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Metal Organic Frameworks (MOFs): An Overview of Synthesis Methods

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Abstract

Metal organic frameworks (MOFs) are crystalline porous organic and inorganic hybrid materials composed with metal centers and organic linkers, creating one-, two-, or three-dimensional networks with high porosity and surface areas that make the compounds very useful in adsorption/separation, catalysis, sensing luminescence, and biomedical applications. This chapter presents a comprehensive, up-to-date overview of the synthesis methods, including conventional solvothermal/hydrothermal synthesis, microwave-assisted, electrochemical, sonochemical, and mechanochemical synthesis of currently available MOFs with specific examples. Recently, newly attempted ionothermal, dry-gel conversion, and microfluidic synthesis methods are also utilized for synthesizing more environmentally benign MOFs. In most of the methods, solvents play an important role, whereas mechanochemical synthesis involves solvent less process or uses a minimum amount of solvent. Most of the MOFs have been synthesized by using aromatic ligands as linkers in conjuction with metal nodes of transition metal ions, alkaline earth metal ions, rare earth metal ions and nitrate, sulphate, acetate, chloride and oxides of metal.

Keywords: *Electrochemical; Mechanochemical; Metal Organic Frameworks (MOFs); Microwave; Solvothermal/Hydrothermal; Sonochemical*

Introduction

In the last few decades, metal organic frameworks (MOFs) have attracted great attention from scientists for their wide range of applications in energy storage, gas adsorption, hydrocarbon adsorption and separation, sensors, catalysis, magnetic and electronic devices, drug delivery, cancer therapy, photoluminescence, etc. due to their high surface area, high pore volumes, and high metal content (Furukawa *et al.,* 2013; Safaei *et al.,* 2019; Chattopadhyay, Mandal & Maiti, 2024). MOFs are crystalline materials made up of organic and inorganic hybrid materials that are formed by joining metals with organic linkers. The organic linkers are called organic secondary building units (SBU), whereas the metal centers act as joints in the MOF structure. The structure has high porosity due to the extended size of inorganic metals and the length of the linker used (Lee, Kim & Ahn, 2013; Wang, 2017). Different types of metals and

ligands are used to synthesize MOFs as secondary building blocks for their flexibility in physical and chemical properties. The atomic-level structural uniformity in network topology and geometry, as well as the excellent chemical stability of MOFs, make them have great potential for their various applications. Different first-row transition metals, such as Co^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+} are used as joints in the formation of MOFs compounds. The synthesis of MOFs also incorporates alkaline earth metal ions and rare earth metal ions (Dey *et al*., 2014). Since MOFs compounds are dependent on the choice of metal ions and ligands, different ligands are used to create large volume and high porosity in the cavity of the MOFs. Sometimes, nitrate, sulphate, acetate, chloride and oxides of metal are also used as precursors for the synthesis of MOFs (Soni, Bajpai & Arora, 2019). The reactivity of the pores is enhanced by incorporating organic units and metal organic complexes through reactions with linkers in post-synthetic modification of MOFs. This chapter comprehensively reviewed different synthesis methods for MOFs with suitable examples (Table 1).

Table1: Some selective MOFs with their synthesis methods

Synthesis method	**MOF**	**Metal salt**	**Ligand**	**Solvent**	**Conditions**	**Ref**
Slow evaporation	$[Cu(pya)_2(H_2O)_2]_n$	$Cu(ClO_4)_2 \cdot 6H_2O$	Hpya	$MeOH/H_2O$	7 days	Du, Li & Zhao, 2006
	$[Hg(pya)Cl]_n$	$HgCl_2$	Hpya	$MeOH/H_2O$	21 days	Du, Li & Zhao, 2006
	MOF-Co/PDA	$CoCl_2 \cdot 6H_2O$	PDA	H_2O/ Pyridine	14 days	Murinzi, Hosten & Watkins, 2017
Slow Diffusion	$Zn_3(BDC)_3 \cdot 6CH_3OH$	$Zn(NO_3)_2 \cdot 6H_2O$	H_2BDC	DMF/Methanol/ n-propanol	12 days	Li *et al.,* 1998
	$[Ag(dpma)(H_2O)](NO_3)$	$AgNO_3$	dpma	$MeOH/H_2O$	14 days	Wu, Chao & Zhong, 2013
Solvothermal	MOF-5	$Zn(NO_3)_2 \cdot 6H_2O$	H_2BDC	DMF/Chlorobenzene	120ºC, 2 days	Eddaoudi *et al.,* 2002
	$[Mg_4(bdc)_4(DEF)_4]_n$	$Mg(NO_3)_2 \cdot 6H_2O$	H_2BDC	DEF	120ºC, 18 hrs	Biswas *et al.,* 2016
	UiO-66	$ZrCl_4$	H_2BDC	DMF	120ºC, 2 days	Abid *et al.,* 2012
	IRMOF-3	$Zn(NO_3)_2 \cdot 4H_2O$	H_2BDC-NH_2	DEF	85ºC, 4 days	Millward & Yaghi, 2005
	Bi-TMA	$Bi(NO_3)_3 \cdot 5H_2O$	H_3TMA	DMF/ Methanol	120ºC,1 day	Nguyen *et al*., 2021
Hydrothermal	HKUST-1	$Cu(NO_3)_2 \cdot 3H_2O$	H_3BTC	$EtOH/H_2O$	180ºC, 12 hrs	Chui *et al.,* 1999
	Hf-MOF-808	$HfClO_2$	H_3BTC	H_2O/ CH_3COOH	100ºC, 37 hrs	Bohigues *et al.,* 2021
Microwave-assisted	UiO-66	$ZrCl_4$	H_2BDC	Acetone	80ºC, 6 hrs	Yahia *et al.,* 2024

	MOF-808	$ZrCl_4$	H_3BTC	Acetone/ H_2O	95ºC, 5 hrs	Yahia *et al.,* 2024
	Cr-MIL-100	Metallic Cr with HF	H_3BTC	H_2O	220ºC, 4 hrs	Jhung, Lee & Chang, 2005
	HKUST-1	$Cu(NO_3)_2 \cdot 3H_2O$	H_3BTC	EtOH	140ºC, 1 hr	Seo *et al.,* 2009
	ZiF-8	$Zn(NO_3)_2 \cdot 6H_2O$	HMeIm	DMF	140ºC, 3 hrs	Park, Park & Jhung, 2009
	Fe-MIL-53	$FeCl_3 \cdot 6H_2O$	H_2BDC	DMF	150ºC, 10 mins	Horcajada *et al.,* 2006
	Co-MOF-74	$Co(NO_3)_2 \cdot 6H_2O$	H_4DHBDC	DMF/ EtOH/H_2O	130ºC, 1 hr	Cho *et al.,* 2012
Electrochemical	HKUST-1	Bulk Cu plate	H_3BTC	MeOH	12-19 V, 1.3A, 150 mins	Mueller *et al.,* 2006
	Al-MIL-53	$Al(NO_3)_3 \cdot 9H_2O$	H_2BDC	H_2O/DMF	90ºC, 10 mA	Martinez Joaristi *et al.,* 2012
	Al-MIL-53-NH_2	$Al(NO_3)_3 \cdot 9H_2O$	H_2BDC-NH_2	H_2O/DMF	90ºC, 10 mA	Martinez Joaristi *et al.,* 2012
	Mn–DABDC	Mn strips	DABDC	DMF/H_2O	20-22ºC, 70 mA, 2 hrs	Asghar *et al.,* 2021
	Fe-MIL-101	$FeCl_2$	H_2BDC/ $TBAPF_6$	DMF	0.75 V, 14h	Wu *et al*., 2021
Sonochemical	MOF-5	$Zn(NO_3)_2 \cdot 6H_2O$	H_2BDC	NMP	60W, 30 mins	Son *et al.,* 2008
	Mg-MOF-74	$Mg(NO_3)_2 \cdot 6H_2O$	H_4DHBDC	DMF/ EtOH/H_2O	500W, 1 hr	Yang *et al.,* 2012
	MIL-53(Fe)	$FeCl_3 \cdot 6H_2O$	H_2BDC	DMF	70ºC, 2 hrs	Lee, Ahn & Kwak, 2022
Mechanochemical	HKUST-1	$Cu(OAC)_2 \cdot 6H_2O$	H_3BTC	-	15 mins	Pichon & James, 2008
	ZIF-8	ZnO	HMeIm	DMF	5-60 mins	Beldon *et al.,* 2010
	ZIF-4	ZnO	HIm	DMF	5-60 mins	Beldon *et al.,* 2010
	MOF-74	ZnO	H_4DHBDC	DMF	2-90 mins	Beamish-Cook *et al.,* 2021

Hpya = 4-pyridylacetic acid, PDA = 2,6-pyridinedicarboxylic acid, H_2BDC = 1,4-benzenedicarboxylic acid, dpma = Di(3-pyridylmethyl)amine, H_2BDC-NH_2 = 2-amino-1,4-benzenedicarboxylic acid, H_3TMA = trimesic acid, H_3BTC=1,3,5-benzenetricarboxylic acid, HMeIm = 2-methyl imidazole, H_4DHBDC = 2,5-dihydroxy-1,4-benzenedicarboxylic acid, DABDC = 2,5-diaminoterephthalic acid, HIm = imidazole.

Methodology

Slow evaporation method

The slow evaporation method is a conventional method where the crystallization of MOFs starts at room temperature by evaporating solvents, making the solution more concentrated. The process needs no external energy, but the process is too slow to get the crystals. The process can be faster by using different solvents or mixtures of

solvents that dissolve the starting reagents, and the low-boiling solvents evaporate more quickly. The major advantage is that the reaction takes place at room temperature (Du, Li & Zhao, 2006).

Slow diffusion method

The slow diffusion method is applied when it is difficult to get a single crystal of MOFs by mixing metal ions and ligand solutions at room temperature. The gentle, steady diffusion of two solutions of metal ions and ligands in appropriate portions of solvents forms single crystals over time as two layers of different densities of solvents diffuse to generate larger and better-quality single crystal at the interface of two solutions (Li *et al.,* 1998; Wu, Chao & Zhong, 2013). This method is useful for microcrystalline powder compounds that are not soluble.

Solvothermal/ hydrothermal synthesis

In solvothermal synthesis, the metal salt and organic linker are mixed in a solvent and heated in glass vials (low-temperature reactions), whereas for high-temperature reactions, Teflon lined auto-clave is used (Wang & Ying, 1999). When water is used as a solvent, the process is called hydrothermal synthesis. The boiling point of the solvents should be high for a solvothermal reaction, in which temperature, pressure, solvent composition, and reagent concentration are the important parameters to get the MOFs (Lee, Kim & Ahn, 2013). The most commonly used solvents are dimethyl formamide (DMF), diethyl formamide (DEF), dimethyl sulphoxide (DMSO), dimethylacetamide (DMA). Different mixtures of solvents are used to avoid the difficulties of dissolving the starting reagents.

Microwave-assisted synthesis

Microwave-assisted synthesis is a rapid process in which the energy is provided in the form of a microwave. It is generally useful in organic synthesis, but in recent times, nanoporous compounds have also been synthesised by using microwaves. In this process, the heating time is generally one hour for getting the nanosized crystals after heating the solution with microwave (Lee, Kim & Ahn, 2013). The alternative name of the process is microwave-assisted solvothermal synthesis for the preparation of MOFs. Fast crystallisation along with phase selectivity, particle size distribution, and morphological controls, are the major advantages of the process.

Electrochemical synthesis

Electrochemical synthesis involves anodic dissolution as a metal source instead of metal salts. Anodic dissolution is the electrosynthesis method in which a high anodic voltage or current is applied to the electrode immersed in supporting electrolytes and organic linkers and metal gets oxidised to metal ions and released into a solution

containing organic linkers (Dey *et al.,* 2014; Ren & Wei, 2022). Mueller and co-workers (2006) introduced the process. The metal ions and the organic linker react on the surface of the electrode as a thin layer of MOF. Different factors, such as the nature of solvents, electrolyte concentration, applied voltage, electro deposition time etc. govern the crystallization process. Polar protic solvents play an important role in electrochemical synthesis, as the solvent ensures hydrogen generation and avoids the reduction of metal ions on the cathode. The nucleation of MOF crystals increases with increasing the rate of applied voltage and regulating the crystal size.

Sonochemical synthesis

Sonochemical synthesis is a rapid, efficient, and promising method in which high temperature and pressure are generated and high-quality MOFs are produced in a short period compared to other conventional methods, as ultrasonic waves can facilitate the nucleation and growth of MOFs in high energy conditions produced by the wave through cavitation (formation of bubbles, growth and collapse due to altering pressure) (Dey *et al.,* 2014). Sonochemical synthesis can produce narrow size distributions of MOFs and it is useful in different applications.

Mechanochemical synthesis

Mechanochemical synthesis is a process in which mechanical force is produced by milling or grinding solid starting materials and thus the chemical reactions proceed with minimal amounts of solvents or without solvents at all. The process is the most environment friendly methodology, as a minimum amount of toxic solvent is used or without using solvents, the reactions are most sustainable for the earth. The solid-solid reaction has potential advantages to get high amounts of MOFs (Stock & Biswas, 2012). However, in purification steps, solvents are used despite solvent-free or solvent less mechanochemical synthesis. This mechanochemical route is considerable interest for the construction of bonds through environment friendly process in modern synthetic chemistry.

Beside these methods as discussed above, Ionic Liquids (ILs) have attained great attention because of their unique properties such as excellent solvating properties as well as high thermal stability and easy recyclability and used as solvent for chemical synthesis (Himeur *et al.,* 2010; Pérez Fernández *et al.,* 2019; Azbell *et al.,* 2023). The majority of the researchers have used ILs derived from 1-alkyl-3-methylimidazolium. Other synthetic method Microfluidic MOF Synthesis (Bendre *et al.,* 2023) is also a continuous, faster and viable processes for MOF synthesis. Dry-gel conversion (DGC) synthesis method has also been used in the preparation of MOFs (Kim, Lee & Ahn, 2013).

Discussion

Different synthetic methods have been used in MOFs synthesis, most of them are liquid phase synthesis, where metal salts and ligand solutions or solvents are added to the mixture. Solvent plays an important role in determining the geometry and shape, i.e., the crystallization process for favouring thermodynamics and activation energy for the reaction process. The reactivity, solubility, stability constant etc. greatly influenced by the solvent used by the solvent used for a particular reaction (Dey *et al.,* 2014). Therefore, different solvents in the same ratio of reactants can proceed to form different MOFs. Researchers also attempted to synthesise MOFs in the solid phase, which is quicker and easier, but the success of obtaining a single crystal is comparatively low. Slow evaporation and slow diffusion methods are well suited for the researchers, but it takes a long time to get single crystals of MOFs, depending on the solvents used. Today, the solvothermal/hydrothermal method is quite common and convenient for synthesising an enormous number of MOF compounds (Table-1). Some of them are MOF-5 (Eddaoudi *et al.,* 2002), UiO-66 (Abid *et al.,* 2012), IRMOF-3 (Millward & Yaghi, 2005), HKUST-1 (Chui *et al.,* 1999). Microwave-assisted synthesis, electrochemical synthesis, and sonochemical synthesis are also used as alternatives to MOF synthesis (Dey *et al.,* 2014; Lee, Kim & Ahn, 2013). Cr-MIL-100 (Jhung, Lee & Chang, 2005) is the first MOF that has been synthesized via microwave method. HKUST-1 (Seo *et al.,* 2009), ZiF-8 (Park, Park & Jhung, 2009), Fe-MIL-53 (Horcajada *et al.,* 2006), Co-MOF-74 (Cho *et al.,* 2012), UiO-66 (Yahia *et al.,* 2024) and MOF-808 (Yahia *et al.,* 2024) are also well-known microwave-assisted MOFs. The process is very useful as both compounds have better CO_2 adsorption abilities. Several metal ions, such as Fe^{3+}, Al^{3+}, Cr^{3+}, V^{3+} containing MOFs have been reported using the microwave method. The first and most often electrochemically synthesized MOF is HKUST-1 or $Cu_3(BTC)_2$ (Mueller *et al.,* 2006). Al-MIL-53 (Martinez Joaristi *et al.,* 2012), Al-MIL-53-NH_2 (Martinez Joaristi *et al.,* 2012), Fe-MIL-101 (Wu *et al.,* 2021), and Mn-DABDC (Asghar *et al.,* 2021) are also synthesized by electrochemical method. Aluminium containing MOFs have been synthesized by using $Al(NO_3)_3.9H_2O$ as metal salt and 1,4-benzene dicarboxylic acid or 2-amino-1,4-benzene dicarboxylic acid or 1,3,5-benzenetricarboxylic acid as ligand. Using sonochemical irradiation, MOF-5 (Son *et al*., 2008) compounds (5-25 mm crystals) obtained in 1-methyl-2-pyrrolidinone (NMP) in 30 min, compounds are similar to the MOF-5 crystals that are obtained in solvothermal or microwave methods. Mg-MOF-74 (Yang *et al.,* 2012), MIL-53(Fe) (Lee, Ahn & Kwak, 2022) are also synthesized by sonochemical method. Using mechanochemical synthesis method, HKUST-1 was successfully obtained without using a solvent (Pichon & James, 2008). ZIF-8 was successfully synthesized by using ZnO and 2-methylimidazole in the presence of NH_4NO_3 in DEF solvent whereas ZIF-4 was successfully produced by using ZnO and imidazole in presence of $NH_4NCH_3SO_3$

using DMF as a solvent (Beldon *et al.,* 2010). MOF-74 was synthesized by using ZnO and 2,5-dihydroxy-1,4-benzenedicarboxylic acid in DMF solvent by mechanochemical process (Beamish-Cook *et al.,* 2021).

Conclusion

The porous coordination polymer or metal organic framework has been widely used in gas adsorption and desorption, separation, sensing, magnetism, catalysis etc. Different synthetic methods, such as slow evaporation synthesis, solvothermal/ hydrothermal synthesis, microwave-assisted synthesis, electrochemical synthesis, sonochemical synthesis and mechanochemical synthesis, have been applied to get porous crystalline MOFs. In most of the methods, solvents play an important role in the synthesis of MOFs as well as in deciding morphology of the MOFs. In solvothermal synthesis, the most common solvents are DMF, DEF, DMA, DMSO, ethanol/methnol, acetonitrile, and acetone, whereas in hydrothermal synthesis, water is used as solvent. MOFs having different morphology are obtained in same reaction condition with varying solvents as degree of deprotonation of organic linker is different in different solvents. Besides, reactions are greatly influenced by the temperature and pH of the reaction medium. The microwave-assisted synthesis of MOFs is comparable to that of conventional methods, but the progress of the reaction is very fast compared to hydrothermal methods. In the electrochemical synthesis method, there is no need to use metal salts, as metal ions are continuously supplied through anodic dissolution. Sonochemical synthesis involves homogeneous solution with formation and collapse of bubbles, termed acoustic cavitation, which produces high local temperature and pressure and results in a in a fine MOF crystal with a reduction in crystallization time. Mechanochemical synthesis, which is an environment-friendly method, produces a quantitative number of small MOFs in short reaction times and in this method, metal oxide is generally used as the starting material. In most cases, the solvent is minimized, or reaction is done without using a solvent. Using Ionic Liquids as a solvent, Microfluidic MOF Synthesis and Dry-gel conversion synthesis are now a days getting attention for more environmentally benign MOF synthesis. The reported methods are confined to very small-scale production with crystal structure analysis and the MOFs that were reported are mostly unstable except Zr-containing MOFs. Therefore, researchers should focus on producing large-scale stable crystals that will be highly demanded in industry.

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