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Review

Carbon Capture Advancements in Metal-Organic Frameworks

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Abstract: Global growth and sustainability highly depend upon the output of industries, corporations, governments, and non-governmental organisations requiring comprehensive energy transition in the face of a worldwide crisis demanding carbon neutralisation. The carbon neutralisation challenges required for energy transition could be overcome by detailed surveying, recording and the analysis of the carbon dioxide emissions. It is crucial to study innovative materials like metal-organic frameworks for their transdisciplinary applications towards carbon capture to have a sustainable strategy to capture harmful emissions. In addition, the CO_2 solubility, adsorption and absorption capacity, and several reinforcing characteristics and factors for carbon dioxide capture using MOFs are discussed in detail. Further, for various multidisciplinary applications towards commercialisation, MOFs solubility, adsorption and absorption parameters were considered. Moreover, the essential organic qualities of MOFs and their organo-derivatives are considerably elaborated. Overall, to align with the current sustainable development goals, it is significant that carbon dioxide emissions must be reduced along with its capture in a scientific manner. Relevant projections for carbon capture through MOFs have been reviewed industrially and universally in alignment with the United Nations Sustainable Development Goals (UNSDGs).

Keywords: metal-organic frameworks; organic chemistry; carbon capture; sustainability; organo-conversions

1. Introduction

As observed and analysed through carbon capture materials, including amines, amino acids, ionic liquids or synthetic materials, there is still an imperative demand for an energy-efficient and sustainable carbon capture material towards neutralising emissions. Traditional solvent-based carbon capture methods require much energy to replenish the carbon-capturing material. In power generation applications, estimates place the energy penalty at up to 35% of the power station's output. Metal-organic frameworks (MOFs) collect carbon primarily through physical, not chemical, processes (Boycheva et al., 2022; Mittal et al., 2024; Pio et al., 2022; Ramasubramanian et al., 2022; Zhang et al., 2022). This "trapping" method requires less energy to replenish the MOFs, allowing for more energy-efficient carbon capture. By utilising MOF-based carbon capture, more generated power may be directed where intended, cutting customer energy prices and CAPEX for generators. However, it's important to note that MOFs have several limitations, which include production challenges and variable cost barriers. MOFs' repeated lattice structures, ultra-high surface areas, CO_2 selectivity, and low desorption energies make them potential contenders for more energy-efficient carbon capture. The process of carbon dioxide capture in metal-organic frameworks is demonstrated in Figure 1 (Geissler and Maravelias, 2022; Bhardwaj, Kumar, and Choudhury, 2022; C. Tan, Tao, and Xu,2022).

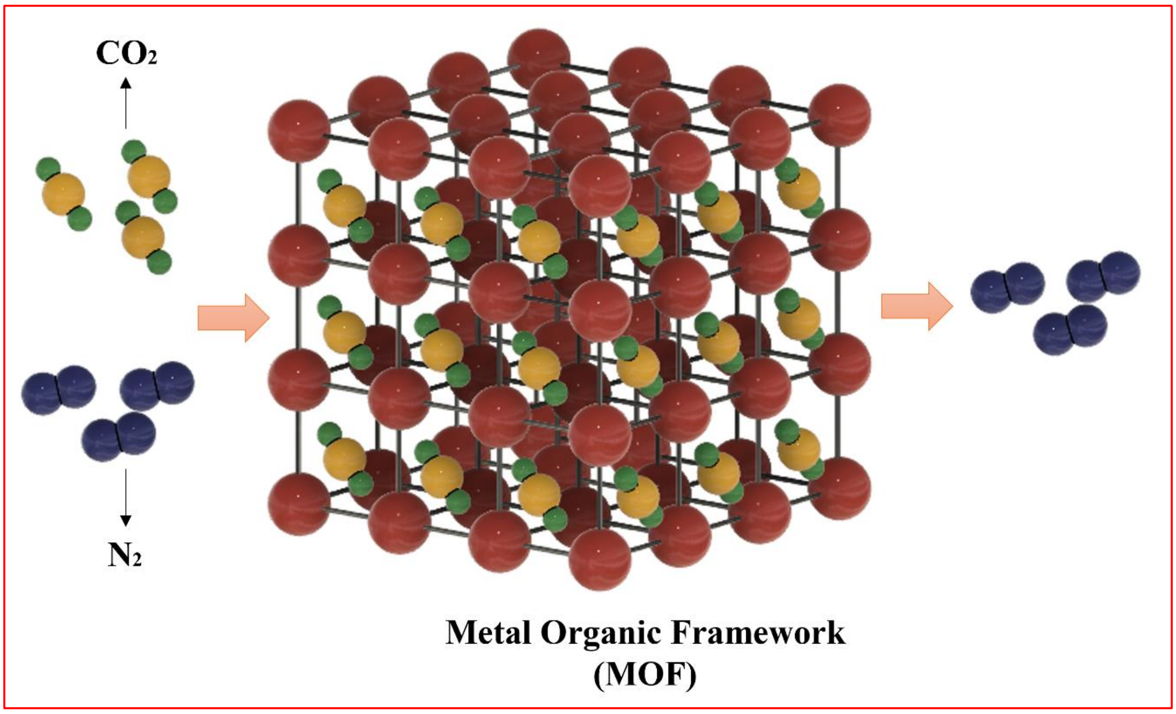

Figure 1. Carbon capture process through Metal-Organic Framework (MOFs) (L. Lu et al., 2015; Rahimi et al., 2022).

1.1. Role of MOFs in Carbon Capture

Metal-organic frameworks are novel materials with unique carbon capture properties (Theo et al., 2016). MOFs are comprised of metal ions or clusters that are connected by organic ligands. These materials possess very high porosity, resulting in a high surface area for gas adsorption. Research and development could alter MOFs' physical and chemical properties, resulting in novel metal-organic frameworks for carbon capture. MOFs also possess high adsorption capacity and are stable in thermal and chemical stability. Metal-organic frameworks also possess multidisciplinary applications besides carbon capture, which involve wastewater treatment and other sustainable novel approaches towards decarbonisation (Meng et al., 2014; Mittal & Kushwaha, 2024c; Moh et al., 2011; J. Sun et al., 2014).

Even though MOFs are being established as some novel material for carbon capture, there has been a lack of research and development specifically for MOFs. Figure 2 (Trinh et al., 2023) signifies the number of publications on carbon capture and carbon capture in MOFs to understand the lack of usage of these materials. Based on the number of patents and publications, we can indicate the amount of attention researchers and industrialists pay towards carbon capture and their respective materials (Mittal & Kushwaha, 2024a).

It is essential to know that carbon capture publications and patents are averaging more than 1400 per year, whereas when we see the research and development status of metal-organic frameworks, less than 5% of the overall research in the carbon capture sector is being done on them. This concludes that ionic liquids and MOFs pursuing such unique properties, as shown above, should also be given the most attention in the research and development sector.

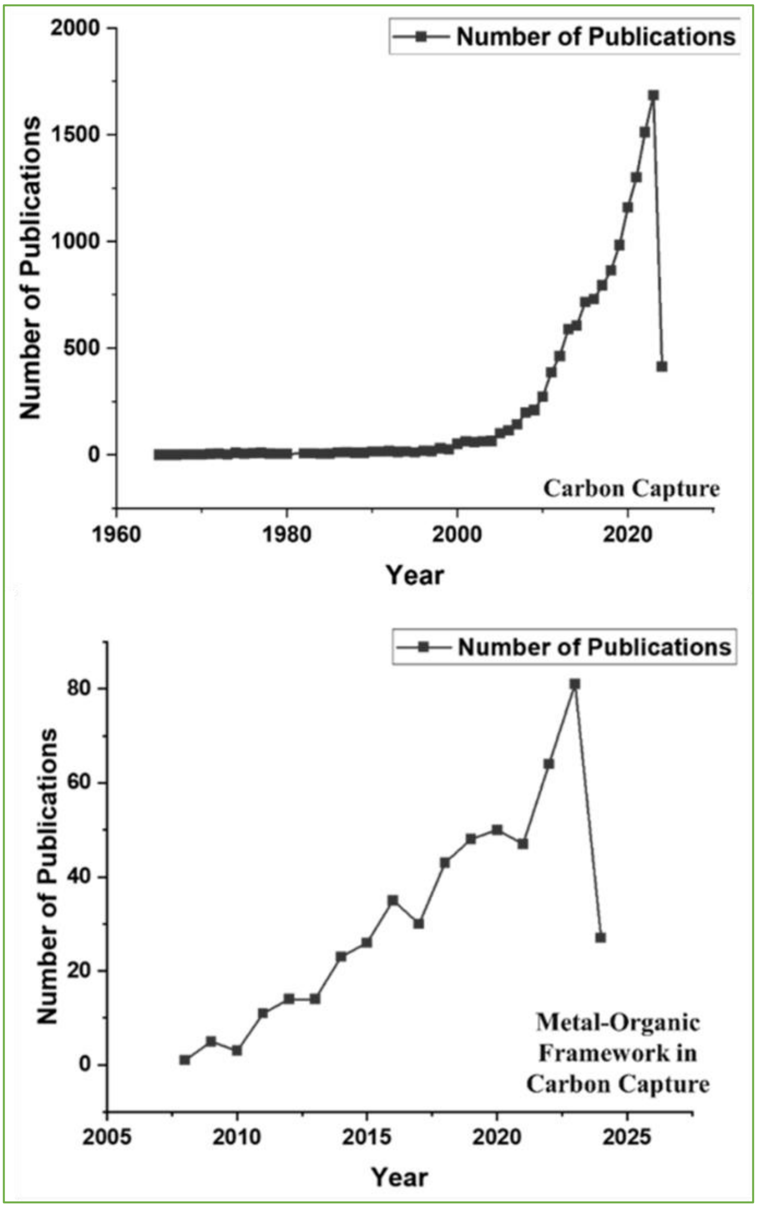

Figure 2. Number of Publications done in carbon capture and carbon capture in metal-organic frameworks (Trinh et al., 2023).

1.2. Pros and Cons of MOFs in Carbon Capture

MOFs have always been the core of futuristic research resulting in the focus of academic research rather than having genuine economic potential. However, because of proprietary reactor designs, continuous synthesis processes, and over a decade of manufacturing experience, several researchers have been currently leading the push for MOFs to be built into carbon capture and other gas separation applications. For the synthesis of metal-organic frameworks, there are usually two classes in which they can be distinguished; these distinctions could be classified as conventional and modern synthesis methods. Traditional Methods for synthesising MOFs include solvothermal, electrochemical and sol-gel methods. These methods are advantageous regarding significant structures, crystal sizes, and good yields but also have disadvantages, such as high energy and costs (Mittal & Kushwaha, 2024b). On the other hand, Modern Methods for synthesising MOFs include spray drying/evaporation, sonication and microwave. Table 1 (Moh et al., 2011; Younas et al., 2020) describes synthesis methods' significant advantages and disadvantages for metal-organic frameworks.

Table 1. Major advantages and disadvantages of the synthesis methods for metal-organic frameworks (MOFs).

Synthesis Methods	Classifications	Advantages	Disadvantages
Conventional Methods	Solvothermal Method	Significant structures, crystal sizes and good yields.	Expensive energy costs and higher durations.
	Electrochemical Method	Faster Synthesis	Fewer surface areas, higher electricity needs, and weak crystal structures.
	Flow chemical methods	Fewer energy needs, sustainable and great yields.	Variable durations on specific reactions.
Modern Methods	Microwave Synthesis	Greater Crystal Sizes, Faster Synthesis and Tunability.	Less yield and scalability issues.
	Sonochemical Method	Faster Synthesis, Tunability	Lesser yields
	Spray Drying	Less energy needs	Longer synthesis duration

MOFs typically have high BET surface areas, an essential common physical feature. MOFs can be used in CC in four forms: pure, functionalised, and combined with adsorbents. The second way MOFs are often investigated in gas separation is with an extra functional group. Research is ongoing to determine the most effective functionalising chemical for CO_2 capture and the optimal loading proportion. Polyethyleneimine is a prominent functionalising chemical that effectively works in integration with MOFs. Most MOFs have high carbon capture uptake values only at low temperatures (273-303 K) (Bhadra et al., 2017).

2. Organic Properties and Carbon Dioxide Uptake Capacity in MOFs

As temperature increases during the capture procedure, Carbon capture values decrease significantly. MOFs have a high moisture sensitivity, which is a significant concern. This substantially reduces their ability to trap other gasses. MOFs lose their crystalline structure when exposed to moisture. There are three techniques to boost carbon capture capacity and mitigate the effects of humidity. Metal ions in MOFs having numerous positive valences demonstrate high adsorption values. Pre-synthetic changes also offer an intriguing way to influence carbon capture values.

Pre-synthetic alterations, such as changing the solvent composition and temperature, can affect the morphology of the MOF and its carbon capture capacity. Post-synthesis functionalisation entails altering MOFs to meet specific needs. This type of modification improves hydrophobicity and selectivity towards CO_2. Several carbon capture conditions (both temperature and pressure) and the carbon dioxide uptake capacity (mmol/g) for most of the metal-organic frameworks are showcased in Table 2.

Table 2. Temperature (in K), Pressure (in atm) and Carbon Dioxide Uptake Capacity (mmol/g) in different metal-organic frameworks for carbon capture.

Metal-Organic Framework	Carbon Dioxide Uptake Capacity (mmol/g)	Temperature (K)	Pressure (atm)	References
pip-γCD-MOF	0.0273	333	1.1	(Zhong et al., 2016)
PVAm(0.4)@MIL-101	3	298	1	(Zhong et al., 2016)
PVAm(0.7)@MIL-101	3.3	298	1	(Zhong et al., 2016)
PVAm(1.0)@MIL-101	2.8	298	1	(Zhong et al., 2016)
Cu-BTC	9.59	273	1	(K. Lee et al., 2022)
Cu-BTC/GO2	9.05	273	1	(K. Lee et al., 2022)
Cu-BTC/GO5	8.46	273	1	(K. Lee et al., 2022)
Cu-BTC/GO10	9.59	273	1	(K. Lee et al., 2022)
HKUST-1	3.3	298	1	(Zhong et al., 2016)
PAN/HKUST-1(40 %) fibers	1.4	298	1	(Prajapati et al., 2022)
PAN/HKUST-1(60 %) fibers	2.5	298	1	(Prajapati et al., 2022)
NH2-β-CD-MOF	0.549	273	1	(L. Lu et al., 2015)
MIL-101(Cr, Mg)	1.9	301	1	(L. Lu et al., 2015)
5% PEI-MIL-101(Cr, Mg)	2.5	301	1	(Álvarez-Murillo et al., 2016)
10 % PEI-MIL-101(Cr, Mg)	3.1	301	1	(Álvarez-Murillo et al., 2016)
20% PEI-MIL-101(Cr, Mg)	3	301	1	(Álvarez-Murillo et al., 2016)
30% PEI-MIL-101(Cr, Mg)	2.6	301	1	(Tsutsumi et al., 2010)
40 % PEI-MIL-101(Cr, Mg)	2.4	301	1	(Tsutsumi et al., 2010)
MIL-101 Cr	1.5	298	1	(Álvarez-Murillo et al., 2016)
TEPA-MIL-101	3.5	298	1	(Tsutsumi et al., 2010)
PEI-MIL-101	2	298	1	(Tsutsumi et al., 2010)
UiO-66/FA_mod	1.5	298	1	(Tsutsumi et al., 2010)
Qc-5-Cu	2.48	298	1	(Álvarez-Murillo et al., 2016)
SIFSIX-3-Cu	1.02	298	1	(Álvarez-Murillo et al., 2016)
Zn(im-P-im)	3.54	298	1	(Álvarez-Murillo et al., 2016)

Ni-4PyC	3.11	298	1	(Smith et al., 2020)
30% PEI-Zn/Co ZIF@450 ◦C	1.4	298	1	(Alabadi et al., 2015)
40% PEI-Zn/Co ZIF@450 ◦C	1.8	298	1	(Alabadi et al., 2015)
f-MWCNTs@Zn/Co-ZIF	-	298	1	(L. Lu et al., 2015)
N-MWCNTs@ZIF-8	-	298	1	(L. Lu et al., 2015)
N-MWCNTs@ZIF-67	-	298	1	(L. Lu et al., 2015)
N-MWCNTs@Zn/Co-ZIF	-	298	1	(L. Lu et al., 2015)
PM24@ MIL-101	2.9	298	1	(North et al., 2010)
PM36@ MIL-101	2.7	298	1	(North et al., 2010)
R-PM24@ MIL-101	3.6	298	1	(North et al., 2010)
NH2-ZIF-8	49.1	298	1	(Olajire, 2013)
18% NH2-ZIF-8	53.57	298	1	(Olajire, 2013)
ZIF-90	2.2	323	1	(Olajire, 2013)
UiO-66	2.32	298	1	(Olajire, 2013)
Cu3(BTC)2	4.4	298	1	(Olajire, 2013)
NH2-UiO-66	3.32	298	1	(Zhong et al., 2016)
NH2-Cu3(BTC)2	3.86	298	1	(Zhong et al., 2016)
UiO-66	2.27	298	1	(Veetil et al., 2015)
UiO-66/GO	3.37	298	1	(Chatelet et al., 2013)
UiO-66-NH2	2.59	298	1	(Hänchen et al., 2008)
UiO-66-NH2/GO	3.8	298	1	(Hänchen et al., 2008)
30TEPA/UiO-66	3.7	348	1	(Hänchen et al., 2008)
NH2-UiO-66	3.15	298	1	(Zhong et al., 2016)
GMA-UiO-66	4.28	298	1	(Hänchen et al., 2008)
MOF-200	1.17	298	1	(C. Martín et al., 2015)
MOF-200/GO	1.34	298	1	(C. Martín et al., 2015)
GO@ZIF-8	0.8	298	1	(C. Martín et al., 2015)
MH-0	4.12	298	1	(Hänchen et al., 2008)
MH-1	3.7	298	1	(Hänchen et al., 2008)
MH-2	4.64	298	1	(Hänchen et al., 2008)
MH-3	4.38	298	1	(Hänchen et al., 2008)
Fe(pz)[Pt(CN)4]	4.7	298	1	(Zhong et al., 2016)

MIL-101(Cr)-NH2	3.4	308	1	(Zhong et al., 2016)
UiO-66(Hf)	1.5	298	1	(Zhong et al., 2016)
UiO-66(Hf)-NH2	2.8	298	1	(Zhong et al., 2016)
UiO-66(Hf)-(OH)2	4.06	298	1	(North et al., 2010)
UiO-66(Hf)-(COOH)2	1.2	298	1	(North et al., 2010)
UiO-66(Hf)-(F)4	0.82	298	1	(North et al., 2010)
GO-TAc/MOF-60	5.62	298	1	(North et al., 2010)
Meso-Tetraphenyl Porphinato–Cu(II)	1.74	298	40	(North et al., 2010)
PPIA-MOF-5(40 %)	3.5	298	1	(North et al., 2010)
Ni(II)-MOF	2.69	298	27	(Amaral et al., 2013)
PAN/HK@HK3-A NFM	3.9	273	1	(Amaral et al., 2013)
Bz@InOF-1	2	298	1	(Amaral et al., 2013)
MIL-96(Al)–Ca1	10.22	273	9.3	(Amaral et al., 2013)
MIL-96(Al)–Ca2	9.38	273	9.3	(Amaral et al., 2013)
50PEI@meso-UiO66– 0.2Cu	1.39	298	1	(Amaral et al., 2013)
Zn(Bmic)(AT)	3.53	353	5	(Amaral et al., 2013)
Zn(BPZ)	5.1	298	1	(North et al., 2010)
PEI(50)@NU-1000	1.75	298	1	(North et al., 2010)
Ca3L2(H2O)2(DMA)2	4.32	298	1	(Sanna et al., 2014)
PCN-250(Fe2Co)	2.23	298	1	(Sanna et al., 2014)
ACN1/3@Cu-BTC	4.32	298	1	(da Costa et al., 2022)
mmen-Mg2(dobpdc)	3.33	298	1	(da Costa et al., 2022)
sod-ZMOF-chitosan	22.23	298	1	(da Costa et al., 2022)
{[(CH3)2NH2][Zn2(L)(H2O)PO4]·2DMF}n	4.99	298	1	(da Costa et al., 2022)
MOF-505@5GO	3.94	298	1	(da Costa et al., 2022)
UTSA-16	4.5	333	1	(Naranjo et al., 2023)
Imi1/3@Cu-BTC	4.4	298	1	(Naranjo et al., 2023)
NbOFFIVE-1-Ni	1.3	298	1	(Ang et al., 2015)
Tb-L	1.84	298	1	(Aresta et al., 2014)
Cu-BTC-PEI-2.5	4.15	298	1	(Aresta et al., 2014)
[Ni-4PyC, Ni9(mH2O)4(H2O)2(C6NH4O2)18.solvent]	8.2	298	10	(Aresta et al., 2014)

LDH@ZIF-67	0.52	303	1	(Sanna et al., 2014)
ZIF-8– 90 100 %	5.22	273	1	(Sanna et al., 2014)
MOF-505	5.51	273	1	(Aresta et al., 2014)
HNUST-7	26.1	273	1	(Sanna et al., 2014)
opt-UiO-66(Zr)-(OH)2	5.63	298	1	(Calò et al., 2002)
[Zn2(NH2BDC)2(dpNDI)]n	1.26	298	1	(Calò et al., 2002)
[Zn5(btz)6(bdc)2(H2O)2]· 7DMA	2.16	298	1	(Calò et al., 2002)
MIL-53	0.05	298	1	(Calò et al., 2002)
MWCNT@MIL-53	0.3	298	1	(Calò et al., 2002)
CNF@MIL-53	0.1	298	1	(Calò et al., 2002)
MWCNT@MIL-101	0.003	298	1	(Calò et al., 2002)
1·MeCN	0.82	298	1	(Calò et al., 2002)
1-mmen	4.13	298	1	(Decortes et al., 2010)
1-en	2.63	298	1	(Sanna et al., 2014)
1-ppz	3.15	298	1	(Sanna et al., 2014)
1000-as	3.31	298	1	(Sanna et al., 2014)
1000- clean	3.22	298	1	(Sanna et al., 2014)
MOF-888	1.07	298	800 torr	(Sanna et al., 2016)
MOF-889	2.46	298	800 torr	(Sanna et al., 2016)
MOF-890	2.59	298	800 torr	(Sanna et al., 2016)
MOF-891	2.59	298	800 torr	(Sanna et al., 2016)
476-MOF	1.68	293	1	(Whiteoak et al., 2013)
477-MOF	1.92	293	1	(Whiteoak et al., 2013)
ɤ-CD-MOF	0.55	303	1	(Whiteoak et al., 2013)
NPC-6	4.83	293	1	(Whiteoak et al., 2013)
TMOF-1	1.45	298	1	(Whiteoak et al., 2013)
[Cu2L(H2O)2]• 4H2O•2DMF	6.65	273	1	(Whiteoak et al., 2013)
Cr-MIL-101-SO3H	2.28	313	150 mbar	(Miller et al., 2013)
MIL-91(Al)	-	303	1	(W. Wang et al., 2011)
Co2L2(AzoD)2·2DMF (1)	0.56	298	1	(W. Wang et al., 2011)
Al-soc-MOF-1	-	298	1	(W. Wang et al., 2011)
PN@MOF-5	3.48	-	1	(W. Wang et al., 2011)

There are a lot of factors that affect the morphology of metal-organic frameworks towards carbon capture. These factors usually involve the temperature of synthesis, enhancers or modifiers, synthesis type, reagents, composition and process parameters. MOF-5, synthesised at 393 and 413 K, exhibits a cube-like crystal structure, smooth morphology, and excellent carbon capture potential. MOFs synthesised at lower temperatures have lesser dimensionality, albeit no clear link exists (Mohan et al., 2006; Tai et al., 2014). Temperature, reagents, and process parameters significantly impact MOFs' crystal structure and morphology. Changing the number of ligands resulted in various forms, including long rods and squatting types. Adding enhancers/modifiers during synthesis affects the morphology of the resulting MOF. MOF morphology and design can be affected by three different synthesis methods. They include deprotonation regulation synthesis, coordination modulation synthesis, and surfactant modulation synthesis (Azdarpour et al., 2015).

Metal-organic frameworks exhibit unique features, which include high surface area, diversity of structures, stability and tunability (both physically and chemically). Synthesis of such metal organic frameworks requires specific properties for MOFs, including lewis bases, functionalisation and selective absorption. Several metrics for the carbon capture performance of metal organics frameworks (MOFs) are adsorption capacity, working capacity, selectivity, adsorption heat, water stability, thermal stability, diffusion coefficient, and heat capacity. The adsorption capacity of MOFs refers to the saturated adsorption capacity of CO_2 at a specific pressure and temperature. This is a crucial criterion for assessing MOFs' carbon capture performance and determining their maximum working capacity. MOFs' CO_2 adsorption depends on their structure, including pore size, volume, and surface area. MOFs often have higher CO_2 adsorption rates than other porous materials like zeolites and activated carbon due to their ultrahigh pore volume and specific surface area. MOFs can improve adsorption performance through structural characteristics such as open metal sites (OMSs), Lewis primary sites (LBSs), and covalently bound polar functional groups. Scholars have undertaken thorough numerical and experimental studies on the adsorption capability of various MOFs at specified pressures and temperatures to meet carbon capture criteria (Clements, 2003; Dweck et al., 2000; L. Hu et al., 2014; Roshan et al., 2012).

While adsorption capacity is commonly tested and presented, operating capacity is a more helpful statistic for carbon capture technologies. The differential in adsorption capacity between adsorption and desorption conditions determines the quantity of CO_2 adsorbed per unit of adsorbent, specifically MOFs, in carbon capture cycles. The MOF's operating capacity determines its potential for industrial applications. MOFs with better working capacity require less adsorbent in the adsorption bed to achieve the same CO_2 separation effect, resulting in lower capital costs and long-term energy consumption for regeneration (Amaral et al., 2013; Liang et al., 2011). In GCMC simulations, force fields rely on Lennard-Jones (LJ) parameters and atomic partial charges. Machine learning can train predictive models from screening data to quickly identify MOFs with good working capacity before GCMC simulations.

3. Carbon Dioxide Storage Sites in MOFs

Their unique structure determines the ability of MOFs to adsorb CO_2 over other gases selectively. Rigid MOFs primarily rely on size exclusion or surface contact, determined by the kinetic diameters and characteristics of adsorbates and pores. In flexible MOFs, selective adsorption is influenced by breathing and gate-opening/closing phenomena, in addition to the previously described two aspects. Due to their unique properties, flexible MOFs may selectively absorb gases at various pressures. When selecting adsorbents for carbon capture, it's essential to evaluate the stability of MOFs to water, as water vapour is present in many industrial flows. Hydrolysis events in coordination bonds can reduce the carbon-capture capacity of MOFs (X.-B. Lu & Darensbourg, 2012; Morales-Flórez et al., 2015; Song et al., 2013). Zeolites, like MOFs, are impacted by their structural properties and the conditions in which they interact with water in water-containing environments. TGA is commonly used to assess the thermal stability of MOFs. TGA analyses the weight change of MOFs at different temperatures to determine their thermal stability, breakdown temperature, and route. TGA measurements can help optimise MOF synthesis for better thermal stability. Guest molecules can also impact the thermal stability of MOFs. Desorption of guest molecules can cause heat degradation in some MOFs, destabilising framework structures. MOFs for high-temperature applications should be manufactured with guest molecules with low desorption temperatures. MOFs' thermal durability is crucial for their practical uses, particularly in high-temperature processes like adsorptive carbon capture. TGA is a valuable approach for evaluating the thermal stability of MOFs. Metal ions, organic linkers, and guest molecules all significantly impact their thermal stability.

More research is needed to improve the thermal stability of MOFs for various applications (Jutz et al., 2009; Whiteoak et al., 2012, 2014).

Adsorption efficiency depends on both equilibrium and kinetics. Consider the diffusion coefficient when analysing an adsorption process. The kinetic characteristics of adsorbents are typically calculated using MD, while the diffusion coefficient is a popular indication of adsorption. This value can also be determined using dynamic gravimetric absorption curves from adsorption studies. The heat capacity of MOFs is primarily determined by the organic ligands in the framework and any guest molecules within the pores. Differential scanning calorimetry (DSC) is a standard experimental technique to measure heat flow into and out of a sample under controlled temperature changes. Another method for measuring heat capacity is adiabatic calorimetry, which measures the temperature change caused by an exothermic or endothermic process within a sample without heat exchange with the environment. This approach is efficient when investigating reactions involving extremely reactive or unstable chemicals. MOFs' heat capacity has applications beyond carbon capture, including gas storage and separation (Daval, 2018; Matter, Stute, Snæbjörnsdóttir, et al., 2016; Matter, Stute, Snæbjörnsdottir, et al., 2016; Sakakura et al., 2007). A MOF's ability to selectively adsorb gases is influenced by temperature, pressure, and the material's heat capacity. The structure of MOFs showcases novel properties in their capture of carbon dioxide molecules, making a polyhedral structure for capturing. It mostly captures carbon dioxide molecules, whereas other gases like nitrogen, methane, SO_x or NO_x are taken out as purges. The storage units inside the MOFs are shown in Figure 3.

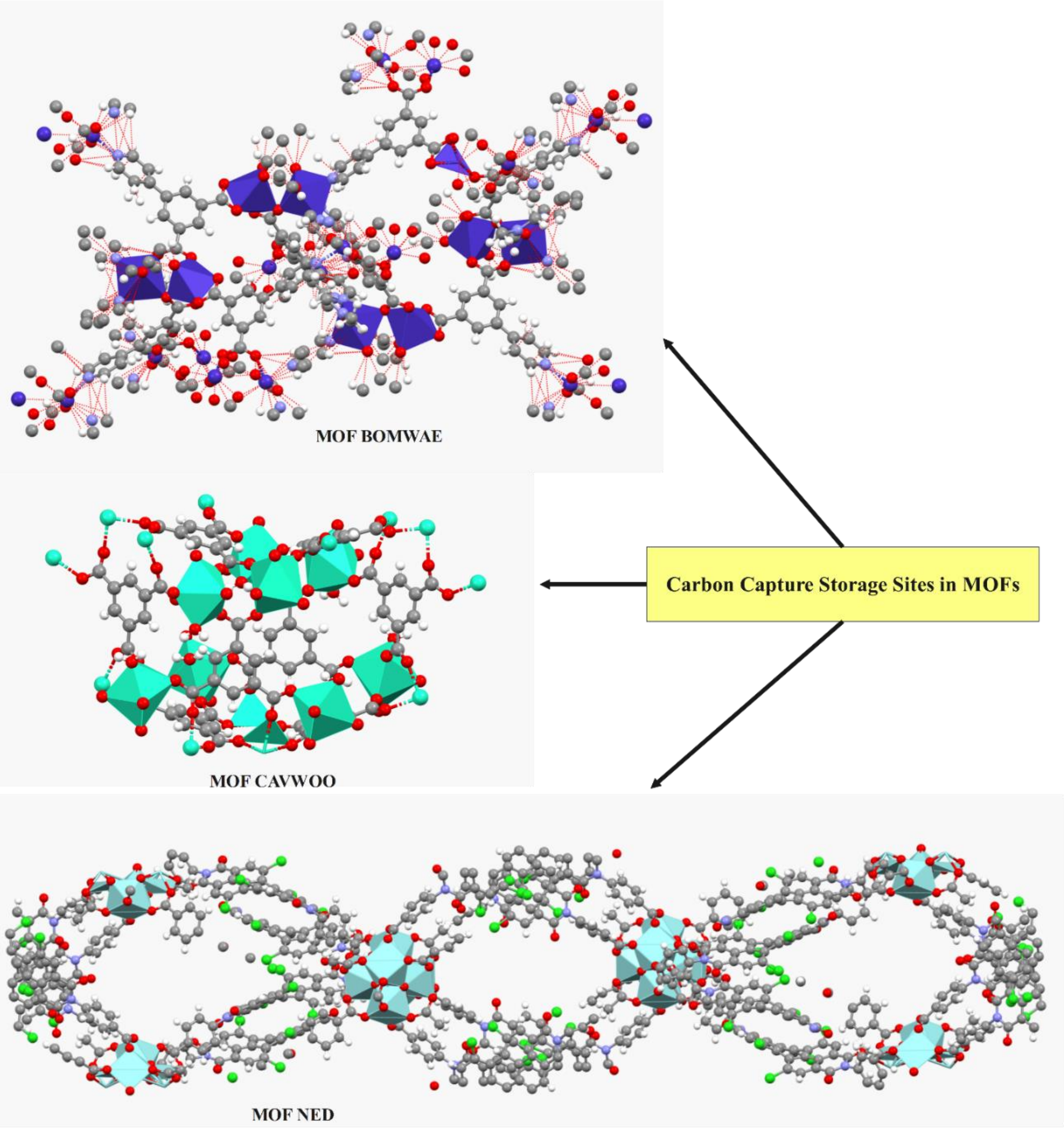

Figure 3. Carbon Capture Storage Sites in Metal-Organic Frameworks.

Due to metal-organic frameworks' high surface area, tunability and stability, it synthesises the captured carbon dioxide inside its structure. It converts carbon dioxide for its possible utilisation and multidisciplinary applications. The primary process through which carbon capture, utilisation and storage occurs is demonstrated in Figure 4.

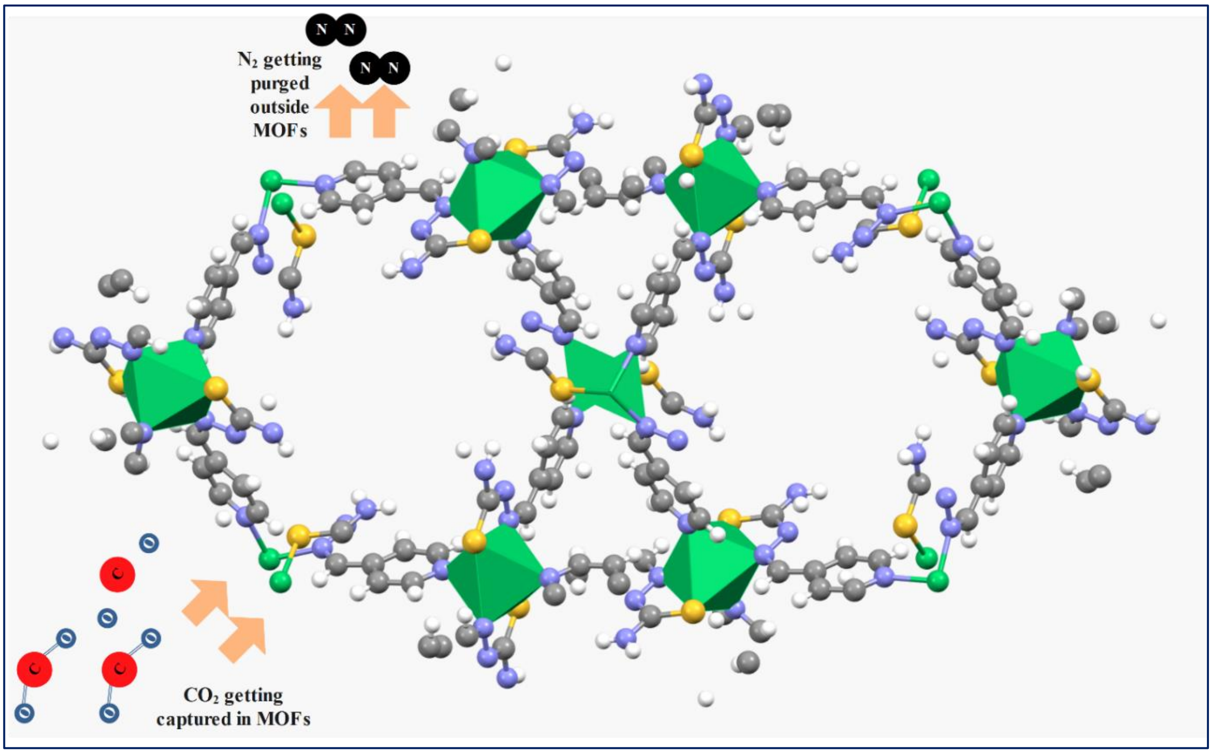

Figure 4. Carbon Capture Process in Metal-Organic Frameworks.

4. Carbon Dioxide Conversion through Metal-Organic Frameworks

Captured carbon dioxide can produce organic carbonates such as dimethyl carbonate (DMC), diallyl carbonate (DAC), diethyl carbonate (DEC), diphenyl carbonate (DPC), cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), cyclohexene carbonate (CC), and styrene carbonate (SC), and polycarbonates such as polypropylene carbonate and bisphenol polycarbonate (BPA-PC). This approach has limitations since it requires considerable catalyst inventory and operates at high temperatures and pressures. Another area for development in this technique is separating the catalyst and the products. Commercially available Aluminium-based catalysts are commonly used in the production of polycarbonates from the reaction of CO_2 and epoxides. Captured carbon dioxide can produce organic carbonates such as dimethyl carbonate (DMC), diallyl carbonate (DAC), diethyl carbonate (DEC), diphenyl carbonate (DPC), cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), cyclohexene carbonate (CC), and styrene carbonate (SC), and polycarbonates such as polypropylene carbonate and bisphenol polycarbonate (BPA-PC). This approach has limitations since it requires considerable catalyst inventory and operates at high temperatures and pressures. Another area for development in this technique is separating the catalyst and the products. Commercially available Al-based catalysts are commonly used in the production of polycarbonates from the reaction of CO_2 and epoxides (Ahmed et al., 2022; Jeffry et al., 2021; Mofarahi et al., 2008; Sinha et al., 2017).

Despite the large market for converting collected CO_2 into chemicals and fuels, the recommended laboratory-scale methods still need to be commercialised for industry usage. This is partly because the materials now being studied are expensive to create but not chemically stable and because, most of the time, the total yields of the primary products and CO_2 conversion rates are low and do not meet the requirements for widespread use. Furthermore, additional understanding of the mechanisms underpinning the chemical reactions responsible for the transformations of CO_2 is required. In this field, evaluating the procedure's requirements and contributing variables is also necessary. Some of the significant challenges of chemical conversions are the high operating conditions, complexity of reaction pathways, catalyst stability for coke formation, less conversion, yield rates of products, regeneration of catalysts, and highly selective catalyst development. Even though there are several challenges for carbon dioxide chemical conversion, several opportunities for chemical modifications include methane dry reforming, formic acid catalytic reduction and its derivative, noble metal doped transition metal catalysts, synthetic fuels through biological pathways and oxidation dehydrogenation (Zheng et al., 2019).

4.1. Organo-Catalysts Pathways through Carbon Capture in MOFs

Carbon dioxide conversion occurs in metal-organic frameworks through organic salts, molten salts, ionic liquids, nitrogen-based heterocycles, and poly(phenolic and alcohol) compounds. After reacting with reductive carbon dioxide coupling, carbon dioxide forms quinazoline-2,4-diones, cyclic carbonates and oxazolidinones, whereas non-reductive carbon coupling formulates methane, formyl derivatives and methanol. Such reactions occur when carbon dioxide is equipped with organo-catalysts that possess tuneable, metal-free, sustainable and generally low-costs. Such conversion process is thoroughly demonstrated in Figure 5 (Guo et al., 2015; C. F. Martín et al., 2011; Serna-Guerrero et al., 2010; Thiruvenkatachari et al., 2009; Wall et al., 2009; Wörmeyer & Smirnova, 2013; Zhao et al., 2013).

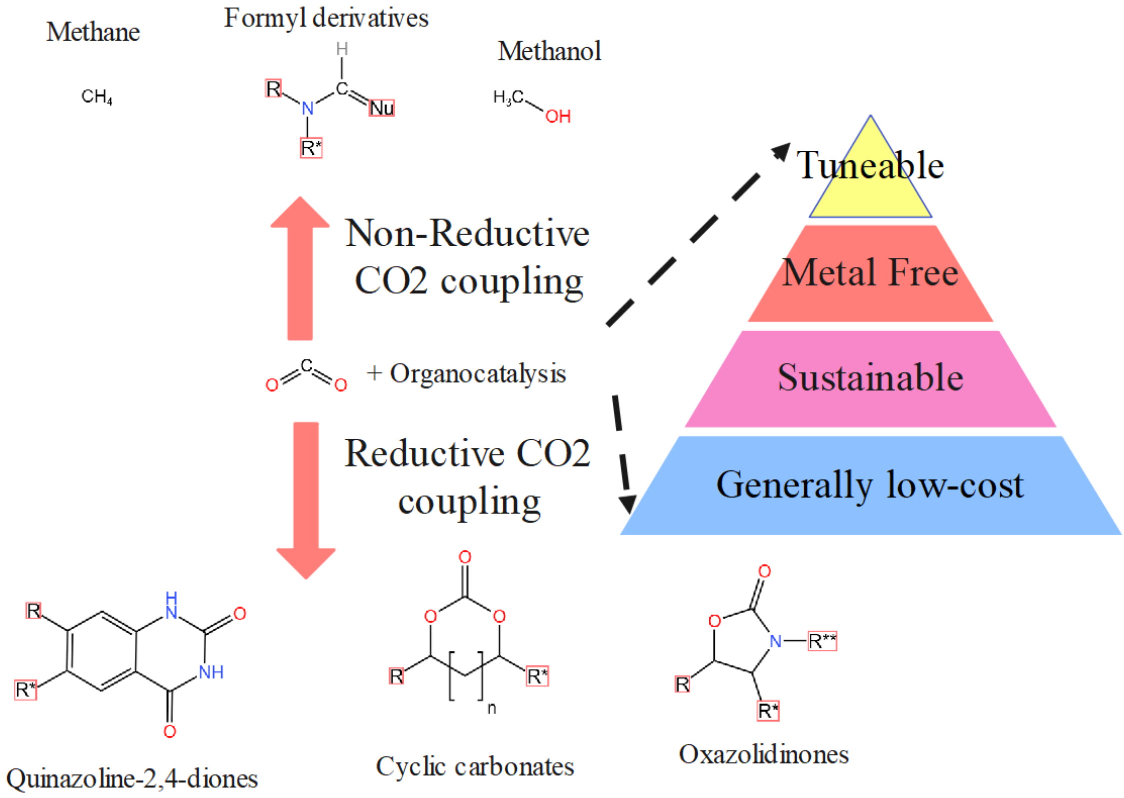

Figure 5. Process and General Pathways of Organo-Catalysts through Carbon Capture stored in Metal-Organic Frameworks (MOFs) (Guo et al., 2015; C. F. Martín et al., 2011; Serna-Guerrero et al., 2010; Thiruvenkatachari et al., 2009; Wall et al., 2009; Wörmeyer & Smirnova, 2013; Zhao et al., 2013).

4.2. Carbon Dioxide Conversion to Organic Compounds

The production of urea, a standard fertiliser, is now the highest usage of CO_2. The annual CO_2 consumption for this chemical synthesis is around 110 megatons. The chemical process that creates urea is referred to as shown in Equation (1).

$$CO_2 + 2NH_3 \longrightarrow CO(NH_2)_2 + H_2O \quad .(1)$$

CO_2 also produces salicylic acid, which has applications in pharmaceuticals and cyclic organic carbonates (Genovese et al., 2013; Kalyanasundaram et al., 2010; J. H. Lee et al., 2016). The principal desired reaction for the production of salicylic acid is caused by sodium phenolate with carbon dioxide, which first produces sodium salicylate and then, through the final addition of sulphuric acid, produces salicylic acid. While aspirin is made from salicylic acid, sodium sulphate is a byproduct. Salicylic acid and aspirin are produced using the following chemical pathway as shown in Equations (2)–(4).

$$CO_2 + C_6H_5ONa \xrightarrow{\qquad} C_6H_5(COONa)OH \text{ [sodium salicylate] } (2)$$

$$(H^+) \xrightarrow{\qquad} C_6H_5(COOH)OH \text{ [salicylic acid] } (3)$$

$$(CH_3CO)_2O \xrightarrow{\qquad} C_6H_5(COOCH_3)COOH \text{ [aspirin] } (4)$$

Carbon dioxide and hydrogen combine with a catalyst to form methanol, which is used as a fuel or a chemical reagent (B. Hu et al., 2013; Hussain et al., 2021; X. Sun et al., 2014). Methanol may also be dried out to create fuels that resemble petrol. A chemical process occurs when CO_2 and H_2 are combined to form methanol, as shown in Equation (5).

$$CO_2 + 3H_2 \xrightarrow{\qquad} CH_3OH + H_2O \; (5)$$

The conversion of CO_2 into usable chemicals has received much attention in recent years because of mechanisms including mineral carbonation, new heterogeneous catalysis, thermochemical, photochemical, electrochemical, and biological reactions, carbonate fuel cells, and plasma-assisted catalysis. These strategies can significantly lower carbon emissions if commercially viable and undeniably appealing economically. Even though several of these methods are still in development, they appear to have promising financial futures.

The metalorganic framework's extremely well-organized structure allows for the distinct spatial separation of active sites. MOF-based catalysts can potentially have a large bulk concentration of active sites due to their high specific surface area. These open spots in the MOF structure provide an exceptionally high metal dispersion. One of the main benefits of MOFs, besides their high metal content, is the uniformity of their active sites, which results from their high degree of crystallinity. Because of these systems' porosity, the catalytic processes on MOFs can thus be selective in both size and form and be mediated by catalytically active sites based on transition metal ions. Furthermore, porous MOFs are distinguished as exceptional candidates for creating heterogeneous catalysts because of their capacity to include functional groups. The synthesis of MOFs typically occurs under mild circumstances, which allow for the direct introduction of different functions into the framework structure. For instance, an efficient asymmetric catalyst can be formed by directly introducing enantiopure chiral ligands or their metal complexes into the MOF framework. Since zeolites and other microporous oxide materials are typically synthesised under severe conditions (such as high-temperature calcination), this procedure cannot be used for them (Gong et al., 2009; Huang et al., 2011; Yokozeki et al., 2008; Yu et al., 2021).

5. Applications of MOFs integrated with Carbon Capture

Their hydrolytic and thermal instability restricts the application of MOFs in heterogeneous catalysis. Despite this, many MOFs show stability at high temperatures, with some even demonstrating resistance up to 450°C. Some of the catalytic application-based metal-organic framework’s utilisation comprises the classical support in a heterogenous catalytic system through MOFs, Utilisation of metal-organic frameworks through active sites in organic ligands, active sites located in the inorganic units of the framework by the running of catalytic processes and introducing the active site through host-guest interaction. Table 3 provides the catalysts based on MOFs.

Table 3. Catalysation Applications on Metal-Organic Frameworks.

Metal-Organic Framework Type	MOF Site of Reaction	Reaction Type	Reactants	References
Pd@[Zn4O(BDC)3] (MOF-5)	MOF as a classical support	Hydrogenation	Cyclooctene	(Chen et al., 2023)
Ru@[Zn4O(BDC)3] (MOF-5)		Oxidation	Benzyl alcohol +O_2	(Jeffry et al., 2021; Mehrpooya et al., 2017; Sinha et al., 2017)
Cu@[Zn4O(BDC)3] (MOF-5)		Methanol synthesis	Syngas	(Ding et al., 2019; Sinha et al., 2017)
Pd@[Zn4O(BDC)3] (MOF-5)		Hydrogenation	Styrene+H_2	(Ahmed Ali et al., 2020; Fei et al., 2011)
Pd@[Zn4O(BDC)3] (MOF-5)		Hydrogenation	Ethyl cinnamate+H_2	(Ahmed Ali et al., 2020; Fei et al., 2011)
Cr3(F,OH)(en)2O(BDC)3(ED-MIL-101)	Post-synthetic modification of the framework	Heck condensation	Iodobenzene+acrylic acid	(Shiraishi & Hirata, 2021)
Cr3(F,OH)(en)2O(BDC)3(ED-MIL-101)		Knoevenagel condensation	Benzaldehyde+ethyl cyanoacetate	(Shiraishi & Hirata, 2021)
[Ni(L-aspartate)bpy0.5]HCl0.9 MeOH0.5		Methanolysis of epoxides	Cis-2,3-epoxybutane	(Shiraishi & Hirata, 2021)
Ti(OiPr)4[Cd3Cl6(L1)3] 4DMF 6MeOH 3H2O	Active side in organic ligand	Addition to carbonyls	ZnEt2 + aromatic aldehyde	(Ahmed et al., 2022)
[Zn2(BPDC)2(L2)] 10DMF 8H2O		Epoxidation	2,1-Dimethyl-2H-chromene + (tert-buthylsulfonyl) iodosilybenzene	(Chen et al., 2023; Escobar-Hernandez et al., 2023)

The state of the art of research indicates that there are distinct applications for metal-organic frameworks compared to their classical counterparts, zeolites. MOFs are still inferior to zeolites when harsh conditions are needed for a catalytic reaction. Their primary application areas include fine organic synthesis, enantioselective synthesis, and valuable substance preparation since these catalytic processes can be completed gently. Examining available data demonstrates that full realisation of all synthesis possibilities is necessary to use the diversity of MOF properties to create catalytic systems. The goal is to develop future catalysts with a high molecular sieve selectivity. These systems need polyfunctional architecture, which is impossible to achieve outside the framework structures of metal-organic compounds. We also think fine-tuning the active site microenvironment, which controls the reactivity, is an intriguing challenge. Future research will thus be able to showcase the unique catalytic qualities that are particular to MOFs.

Recently, there has been a renewed interest in MOF applications in materials science and chemistry for fuel storage, photo-induced hydrogen evolution, fuel cells, batteries, and supercapacitors. According to research on their many applications, MOFs are promising porous materials for energy storage and conversion technologies. Moreover, MOFs have served as sacrificial materials for synthesising different nanostructures for energy applications and as support substrates for metals, metal oxides, semiconductors, and complexes. We provide the most recent research highlighting energy applications based on MOFs, their derivatives, and composites. The term "chemical hydrogen storage" refers to the potential practice of storing hydrogen in chemical bonds for fuel-cell applications. It is also a reliable and effective substitute for actual hydrogen storage. Over the past few decades, much research has been done on the chemical storage of hydrogen in both liquid and solid phases. Chemical hydrides can be contained in MOFs' nanopores, releasing hydrogen under benign circumstances with less unwanted volatile byproducts. Furthermore, MOF-supported metal nanoparticle catalysts improve the kinetics of hydrogen liberation of liquid-phase chemical hydrides (Bhadra et al., 2017).

A prevalent issue in research circles is the evolution of hydrogen from water in the presence of a photocatalyst to help replace fossil fuels. With the aid of $Ru(bpy)_3^{2+}$ (as a photosensitiser), MV^{2+} (as an electron relay), and $EDTA\text{-}Na_2$ (as a sacrificial donor), the first MOF photocatalyst, $\{Ru_2(1,4\text{-}BDC)_2\}n$ (1,4-BDC = 1,4-benzenedicarboxylic acid), was used in 2009 to induce hydrogen evolution from water under the irradiation of visible light. Here, bpy, MV, and EDTA are, respectively, 2,20-bipyridine, N, N0 -dimethyl-4,40-bipyridinium, and EDTA. Another exciting use for MOFs is in solar cells, also called photovoltaic cells, which are electrical devices that directly convert sun energy to electricity. Solar cells' effectiveness largely depends on the regular arrangement of photoactive molecules. Liquid phase epitaxy was used to create a highly porous, crystalline, and monolithic porphyrin-based MOF thin film of $Zn\text{-}SURMOF_2$ on a conductive fluorine-doped tin oxide (FTO) substrate (as the bottom anode).

Regarding energy storage and conversion technologies, fuel cells are crucial because they work as electrochemical converters, turning fuels like methanol, hydrogen, and natural gas into electricity that can be used to power portable electronics, stationary buildings, and automobiles. However, the USDOE's 2016 fuel-cell development targets for price, efficiency, and durability are still far from what the existing fuel cells can achieve. This necessitates improving the fuel cell's auxiliary features and developing the electrolyte membranes and electrode catalysts now in use. MOFs, MOF derivatives, and MOF composites are possible electrode catalysts and electrolyte materials in the fuel cell industry. Due to their extended lifespan and high-power density, supercapacitors (SCs), electrochemical or ultracapacitors, have garnered significant scientific interest. Pure MOF SCs often have low specific capacitance because of weak conductivity, even with their high porosities. To improve MOF conductivity, a new approach to enhancing SC performance involves incorporating MOFs with conductive materials, like graphene and conductive polymers.

Water electrolysis, encompassing the OER and the hydrogen evolution reaction, has been the subject of extensive research in the past few years. Catalysts are needed to lower their overpotential to drive these reactions at the requisite high catalytic current densities. Using MOFs, MOF derivatives, and MOF composites to facilitate the efficient evolution of hydrogen from electrolytic water splitting has become a significant approach to producing clean, renewable fuel. HER catalytically active components can be successfully integrated into MOFs to investigate high-performance electrodes. Conjugated ligands of benzenehexathiol and triphenylene-2,3,6,7,10,11-hexathiolate, respectively, have been used to develop and fabricate 2D ordered MOF films with cobalt dithiolene catalytic sites with substantial HER catalytic activity. Under acidic circumstances, metal-organic frameworks based on ε-Keggin polyoxometalate are robust HER electrocatalysts. In short, the bio-applications of metal-organic frameworks are demonstrated Figure 6 (Moh et al., 2011; H. Wang et al., 2017).

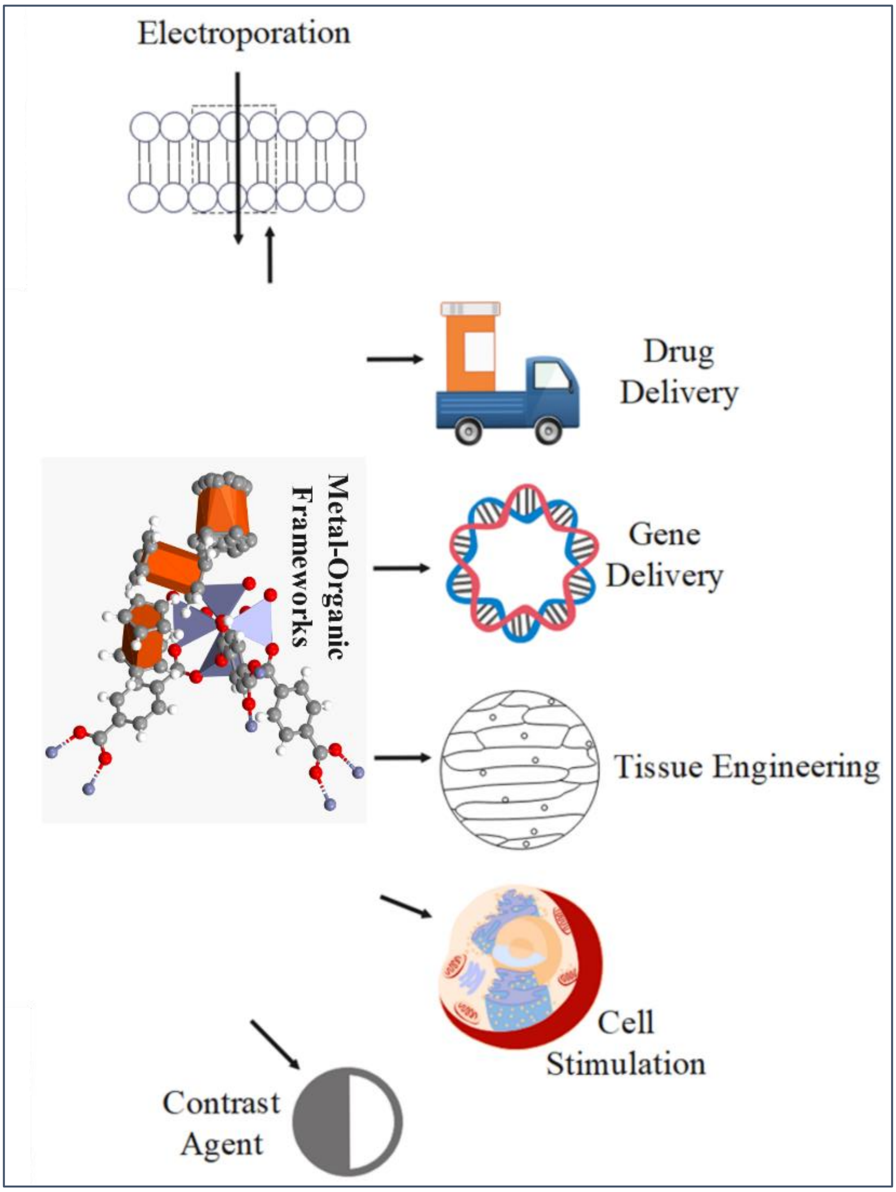

Figure 6. Metal-Organic Frameworks bio-applications (Moh et al., 2011; H. Wang et al., 2017).

6. Conclusions

Clearly, the current scenario not only demands an alternative to reduce emissions but also to eliminate the existing atmospheric carbon dioxide; the realistic portrayal of the globe must be entirely on the path of GHG emissions reduction even though significant global investments have been made for cleaner energy and gradually going towards the energy transition of renewable energies like wind energy, hydrogen fuels, biogases, biofuels etc., from conventional energy sources like fossil fuels, crude oil, natural gas, petrol, diesel etc. Several critical and novel points were concluded through discussions, observations, study and reviews, which are as follows-

1) Several advantages and disadvantages of synthetic methods for metal-organic frameworks were concluded, with faster synthesis, fewer energy needs, excellent yields, and more significant crystal sizes being some pros. Expensive energy costs, higher durations, fewer surface areas, lesser yield, scalability issues, and longer synthesis duration are some of the disadvantages of metal-organic frameworks (MOFs).

2) The carbon uptake capacity of metal-organic framework materials was maximum in sod-ZMOF-chitosan, MIL-96(al)-Ca1, 18% NH_2-ZIF-8, and Cu-BTC.

3) Based on different reactants and reaction types along with the carbon dioxide uptake capacity, the industrialisation of carbon capture materials can be scaled up with higher efficiencies.

As a fresh research area that majorly ignited after COVID, it is essential to bridge the gaps in CCUS to reach net zero emissions as soon as possible and focus on alternate energy transition to eliminate emissions.

List of Abbreviations.

UNSDGs	United Nations Sustainable Development Goals
CO_2	Carbon Dioxide
MOF	Metal Organics Framework
CC	Carbon Capture
ZIF	Zeolitic imidazolate frameworks
BET	Brunauer-Emmett-Teller
LBS	Lewis Primary Sites
USDOE	United States Department of Energy
DMC	Dimethyl Carbonate
DAC	Diallyl Carbonate
DEC	Diethyl Carbonate
DPC	Diphenyl Carbonate
EC	Ethylene Carbonate
PC	Propylene Carbonate
CC	Cyclohexene Carbonate
SC	Styrene Carbonate

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