



SYNTHESES AND APPLICATIONS OF METAL-ORGANIC FRAMEWORKS MATERIALS : A REVIEW

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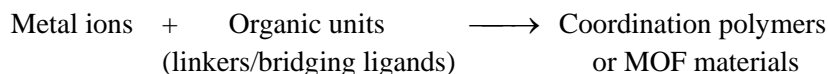
ABSTRACT

Metal-organic frameworks are a class of porous polymeric material, consisting of metal ions linked together by organic bridging ligands. They are recently emerging on the interface between molecular coordination chemistry and material science. The very high sorption behaviors, and excellent reversibility kinetics is a result of their many favourable attributes, such as reproducible and facile syntheses, high porosity, chemical modification and amenability to scale-up. However, these materials can be employed in different applications depending on the appropriate choice of metal ions and the organic compound, and also can function best at very low temperature. The synthetic approaches to these materials, investigations of their properties and applications are reviewed.

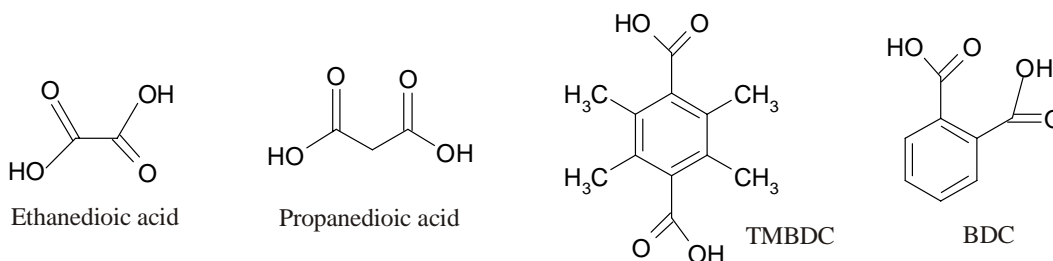
Key words: Sorption, Gas storage, Metal-organic frameworks, Microporous materials.

INTRODUCTION

A metal-organic framework (MOF) material can be thought of as the composition of two major components: a metal ion (or cluster of metal ions) and an organic molecule called a linker (or bridging ligands)¹.



The organic ligands or linkers are groups that can donate multiple lone pairs of electrons (polydentate) to the metal ions, whereas the metal ions are made up with vacant orbital shells that can accept these lone pairs of electrons to form a metal-organic framework material. The molecular structures of organic linkers used for the synthesis of MOF materials are shown in Fig. 1 below:



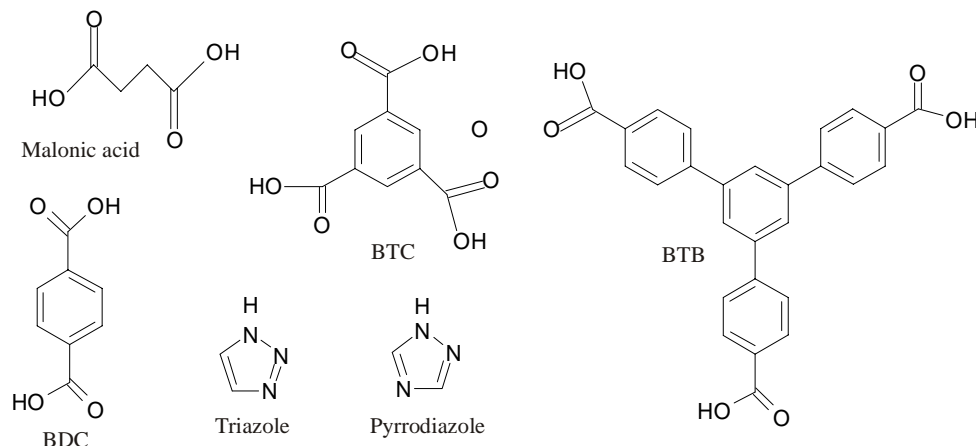


Fig. 1: Structural representation of organic linkers

Abbreviations: BDC-benzene-1,4, dicarboxylate, BTB-benzenetricarboxylate, TMBDC-tetramethylbenzene-1,4-dicarboxylate.

Metal organic framework (MOF) materials are potential storage materials (energy carriers) suitable for gas uptake such as hydrogen, carbon dioxide, methane etc.² The design of low-cost, light-weight metal-organic framework (MOF) materials can probably reduce the escalating atmospheric level of carbon dioxide caused by fossil fuels³.

Metal-organic framework materials are well-defined, adjustable and highly porous materials (see Fig. 2 below), with spatial confinement, often crystalline, sensitive to air and resistant to structural collapse upon heating⁴.

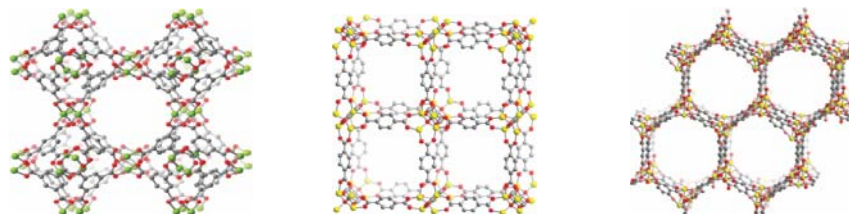
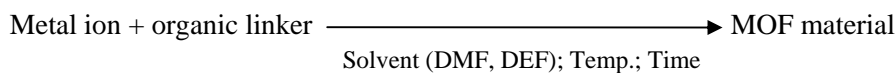


Fig. 2: Crystal structures of metal organic framework materials

Either infinite extended polymeric or discrete closed oligomeric structures can arise from the synthesis, depending on the nature of the system used. The most detailed structural information is obtainable from single crystal X-ray crystallography⁵.

Synthesis: Two methods are adopted, namely conventional and unconventional methods.

1. Conventional synthesis is frequently performed by Solvo-thermal methods; i.e heating a mixture of organic linker and metal salt in a solvent system that usually contains formamide functionality⁶. The materials produced from this method are thermally unstable or reactive to solvent used, and this could lead to breaking of bonds or creation of metal sites for guest species such as gases to gain access into the framework's micropores/mesopores/macropores. In some cases, assisted microwave-solvothermal synthesis can be used, to monitor or regulate the temperature whilst the reaction is in progress.



A representation of MOF synthesis flowsheet is shown in figure 3 below. Precipitation and crystallization follows immediately after heating a mixture of a chosen metal ion and organic linker in the presence of a solvent. Thereafter, filtration and drying follows after word.

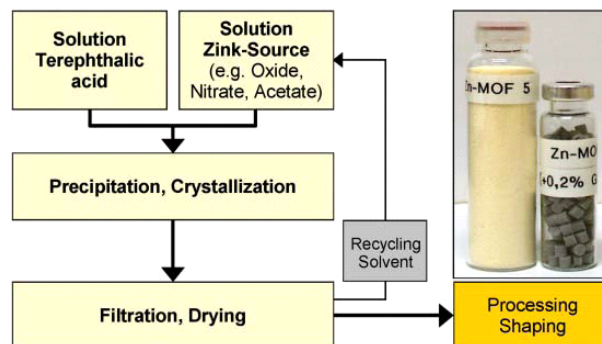
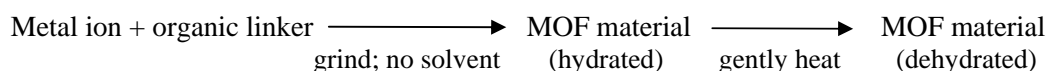


Fig. 3: The synthesis flowsheet of $Zn_4O(BDC)_3$

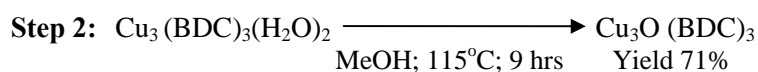
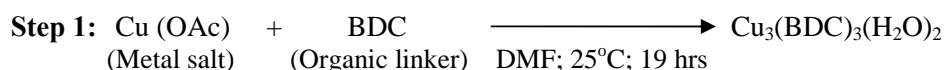
The slow growth of crystal allows defects to be re-dissolved, resulting in a material with millimeter-scale crystals and equilibrium product⁶.

2. Unconventional Synthesis is frequently performed by grinding a mixture of organic linker and metal salt in an agate mortar and pestle or in a ball mill and in the absence of solvent⁷. This method is known as mechanochemical method.

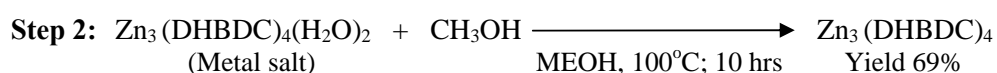


The metal sites are exposed when the mixture is gently heated, thus allowing gases such as hydrogen to bind at these sites. The mechanochemically initiated reactions are comparable to those of solvent reactions. The method is known to be environmentally-friendly and can possibly give high yield of products^{8,9}.

Review: One of the early MOF materials are metal terephthalate such as $Cu_3O(BDC)_3$ synthesized by Cueto et al.¹⁰ by using a metal salt with terephthalic acid (BDC) as organic linker or bridging ligand and dimethylformamide (DMF) as solvent. The copper terephthalate has a large surface area and high sorption behavior.

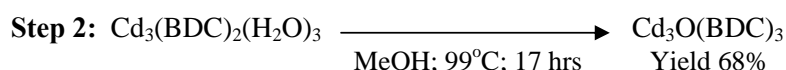
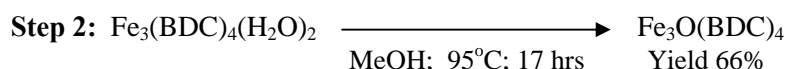


Jefrey et al.¹¹ synthesized $Zn(DHBDC)$ by using zinc acetate with 2,5-dihydroxyterephthalic acid – DHBDC (239 mg, 1.2 mmol) as organic linker and 20 mL dimethylformamide as solvent. The DHBDC was added to the zinc acetate (686, 3.12 mmol) continuously while stirring over 10 minutes.

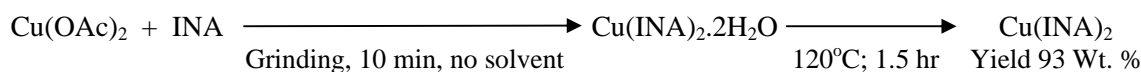


The reaction was monitored by PXRD analysis. The simulated PXRD shows pure Zn(DHBDC)(OAc)₂. The product in step 1 was centrifuged and the mother liquor was decanted and washed with 320 mL DMF, and immersed in 220 mL methanol overnight, later decanted and was heated over 100°C for 10 hours. Thereafter, the product was cooled to room temperature over 2 hours giving a yield of 269.5 mg, 69% and high sorption behavior.

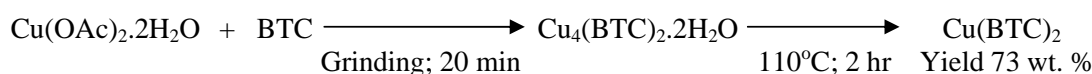
The following metal terephthalates such as Fe, Cd, Cu, Ag, Zn were synthesized by Sherif et al.¹² The method above was adopted for the synthesis.



Pichon and James et al.⁹ described the synthesis of crystalline MOF material called [Cu(INA)₂]- (copper isonicotinate) by simply grinding copper acetate and INA (isonicotinic acid) in the absence of solvent with a ball-mill. The formation of a reaction product [Cu (INA)₂] was indicated by a change in colour from green to blue and the characteristic colour of acetic acid, released as a by-product. The progress of the reactions was monitored by XRPD and X-ray crystallography.



Braga et al.⁸ synthesized Cu₃(BTC)₂ in this way - solventless synthesis- by using copper acetate and BTC. The reaction is quick with quantitative yield, the metal-complexes of the ligand was monitored with XRPD and elemental analysis. The morphology synthesized product (Cu₃(BTC)₂) was the same as the industrial made, Basolite C300 (Copper benzene-1,3,5-tricarboxylate).



Applications

1. Gas Separation: MOF materials could possibly be used to separate mixtures of rare gases by adsorption¹². For example in cryogenic air separation units, xenon and krypton was separated. Xenon was separated as narcotic medical gas and krypton as filler for lamp industry.

2. Catalysis: MOF materials can act as catalysts. Successful catalysis on zinc-containing MOFs in the activation of alkoxides and carbon dioxide into polypropylene carbonate has already been reported¹². However, the shape, size selectivity, accessible bulk volume, and porous architecture of MOF materials make catalysis possible.

3. Gas Storage: Nathaniel et al.¹³ reported the use of Zn₄O(BDC)₃ (BDC = 1,4-benzenedicarboxylate) with a cubic three-dimensional extended porous structure as storage material at room temperature. The Zn₄O (BDC)₃ adsorbed hydrogen up to 4.5 wt. % (17.2 hydrogen molecules per formula unit) at 78 K and 1.0 wt. % at room temperature and pressure of 20 bar.

4. Hydrogen storage. Many reports have dealt with the use of hydrogen as a fuel and its storage in metal organic framework materials. (Yaghi et al.¹⁴). Properties regarding hydrogen storage capacity of some MOF materials are shown in Table 1 below.

Table 1

MOF Material	S _{BET} [m ² g ⁻¹]	S _{Langmuir} [m ² g ⁻¹]	H ₂ Uptake at 77 K (wt. %)	Pr. [bar]	Max ΔH ^o _{ads} [KJ/mol]
Cu ₃ (btc) ₂	1507	2175	2.5	1	6.8
NaNi ₃ (OH)(sip) ₂	700	-	0.94	1	6.8
Zn ₂ (dhtp)	870	-	2.8	30	8.8
Ni ₂₀ (OH) ₁₂ [(HPO ₄) ₈ (PO ₄) ₄]	500	-	0.53	0.79	-
HCu[(Cu ₄ Cl) ₃ (btt) ₈].3.5HCl	1710	1770	4.2	90	9.5

Abbreviations: SA = apparent surface area; btt = 1,3,5-benzenetristetrazolate;
sip = 5-sulfoisophthalate; btc = 1,3,5-benzenetricarboxylate; dhtp = 2,5-dihydroxyterephthalate

The porosity data and H₂ storage properties for some microporous metal–organic frameworks with coordinatively unsaturated metal centers¹⁵.

Table 2

Material	Metal building unit formular	S _{BET} [m ² g ⁻¹]	S _{Langmuir} [m ² g ⁻¹]	H ₂ Uptake at 77 K (wt. %)	Pr. [bar]	Max ΔH ^o _{ads} [KJ/mol]
Li+@Zn ₂ (ndc) ₂ (diPyNI)	Li+ intercalation	756		1.63	1	6.1
Mg ₃ (ndc) ₃	Mg ₃ (O ₂ CR) ₆	10		0.46	1.2	9.5
Cr ₃ OF(btc) ₂	Cr ₃ (3-O)(O ₂ CR) ₆		2700	3.3	25	6.3
Mn ₃ (bdt) ₃	Mn ₃ (N ₄ CR) ₆	290		0.97	1.2	8.4
Ni ₂ (dhtp)	Ni(O ₂ CR, O) chains	-	1083	1.8	70	-
Cu ₂ (tptc)	Cu ₂ (O ₂ CR) ₄	-	2247	2.52/6.06	1/20	-
Cu ₂ (bptc)	Cu ₂ (O ₂ CR) ₄	-	1830	2.47	1	-
Zn ₃ (bdt) ₃	Zn ₃ (N ₄ CR) ₆	640	-	1.46	1.2	8.7
Mo ₃ (btc) ₂	Mo ₂ (O ₂ CR) ₄	1280	2010	1.75	1	-
Cu ₃ (tatb) ₄ (noncatenated)	Cu ₂ (O ₂ CR) ₄	-	2700	1.62	1	-
Cr ₃ OF(bdc) ₃	Cr ₃ (3-O)(O ₂ CR) ₆	-	5900	4.5	30	-

Abbreviations: ndc = 2,6-naphthalenedicarboxylate; diPyNI = N,N'-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide; btc = 1,3,5-benzenetricarboxylate; bdc = 1,4-benzenedicarboxylate;
bdt=1,4-benzeneditetrazolate; dhtp =2,5-dihydroxyterephthalate; bptc = 3,3',5,5'-biphenyltetracarboxylate;
tptc=3,3'',5,5''-terphenyltetracarboxylate

6. Gas adsorption: The highly porous nature of MOF materials is manifested by their large specific surface areas and capacity to adsorb gases. The gas adsorption and vapour experiment was carried out for the separation and removal of harmful vapors i.e benzene on M (btc) species (M = Ni, Zn). The specific surface areas for Ni(btc) and Zn(btc), respectively, as obtained by the BET method are shown in Table 3 below¹⁶.

Table 3

Compound	BET (m ² g ⁻¹)	N ₂ (mmol g ⁻¹)	Ar (mmol g ⁻¹)	CO ₂ (mmol g ⁻¹)	CH ₄ (mmol g ⁻¹)	Benzene (mmol g ⁻¹)	Porevads (cm ³ g ⁻¹)	Porevercryst (cm ³ g ⁻¹)
Ni (bpb)	1600	12.0	13.7	10.0	3.7	5.8	0.38	0.67
Zn (btc)	2200	22.5	22.7	9.1	2.4	3.8	0.71	0.92

5. Gas Purifications: Attempts have been made to remove tetrahydrothiophene – THF (sulphur odourant component) from natural gas, by using Cu-BTC-MOF¹⁵. In a fixed bed reactor vessel (inner diameter of 10 mm) about 10 g of granular Cu-MOF of a particle size fraction of 1–2 mm were thoroughly packed. Before twinkle of an eye, at a temperature of 25°C, a gas stream of methane was separated from tetrahydrothiophene (THT), which was fed over the packing of granular Cu-MOF. The effluent was analyzed by means of gas chromatography, and it confirmed breakthrough had occurred.

6. Ion-Exchange: This is the introduction or impregnation of extra equivalents of metal ions to to an existing MOF to produce materials of different types. E.g M₃[(Mn₄Cl)₃(btt)₈-(CH₃OH)₁₀]₂· was separated with MCl₂ where (M=Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺; x= 0–2). The new materials exhibit large variation in the H₂ adsorption enthalpy, ranging from 8.5 KJ mol⁻¹ for the Cu²⁺-exchanged frameworks to 10.5 KJ mol⁻¹ for the Co²⁺-exchanged phase¹⁶.

7. Sensor Materials in the gas phase: The detection of hydrophilic gases like ethanol, methanol at a temperature range of 120°C-240°C and frequency range (1 Hz -1 MHz) can be achieved by using a sensor spectroscopy. Cross sensitivity of the MOF on ethanol and methanol can be evaluated and compared to the relative sensor response for 1 vol % of the interfering gas species¹⁷. The sensor response can be determined by impedance-derived measurands (|Z|, Z', Z'', and C) at 1 Hz¹⁸.

$$CSF_{Interfering\ gas} = \frac{|Z(C_{interfering\ gas})| - |Z(C_{interfering\ gas} = 0)| \cdot 1/C_{interfering\ gas}}{|Z(C_{H_2O})| - |Z(C_{H_2O} = 0)| \cdot 1/C_{H_2O}}$$

CSF = cross sensitivity factor. The absolute value |Z| = impedance response

CONCLUSION

Several reports and attempts have shown that MOF materials can be used for gas storage such as carbon dioxide capture, for gas separations, as sensor materials and as catalysts. Exchange of the diethylformamide solvent with a more volatile solvent (chloroform) gives a small surface area (470 m² g⁻¹) suitable for gas adsorption or separation. BET (Brunauer–Emmett–Teller) equation and Langmuir equation can help to evaluate the adsorption isotherm of gases and surface areas in the materials' surface sites at the temperature of adsorption. Thermally driven removal of the solvent could lead to the collapse of the inter-particle mesoporosity, which aids mass transport of the guests to access micropores; this could create lattice points for effective adsorption of gases.

Increasing effort should be put forth to use MOF materials as adsorbent for oil spillage in Nigeria. More research and rapid effort should continue on how to develop a detailed characterization of MOF materials; study the interaction between H₂, Methane, CO₂ and a number of existing MOFs; compute adsorption isotherms and transport diffusivities of pure and mixed gases in various MOF from atomic-scale simulations; develop a macroscopic model for transport of gas mixtures through a model MOF membrane; identify candidate structures that increase the selective permeability of CO₂ through MOF membranes and to

bring the operating conditions closer to ambient temperature and pressure purposely for an application in automobile industries.

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