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A structural description of selected MOFs and an overview of their capacity to store carbon dioxide – A review study

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Abstract: Carbon dioxide capture, transportation and storage is still being prioritised in studies because of the increasing concentration of Carbon dioxide in the atmosphere. One of interest field to authors is adsorbent for high Carbon dioxide storage. Metal-organic frameworks (MOFs) are widely studies due to their porous crystalline structures, high surface areas, and versatility in gas storage and separation. Ten popular MOFs were collated from different sources that conducted experimental work detailing their synthesis processes, specific reactants, and modification methodologies. Among the ten MOFs reviewed, MOF-177 is reported to have the highest CO_2 storage capacity with a maximum of 39.9 mmol/g. This is due to its highly porous structure and large surface area. Solvothermal synthesis is the most preferred method for modifying MOFs due to its effectiveness in controlling the structural and functional properties of MOFs material, precise tuning of pore size, material, and CO_2 adsorption enhancement.

Index Terms: CO_2 adsorption, Metal-organic frameworks, MOF-177, porous materials, solvothermal synthesis.

1. INTRODUCTION

MOFs are made-up of metal-containing nodes linked by organic ligand bridges meaning its molecule donates a pair of electrons to the central metal atom and assembled primarily by strong coordination bonds (Elhenawy, 2020). Millions of distinct metal-organic frameworks (MOFs) can be made by combining metal nodes and organic linkers (Moosavi, 2020). Metal organic frameworks are one of the best-used porous materials in carbon capture technologies. Porous metal–organic frameworks have attracted substantial attention during the past decades in the field of gas adsorption/separation both experimentally and theoretically (Yang, 2012). At present, over 90,000 MOFs have been synthesised and over 500,000 predicted (Moosavi, 2020). A vast library of metal–organic framework designs, which range in shape, size, and chemical functionality exist (Grissom, 2019).

The high number of modified MoF indicates their flexibility to change to a form which best suite various conditions. There are different types of MoFs bases namely; Iron based MoF (Fe-MoF), Zinc based MoF(Zn-MoF), Cobalt based MoF (Co-MoF), Nickel based MoF (Ni- MoF), Indium based MoF (In-MoF), Titanium based MoF (Ti-MoF), Copper based MoF (Cu-MoF), Chromium based MoF (Cr-MoF),

Aluminium based MoF (Al-MoF) and Zirconium based MoF (Zr-MoF). Some will be discussed underneath. MOFs have been considered as promising materials for carbon dioxide (CO_2) adsorption due to their excellent chemical stability, large pore volume, and high surface area (Alrubaye. 2019). The different advantages and disadvantages of MOFs have been investigated by several researchers, and they reported how the architecture and active functional groups of MOFs could be controlled. This study looks at the structural description of ten popular MOFs and their capacity to store CO_2.

The increasing concentration of CO_2 in the atmosphere, necessitates the development of efficient carbon capture and storage technologies. MOFs have emerged as promising materials for CO_2 adsorption due to their highly porous structures, tunable chemical properties, and exceptional surface areas (Ma, 2020). The study contributes to the gap of systematically evaluating and comparing the structural characteristics and CO_2 storage capacities of various MOFs to identify the most effective candidates for practical applications and experimental works. By analysing the synthesis methods, physical properties, and adsorption performance of selected MOFs, this study aims to provide valuable insights into their potential for mitigating greenhouse gas emissions, guiding future research and development in advanced porous materials for carbon capture.

2. TYPES OF MOF BASES AND THEIR CHARACTERISTICS

a. Fe-based MoF

They have developed promptly in recent years and are foreseen as the most promising compound to overcome the disadvantages of traditional water depolluting practices (Joseph, et al., 2021). They have also attracted a great deal of attention in the areas of gas separation, catalytic conversion, and drug delivery (Mahdipoor, et al., 2021). Fe-based MOFs are mostly used because of their intriguing structural architectures, excellent stability, durability, function, high surface area, activity, as well as the non-toxicity (Zhang, et al., 2021; Mahdipoor, et al., 2021). Fe-based MOFs are synthesized by a solvo- thermal method for carbon dioxide adsorption (Mahdipoor, et al., 2021), Adsorption of CO_2, N_2 and CH_4 on a Fe-based metal organic framework, MIL-101(Fe)-NH_2).

b. Zr-based MoF

The Zr-MOF is partially amorphous meaning it has no shape, a strong solid with a thermal stability of 180 °C , a surface area of 295 m^2g^{-1}, a wide pore size distribution which ranges from 0.2 to 1.2 nm and a pore volume of 0.6 cm^2g^{-1} (Subramaniyam, Thangadurai, & Lee iii, 2022). Zirconium-based MOF such as UiO-66 are stable in humid and acidic environments, can withstand temperatures higher than 375 °C, and are mechanically robust. In addition, a wide variety of functionalized ligands can easily be incorporated into the framework of UiO-66 MOF through a pre- or post-synthetic modification, which allows for optimization of the materials (Grissom, et al., 2019). Another synthesised Zr-based MOF using water as solvent and HCOOH as modulator was qualified as a good candidate for H_2 storage applications because of its easy production (Rena, et al., 2015).

c. Cr-based MoF

Cr-based MOFs are known as being stable at air and are not destroyed or easily altered when treated with various organic solvents at ambient temperature or in solvothermal conditions (Mahdipoor, et al., 2021) . MIL-101(Cr) is one of the most well-studied chromium-based metal-organic frameworks, which consists of metal chromium ion and terephthalic acid ligand. Cr-based MOF has ultra-high specific surface area, large pore size, contains unsaturated Lewis acid sites in its structure, good thermal, chemical, and water stability (Zou, et al., 2022).

d. Cu-based MoF

Cu-based MOFs predominantly draws countless consideration because they can be synthesized with commercially available reagents, and they possess a high surface area. Cu was selected as a standard transition metal because it is considered to be one of the most attractive elements in the preparation of MOFs due to its abundance, low cost, non-toxic properties, and its high complexation strength (Bagheri & Ghaedi, 2020). The most recognized features of Cu-based Metal organic frameworks are distinct pore dimensions, different proportions, compatibility, variable configuration, measurements, high loading capacity and upgraded biocompatibility (Singh & Thakur, 2022).

e. Zn-based MoF

Zn-based MoF is formed using Zn and its derivatives as metal clusters and organic ligands. Zn-based MOFs have appeared to be safe as elucidated by different cytotoxicity assays for targeted improved drug delivery, this was found by enhanced efficient detection (Ali, Meng, & Li, 2022). The zinc-metal organic framework compound of the current discovery can be used as a carbon dioxide adsorbent by a method of selectivity. The metal organic framework can be used as a heterogeneous catalyst for transesterification capable of being easily reused and being efficient in transesterification (Kim, Huh, Kim, & Kim, 2017).

3. OVERVIEW OF THE MOST POPULAR MOF FOR CARBON DIOXIDE ADSORPTION

Table 1 provides a comprehensive overview of ten popular MOFs evaluated for their CO_2 adsorption capabilities. The table summarizes key aspects of each MOF, including the reactants used in their synthesis, the synthesis or modification methodologies applied, their physical properties such as pore size, specific volume, stability temperature, and specific surface area, and their CO_2 storage capacities under specified conditions. These MOFs, which include a variety of base metals and organic ligands, were selected based on experimental studies highlighting their structural characteristics and performance in CO_2 capture. This comparative analysis underscores the diversity in MOF design and their potential for effective CO_2 adsorption, with detailed insights into how synthesis methods and physical properties influence their adsorption performance.

Table 1: Overview of the most popular MoF for carbon dioxide adsorption

MoF (Mental organic framework	**Reactants**	**Synthesis / modification methodology**	**Physical properties**	**Ability to capture Carbon dioxide - Storage capacity**
MOF-199 – $CU_3(BTC)_2$, HKUST-1 (Loera-Serna, et al., 2012)	Copper nitrate + 1,3,5-benzenetricarboxylic acid	solvothermal method in DMF(-dimethylformamide) (Nguyen, et al., 2012)	•Porous size – 1.18 nm (Nguyen, et al., 2012) •specific volume of 0.693 $x10^{-6}\ m^3g^{-1}$ (Nguyen, et al., 2012) •Stability temperature: 333 ^oC (Nguyen, et al., 2012) •Specific surface area - 1448 m^2g^{-1} by Brunauer–Emmet–Teller (BET) method and 2028 m^2g^{-1}. (Nguyen, et al., 2013)	4.9 $mmol.g^{-1}$ At 5 bar and 36 ^oC (Alrubaye & Kareem, 2019)
MOF-177	Zn_4O(-COO)6 + triangular 1,3,5-benzenetribenzoate (BTB)	Impregnation method with amines (Gaikwad, et al., 2021),	• Porous size – 1.18 nm (Ullah, et al., 2019) • Specific volume of 2.65 $x10^{-6}\ m^3g^{-1}$ (Saha & Deng, 2010) • Stability temperature: 24.85 ^oC (Ullah, et al., 2019) • Specific surface area – 1721 m^2g^{-1} (Ullah, et al., 2019)	39.9 $mmol.g^{-1}$ At 42.5 bar and 24.5 ^oC (Abdi, et al., 2021)
Mg - MOF-74	$Mg(NO_3)_2$ ·$6H_2O$ + 2,5-dihydroxyterephthalic acid (Tao, et al., 2017)	Solvothermal method (Tao, et al., 2017), Sono-chemical method (Yang, et al., 2012)	• Porous size – 1.02 nm (Bao, et al., 2011) • Specific volume of 49 $x10^{-6}\ m^3g^{-1}$ (Kamal, et al., 2021) • Stability temperature: 6.8 ^oC - 36.85 ^oC (Ullah, et al., 2019) • Specific surface area – 1332 m^2g^{-1} (Ullah, et al., 2019) , 1525 m^2g^{-1} (Yang, et al., 2012)	13.55 $mmol.g^{-1}$ At 31.63 bar and 36.85 ^oC (Abdi, et al., 2021)

MIL-101 (Cr) chromium terephthalate metal–organic framework	benzene-1,4-dicarboxylate+Cr (NO_3) (Bhattacharjee, et al., 2014)	Template synthesis (Zou, et al., 2022) Hydrothermal method	• Porous size – 1.02 nm (Yulia, et al., 2019) • Specific volume of 1.4 $x10^{-6}$ m^3g^{-1} (Yulia, et al., 2019) • Stability temperature: Varying temperature up to a max of 51.85 ^oC (Yulia, et al., 2019) • Specific surface area – 3000 m^2g^{-1} (Yulia, et al., 2019)	7 $mmol.g^{-1}$ At 10 bar and 25 ^oC (Yulia, et al., 2019)
Fe- BTT (BTT^3-1,3,5-benzenetristetrazolate) (Asgari, et al., 2018)	$FeCl_2$ + H_3 BTT. 2HCl (Sumida, et al., 2010)	Solvothermal method (Sumida, et al., 2010)	• Porous size – 1.88 nm (Sumida, et al., 2010) • Specific volume of 1.06 $x10^{-6}$ m^3g^{-1} (Yan, et al., 2018) • Stability temperature: 24.85 ^oC (Asgari, et al., 2018) • Specific surface area – 2010 m^2g^{-1} (Asgari, et al., 2018), (Sumida, et al., 2010)	3.07 $mmol.g^{-1}$ At 1 bar and 24.85 ^oC (Li, et al., 2020)
NH_2-MIL-125 (Ti)	Titanium tetrabutoxide $Ti(BuO)_4$	Reflux reaction	• Porous size – 0.6-0.8 nm (Bioparticles, 2023) • Specific volume of 0.6622 $x10^{-6}$ m^3g^{-1} (Sohail, et al., 2017) • Stability temperature: 24.85 ^oC (Asgari, et al., 2018) • Specific surface area – 1492 m^2g^{-1} , 1509 m^2g^{-1} (Li, et al., 2020)	4 – 5.64 $mmol.g^{-1}$ At 1 bar and 24.85 ^oC (Li, et al., 2020)
MOF-5 Zn_4O (BDC)	Zn_4O + 1,4-benzodicarboxylate (Nagappan, et al., 2012)	Solvothermal method (Nagappan, et al., 2012)	• Porous size – 1 nm (Kaye, et al., 2007) • Specific volume of 0.24 $x10^{-6}$ - 0.33 $x10^{-6}$ m^3g^{-1} (Kukulka, et al., 2019) • Stability temperature: 25 ^oC (Kukulka, et al., 2019) • Specific surface area – 1884 m^2g^{-1} (Kukulka, et al., 2019)	2.43 $mmol.g^{-1}$ At 1 bar and 25 ^oC (Kukulka, et al., 2019)
Ni-MOF-74	$Ni(NO_3)_2$ ·$6H_2O$ + 2,5-dihydroxyterephthalic acid	Solvothermal process on the surface of a CNTF	• Porous size – 1.1 nm (Man, et al., 2019) • Specific volume of 0.38 $x10^{-6}$ m^3g^{-1} (Harandizadeh, et al., 2022)	2.43 $mmol.g^{-1}$ At 1 bar and 22 ^oC

	(Man, et al., 2019)	(Man, et al., 2019)	• Stability temperature: 22.85 ^{o}C (Li, et al., 2020) • Specific surface area – 1070 m^2g^{-1} (Li, et al., 2020)	(Li, et al., 2020) (Harandizadeh, et al., 2022)
MOF-200	1,3,5-tris(4-carboxy[1,2-biphenyl]-4-yl)-benzene) + ($Zn\text{-}(NO_3)_2\cdot 6H_2O$) (Ullah, et al., 2020)	Solvothermal method, catalyst free (Ullah, et al., 2020)	• Porous size – 4.8 nm (Furukawa, et al., 2010) • Specific volume of 3.59 $x10^{-6}$ m^3g^{-1} (Xuan, et al., 2012) • Stability temperature: 22.85 ^{o}C (Li, et al., 2020) • Specific surface area – 4530 m^2g^{-1} (Xuan, et al., 2012) (Li, et al., 2020)	16.79 $mmol.g^{-1}$ At 50 bar and 22.85 ^{o}C (Li, et al., 2020)
UiO-67(Zr)	biphenyl-4,4-dicarboxylic acid + $ZrCl_4$ (Bailey, et al., 2021)	Solvothermal method (DMF as a solvent) (Bailey, et al., 2021)	• Porous size – 2.114 nm (Zhan, et al., 2018) • Specific volume of 10.63 $x10^{-6}$ m^3g^{-1} (Zhan, et al., 2018) • Stability temperature: 23 ^{o}C (Abida, et al., 2013) • Specific surface area – 1139 m^2g^{-1} (Zhan, et al., 2018)	9 $mmol.g^{-1}$ At 0.988 bar and 0 ^{o}C (Abida, et al., 2013)

Metal-organic frameworks (MOFs) are a type of porous, crystalline material with numerous applications. MOFs are made up of metal ions or clusters that act as joints and are bound by multidirectional organic ligands that act as network linkers. Table 1 is the overview of the selected most popular MOFs to capture Carbon dioxide. The focus is on the reactants of synthesizing the MOFs, Process of modification and synthesis, Physical properties, ability to capture carbon dioxide or storage capacity and the structure of the MOFs. All metal organic frameworks have their base metal. The study reviewed ten metal organic framework of different ligand. 5 methods of synthesizing the MOFs were quoted in the table 1 namely Solvo-thermal, Template synthesis, Reflux reaction, Impregnation method, and hydrothermal method and Sono chemical method. According to (Feng and Li) hydrothermal and solvothermal syntheses are important branches of inorganic synthesis.

Hydrothermal and solvothermal methods play a versatile role in materials synthesis and growth applications. These techniques are not confined solely to generating conventional and advanced materials but rather take on a diverse array of forms. Based on a survey of the most common synthesis approaches, seven out of ten utilize solvothermal synthesis when fabricating MOFs. This strong adoption of the solvothermal technique highlights its favoured status among researchers for the synthesis of MOFs. The solvothermal practise offers a high optimisation route for controlling the self-assembly of the MOF nanocrystals and microcrystals from the molecular building blocks. Through careful selection of solvents, temperatures, pressures and other reaction parameters, solvothermal synthesis affords material designers reliable production of MOFs with tailored compositions, structures, and properties. Its flexibility and ability to yield MOFs with high purity and crystallinity under relatively mild conditions have made solvothermal synthesis the premier choice for scalable MOF manufacturing.

Fig.1 illustrate the comparison of the ten reviewed MOF's ability to capture carbon dioxide. MOF-177 has the highest ability with a storage capacity of 39.9 mmpl/g as per the cited author's results in table 1.

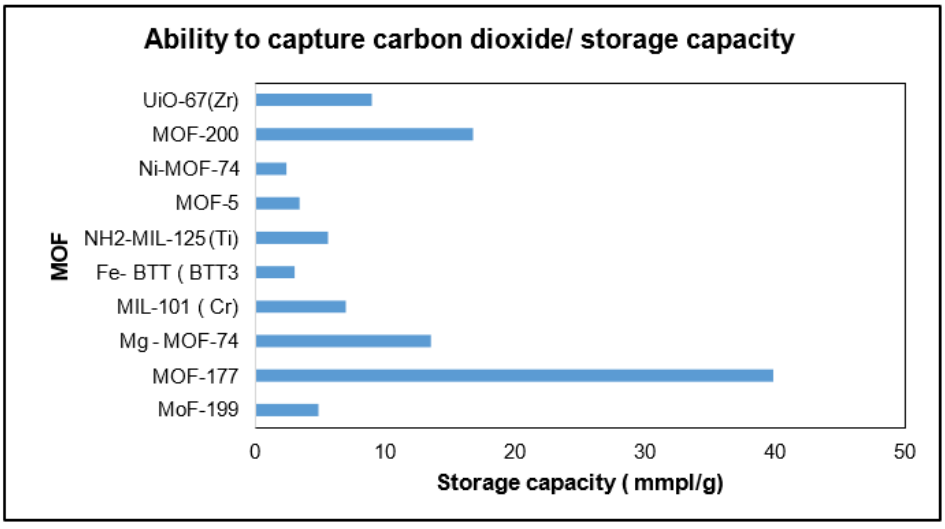

Fig .1. Comparison of 10 different MOFs' ability to capture carbon dioxide

4. STRUCTURAL DESCRIPTIONS OF TEN MOFs WITH (ASCII)

Below are textual descriptions and simplified American Standard Code for Information Interchange (ASCII) art representations of the ten metal-organic frameworks (MOFs) reviewed in the article for their CO_2 adsorption capabilities. Each MOF is described in terms of its metal nodes and organic linkers, with ASCII art illustrating the basic connectivity pattern. Note that MOFs have complex 3D porous structures, so the ASCII art simplifies the repeating unit or node-linker interactions.

4.1 MOF-199 ($Cu_3(BTC)_2$, HKUST-1)

MOF-199, also known as HKUST-1, consists of copper(II) ions forming paddlewheel-shaped dinuclear Cu_2 clusters as metal nodes (.Loera-Serna,2012). These are connected by 1,3,5-benzenetricarboxylic acid (BTC) linkers, forming a cubic framework with large pores (1.18 nm). The BTC ligand has three carboxylate groups, each binding to a Cu_2 cluster, creating a highly connected network (Nguyan, 2012).

```
[Cu2]
 | |
-BTC-          (Cu2 = Cu2 cluster, BTC = benzenetricarboxylate)
 | |
[Cu2]
```

4.2 MOF-177

MOF-177 features Zn_4O clusters as metal nodes, coordinated with triangular 1,3,5-benzenetribenzoate (BTB) linkers (Gwaikwad, et al., 2021). The Zn_4O clusters are tetrahedrally coordinated, and BTB's three carboxylate groups link multiple clusters, forming a highly porous structure (pore size 1.18 nm) ideal for CO_2 adsorption (39.9 mmol/g) (Ullah et al, 2019).

```
 [Zn4O]

  /|\
 / | \                    (Zn4O = Zn4O cluster, BTB = benzenetribenzoate)
-BTB-BTB-
  \|/
 [Zn4O]
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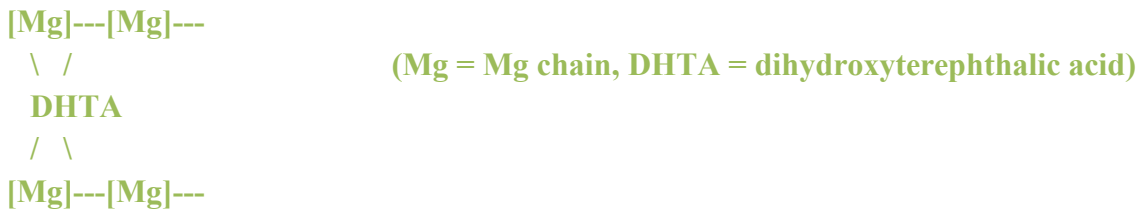
4.3 Mg-MOF-74

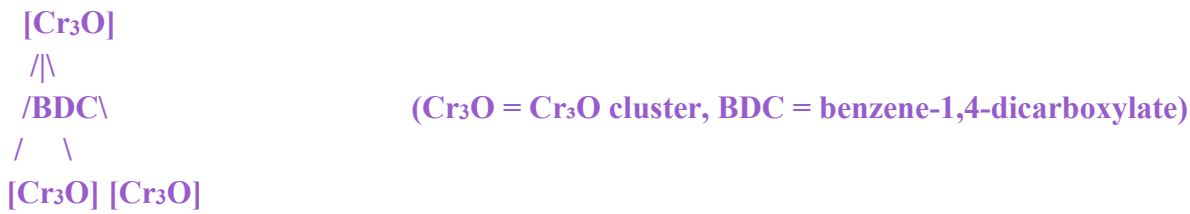
Mg-MOF-74 uses magnesium(II) ions forming one-dimensional rod-like metal chains, coordinated with 2,5-dihydroxyterephthalic acid (DHTA) linkers (Tao, et al., 2017). The linkers connect the Mg

chains into a honeycomb-like framework with open metal sites, enhancing CO_2 binding (pore size 1.02 nm) (Bao, et al., 2011).



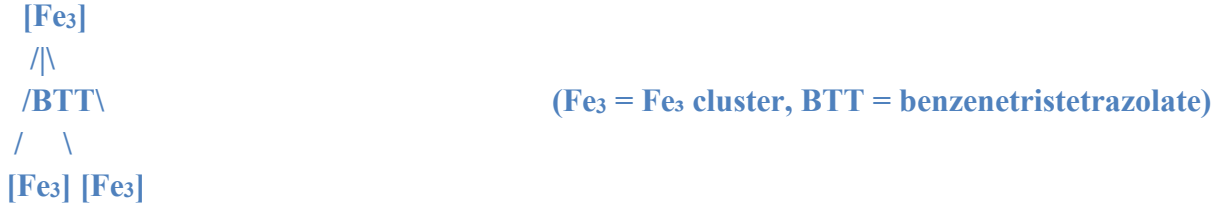
4.4 MIL-101(Cr)

MIL-101(Cr) comprises chromium(III) ions forming trinuclear Cr_3O clusters, linked by benzene-1,4-dicarboxylate (BDC, terephthalic acid) ligands (Bhattacharjee, et al., 2014). The structure forms large cages with a pore size of 1.02 nm with unsaturated Lewis acid sites, contributing to its high surface area of 3000 m^2/g (Yulia et al., 2019).



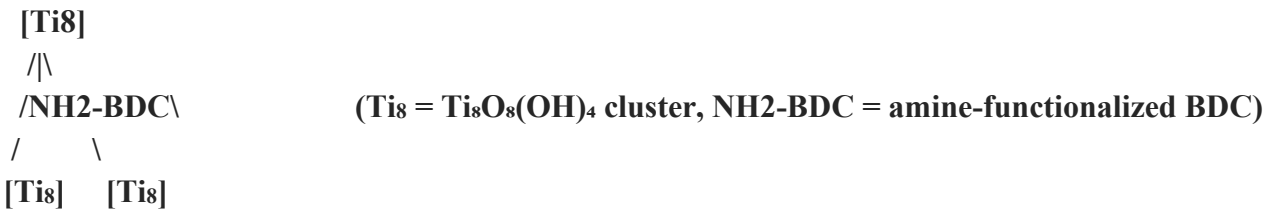
4.5 Fe-BTT

Fe-BTT uses iron(II) ions forming Fe_3 clusters, coordinated with 1,3,5-benzenetristetrazolate (BTT) linkers. (Sumida, et al., 2010). The tetrazolate groups provide strong coordination, forming a porous framework with the pore size of 1.88 nm suitable for gas adsorption ISumida, 2010).



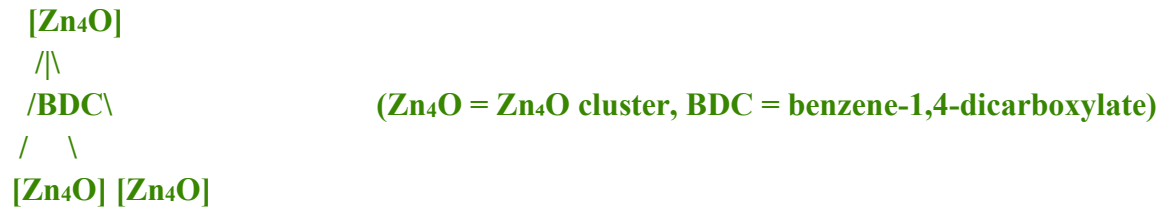
4.6 NH_2-MIL-125(Ti)

NH_2-MIL-125(Ti) features titanium(IV) ions forming $Ti_8O_8(OH)_4$ clusters, linked by amine-functionalized 1,4-benzenedicarboxylate (NH_2-BDC) ligands. The amine groups enhance CO_2 interactions, and the structure has smaller pores ranging between 0.6–0.8 nm (Bio particles, 2023).



4.7 MOF-5

MOF-5 consists of Zn_4O clusters as metal nodes, connected by 1,4-benzenedicarboxylate (BDC) linkers. The tetrahedral Zn_4O units form a cubic framework with moderate pore size (1 nm) and high surface area (1884 m^2/g).



4.8 Ni-MOF-74

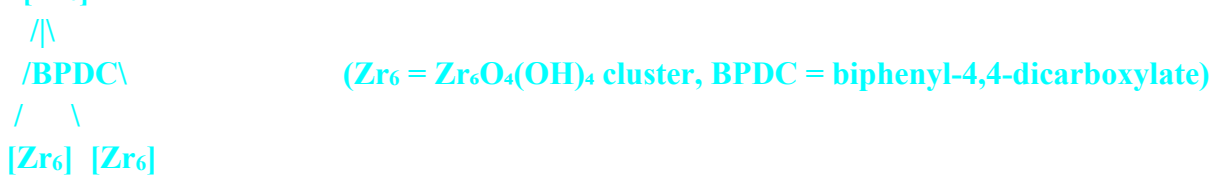
dimensional rod-like chains, coordinated with 2,5-dihydroxyterephthalic acid (DHTA) linkers. The open Ni sites enhance CO_2 adsorption in its honeycomb-like structure with pore size of 1.1 nm (Nagappan, et al., 2012).

4.9 MOF-200

MOF-200 uses Zn_4O clusters, coordinated with 1,3,5-tris(4-carboxy[1,2-biphenyl]-4-yl)-benzene (BCBPB) linkers (Man, et al., 2019). The extended linkers create a highly porous framework with a pore size of 4.8 nm (Furukwa, 2010).

4.10 UiO-67(Zr)

UiO-67(Zr) features zirconium (IV) ions forming $Zr_6O_4(OH)_4$ clusters, linked by biphenyl-4,4-dicarboxylic acid (BPDC) ligands (Bailey et al., 2021). The robust Zr clusters create a stable framework with larger pores sizes of 2.114 nm, ideal for gas adsorption (Zhan, et al., 2018)



5. Conclusion

A review was conducted on ten different MOFs with regard to their potential for carbon dioxide adsorption capabilities. Through a careful evaluation and desktop analysis of each MOF's structural and chemical composition and modification process, adsorption capacity and ability to selectively capture carbon dioxide, the review determined that MOF-177 exhibited the most promising attributes for effective carbon dioxide capture. MOF-177 structure which contains zinc oxide centres interconnected by terphenyl dicarboxylate ligands, facilitates highly favorable interactions and uptake of carbon dioxide molecules. It can be concluded based on the review that MOF-177 possesses the greatest suitability for practical applications involving post- combustion carbon dioxide separation technologies or carbon dioxide capture from industrial flue gasses and natural gas mixtures compared to the other nine MOFs reviewed. MOF-177 represents a significant step forward in the development of advanced porous materials for carbon dioxide sequestration and mitigation of greenhouse gas emissions. Their

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