-BPYDC: [(CH₃)₂NH₂]₂[Eu₆(μ₃-OH)₈](TCPP)_{1.5}(BPYDC)₃
- PCN-900(Eu)-CoTCPP: [(CH₃)₂NH₂]₂[Eu₆(μ₃-OH)₈](CoTCPP)_{1.5}(DCDPS)₃
- PCN-900(Eu)-CoTCPP-CoBPYDC: [(CH₃)₂NH₂]₂[Eu₆(μ₃-OH)₈](CoTCPP)_{1.5}(CoBPYDC)₃

porph@MOM-11: [Cd₄(BPT)₄][Cd(TMPYP)]
 Re₃-MOF: Zr₆O₄(OH)₄[Re(CO)₃(bpydc)Cl]_{0.72}(BPDC)_{5.28}
 SHF-61: (Me₂NH₂)[In(NH₂-BDC)₂]
 SNU-5: {Cu₂(abtc)}₃
 SNU-30: {[Zn₂(TCPBDA)-(H₂O)₂]}₃·30DMF·6H₂O)_n
 SNU-31: {[Zn₂-(TCPBDA)(bpta)]}·23DMF·4H₂O)_n
 SNU-70: [Zn₄O-(CVB)₃]}₃·13DEF·2H₂O
 SNU-71: [Zn₄O-(CEB)₃]}₃·6DEF·H₂O
 SUMOF-2: [Zn₄O(BDC)₃]}₃·(ZnO)_{0.125}
 SUMOF-3: [Zn₄O(NDC)₃]}₃
 SUMOF-4: [Zn₄O(BDC)₂(BPDC)(H₂O)]
 TMOF-1: [Cu(4,4'-bpy)₂(EDS)]_n
 TMOF-3: [Cu(bpy)₂(1,2,4,5-BTMS)_{0.5}(H₂O)_{0.5}]_n
 UiO-66: [Zr₆O₄(OH)₄(BDC)₆]
 UiO-66-allyl: [Zr₆O₄(OH)₄(BDC-allyl)₆]
 UiO-67: [Zr₆O₄(OH)₄(BPDC)₆]
 UiO-bpy: Zr₆(μ₃-O)₄(μ₃-OH)₄(μ₁-OH)(H₂O)-(bpydc)₅(HCO₂)
 USTC-253: [Al(OH)(Sbpdcc)]
 UTSA-16: [K(H₂O)₂Co₃(cit)(Hcit)]
 ZIF-7: Zn(bIm)₂
 ZIF-8: Zn(MeIm)₂
 ZIF-9: Co(PhIm)₂
 ZIF-67: Co(MeIm)₂
 ZIF-78: Zn(nbIm)(nIm)
 ZIF-108: ZIF-8: Zn(nIm)₂
 ZJNU-40: [Cu₂L(H₂O)₂] (L = 5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)diisophthalate)
 ZJNU-43: [Cu₂L₁(H₂O)₂]}₃·3DMF·2EtOH·4H₂O (L₁ = 5,5'-(quinoline-5,8-diyl)-diisophthalate)
 ZJNU-44 ([Cu₂L₂(H₂O)₂]}₃·3DMF·3CH₃CN·3H₂O) (L₂ = 5,5'-(isoquinoline-5,8-diyl)-diisophthalate)
 ZJNU-45 ([Cu₂L₃(H₂O)₂]}₃·3DMF·3MeOH·3H₂O) (L₃ = 5,5'-(quinoxaline-5,8-diyl)-diisophthalate)
 ZnGlu: {[Zn(H₂O)(C₅H₇NO₄)]}·H₂O)_n
 ZnPC-2: {[Zn₃(pbdc)₂]}₂·H₃O)_n
 ZrPP-1-Co: [Zr₂(THPP-Co)]_n
 ZTF-1: [Zn(CN₅H₂)₂]

Conflicts of interest

There are no conflicts to declare.

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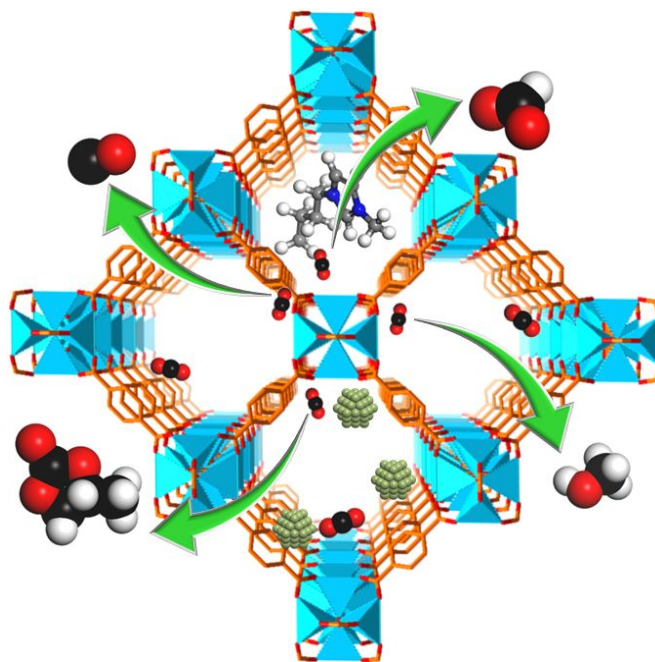
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Graphical Abstract



This review summarizes recent advances and highlights the structure-property relationship on metal-organic framework-based materials for carbon dioxide capture and conversion.