

Synthetic approaches and applications of Metal–organic frameworks: A review

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Abstract

Metal–organic frameworks (MOFs) are the typical class of ultrahigh porous materials consisting of metal clusters bonded with organic ligands to form normally three-dimensional structures having enormous internal surface areas. Due to the wider surface area, huge pore size, crystalline nature, and tunability with variable structures, make MOFs for potential applications in clean energy storage, gas storage and delivery, drug delivery, rechargeable batteries and supercapacitors. They are also applied in separation membranes, thin-film devices, constant and inexpensive catalysis, bifunctional electrocatalyst and biomedical imaging. Furthermore, the application of MOFs in different fields such as the removal and separation of toxic compounds from gas and liquid, environmental applications, biological and medical applications, and optoelectronic equipment is included. In this review various properties of MOF, their synthesis techniques, structure and various applications have been discussed. The future scope is discussed along with opportunities for the synthesis and application in multidisciplinary research area.

Keywords: Metal–organic frameworks, MOF, solvothermal, porosity, gas storage.

1. Introduction

Since last five decades porous materials and metal organic frameworks (MOFs) are being attracted by the researcher day by day due to its extensively growing interest in the field of green energy sector. Metal ions or clusters bonded with organic linkers to form one, two or three-dimensional structures are referred to as metal–organic frameworks (MOFs). The periodic cage like network, crystalline structures with high porosities and large surface areas promote their applications in various fields.

Different types of metal oxo clusters connected by multi-dentated organic ligands construct wide range of MOFs having high porosity and storage capacity. In the inorganic-organic hybrid constituents, the organic linkages are considered as organic Secondary Building Unit (SBU), which are called 'strut'. Whereas central metals are known as inorganic SBU which known as 'joints' in MOFs structures. If zeolite topology are maintained, MOFs framework having larger pores than zeolites. Larger pore size is due to expansion of volume of inorganic SBUs and the higher dimensional network by larger metal clusters. In addition with this, the longer linkage skeleton between inorganic SBU is developed from high porosity and longer organic ligands matched with large pore diameter. Variation of metal centres and multifunctional ligands produce MOFs as molecular building units and resulting a suitable flexibility as desirable physical

and chemical features [1,2]. The higher pore size and specific surface area of synthesized MOFs are considered as a better platform of static molecular catalysts on conductive materials. It also can be adjusted these materials to have high selectivity for a specific chemical reaction. Theoretical estimations predicted that the optical band gap of MOFs semiconductors are in the range of 1.0–5.5 eV. Interatomic bonds are not only confined limited to one dimensional plane; metal clusters and rigid organic molecules linked together by coordinative bonds and undergo self-assembled polymerization, that results crystal-like 3D structures [3,4]. Typically, MOFs appearance is familiar as replica of inorganic constituents like zeolites. So, this is a overview of the actual results in design and creation of extended hybrid constituents with suitable microporosity [5]. Unlike MOFs, Zeolites do not occur close control of the functionality, shape and size of pores. These materials that can be simply prepared, have uniformity, and are easily applied in different field of science and technology are recognized as the ideal MOF constituents. It can be met in a simple manner by selection of synthetic design and careful primary selection of metal centres and ligands. The vast diversity of such basic components can offer the infinite world of hybrid inorganic-organic combinations.

This review study is an attempt to present the structure, synthesis and applications of metal–organic frameworks (MOFs) briefly. Standardization the synthesis

conditions to have the suitable properties for real life application is the main challenge of this study.

2. Classification of MOFs

Depending on the component unit MOFs could be divided into following groups [6]. Functional diversity can be obtained by choosing the materials like metal oxides, carbon materials, polyoxometalates, polymers etc.

2.1 Isorecticular MOFs: When a series of aromatic carboxylates and $[\text{Zn}_4\text{O}]^{6+}$ SBU are mixed together to synthesize MOFs that is isorecticular type. These are octahedral microporous crystalline in nature. Recently such type isorecticular MOFs in form of nanosheet has been used in recognition of 2,4,6-trinitrophenol in wastewater for its magnificent sensitivity and selectivity [7]

2.2. Zeolitic Imidazolate Frameworks (ZIFs): Zeolite topological structured MOFs are synthesized using various elements having valence electrons and imidazole derivatives. ZIFs comprise ZIF-8, ZIF-L, ZIF-7, ZIF-67, ZIF-71, ZIF-90 etc. [8]. ZIFs have a larger pore size and selective chemical composition and thermal stability that are to develop novel MOFs. ZIF-8 MOF are used for detection of the HIV-1 DNA [9].

2.3. Porous Coordination Networks (PCNs): Porous coordination networks with a hole-cage-hole topology are stereo-octahedron materials. PCN-333, PCN-222, PCN-224, and PCN-57 are common example of this class [8]. Selective electrochemical sensing ability applied to detect DNA by using PCN-222. [10].

2.4. Materials Institute Lavoisier (MIL) MOFs. Using various elements having valence electrons and an organic ligands containing two carboxylic functional groups Materials Institute Lavoisier MOFs are formed. These type MOFs contain MIL-101, MIL-100, MIL-125, MIL-53, MIL-88, etc. [8]. MIL composites are used as chemical sensors to immobilize proteins.

2.5. Porous Coordination Polymers (PCPs). Porous polymeric materials are synthesized by carboxylic acid, pyridine, along with its derivative as the PBU and transition metal ions as the secondary building unit [8]. It exhibits magnificent characteristics in biomacromolecule separation and heterogeneous catalysis.

2.6. University of Oslo (UiO) MOFs. This type of MOF is based on dicarboxylic acid as the PBU and $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})$ as the SBU [11]. It is constructed by a solvothermal method from ZrCl_4 and BDC with both octahedral and tetrahedral pore cavity.

3. Synthesis Procedures

There are so many methods for synthesis of MOFs like traditional synthesis including solvothermal, microwave, electrochemical, mechanochemical and sono-chemical. Since last two decades, different synthetic schemes have developed to prepare MOFs that are classified as (i) conventional solvothermal methods, (ii) unconventional methods, and (iii) alternative methods.

3.1 Conventional methods: solvothermal and non-solvothermal method

Solvothermal and non-solvothermal methods are two classes of traditional synthetic procedure. The term 'solvothermal' indicates the use of any solvent and the process is more general than the term hydrothermal where water is used as solvent.

In conventional solvothermal synthesis, the mixture of metal ions and organic linkers in proper solvent is heated in glass vials in case of lower temperature reaction and in Teflon lined autoclaves or bomb reactor in case higher temperature ($> 400\text{ K}$) [12]. Some MOFs, such as MOF-177, MOF-74, MOF-5, HKUST-1 ZIF-8, are synthesized at ambient condition [13]

Non solvothermal synthesis occurs at below the boiling point at atmospheric pressure, whereas solvothermal synthesis is carried out at above the boiling temperature of solvent in typical chemical reactors at elevated pressure.

3.2 Unconventional methods: Mechanochemical method

The mechanochemical method for the preparation of MOFs is easier than the other methods. In this synthetic process, chemical reaction takes place through mechanical intramolecular bonds breaking. This reaction occurs at room temperature, where organic solvents could be avoided. Here metal salt and organic ligand is ground in ball mill or mixed well using mortar and pestle in the absence of solvent; then, ground mixture is heated to evaporate volatile compounds and water [14]. In 2006, the first MOF synthesis through mechanochemical approach was reported [15] and various kinds of MOFs are being prepared through this method.

3.3 Alternative synthesis methods

In addition to conventional methods, alternative methods have also been attempted. These routes can lead to adsorption properties as well as morphologies along with different crystallization rate, particle size, size distribution. Popular alternate routes are categorised as following:

3.3.1 Microwave synthesis

Under hydrothermal conditions; MOFs can be rapidly synthesized by assistance with microwave where small metal and oxide particles are produced. To prepare nanosized metal crystals, the temperature of the reaction mixture could be

elevated by subject to undergo microwaving for more than 24 hours. In this process, a substrate mixture with suitable solvent is kept in Teflon vessel, and the vessel placed in the microwave for adequate temperature and exposure time. Microwaves with frequencies between 300 to 300000 MHz are applied the electromagnetic radiation. Attention should be paid to the choice of appropriate solvent; particular microwave frequency input for uniform size nanocrystals. Microwave-assisted synthesis is focused on rapid crystallization and creation of nanoscale products desirable purity and polymorphs [16].

3.3.2 Electrochemical synthesis:

The electrochemical method has been widely applied for the synthesis of a vast number of MOFs. The first synthesized MOF was HKUST-1 (Hong Kong University of Science and Technology) by BASF in 2005 which was built up of dimeric metal units connected by benzene-1,3,5-tricarboxylate linkage molecules [17] electrochemical method is a green chemistry approach for MOFs preparation. MOFs using Cu, Zn, Mg, Co as cathode material 1,2,3-H₃BTC and 1,3,5-H₃BTC, H₂BDC and H₂BDC-(OH)₂ as linkers have been reported [18]. In electrochemical synthesis, metal ions generally supplied through anodic dissolution as a metal source instead of metals salts that interacts with the dissolved linker and a conducting salt. To avoid deposition of metal on cathode, protic solvents are used, but H₂ is evolved in this process. MOFs comprising ionic liquids as linker like [Zn(BIm)₂] and [Zn(MIm)₂] are also synthesized by electrochemical route [19]

3.3.3 Sonochemical synthesis:

Another important environment friendly method is sonochemical synthetic method where ultra sonic radiation (20 kHz – 10 MHz) is used for preparation of MOFs. When high energy ultrasound interacts with liquid, cavitation including bubble formation, growth and collapse under altering pressure takes place to provide energy with high temperature ($\approx 5000\text{K}$) and pressure (≈ 1000 bar). Chemical reaction take place when ultrasonic radiation is exposed to homogenous liquid. A MOF of [Zn₃(BTC)₂] synthesized sonochemically in ethanol which can be applied in selective sensing towards organoamine [20].

3.3.4 Layer by layer synthesis

Layer by layer method is applied for preparation of MOF thin films. This method is based on surface chemistry where organic surface is deep successively into the solutions of metal ion followed by organic linker. The orientation of thin film depends on that sequence through which the reactants are added [21]. Concentration of metal ions and surface termination control the growth of MOF film [22] and orientation depends on different functional groups such as -

COOH, -OH etc. present in organic linker. Fe-based MOF which is prepared by Fe-metallogels via gel degradation [23].

4. Major applications of MOFs

MOFs are applied in gas storage, catalysis, drug delivery, as sensor in technology due to its unique combination of crystallinity, porosity and existence of strong metal-ligand interaction.

4.1 Gas storage and separation:

Tuneable pore structure makes MOFs preferable compared to other porous materials. Most of the MOFs have been tried for H₂ storage. MOF-177 is one of the promising MOFs for storage purpose. It consists of [Zn₄O] clusters and 4,4',4''-benzene-1,3,5-triyltribenzoate (BTB) [24]. For huge surface area ($\sim 5000\text{ m}^2\text{g}^{-1}$) and larger pore volume it can uptake gravimetric H₂ of 7.5 wt % at 70 bar and 77 K. Similarly MOF-5 (IRMOF-1), which is prepared from [Zn(OAc)₂] and terephthalic acid having BET surface area of $3800\text{ m}^2\text{g}^{-1}$ uptakes up 7.1 wt% at 40 bar and 77 K. Other MOFs like MOF-210, MIL-101, NU-100, PCN-12, HKUST-1, NOTT-102 and MOF-205 are also good agent for H₂ storage [25-28].

Not only H₂ storage; MOFs are also useful for absorption CO₂ level in atmosphere. MOF-210 is the highest surface area ($10450\text{ m}^2\text{g}^{-1}$) which is synthesized from 4,4',4''-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)] tribenzoate (H₃BTE), biphenyl-4,4'-dicarboxylate (H₂BPDC), and zinc (II)nitrate hexahydrate [28] and performs uptake of CO₂ 74.2 wt%, 50 bar at 298K. Like MOF-210; MOF-200 has a similar CO₂ uptake capacity under same experimental conditions [28].

From gas mixtures, hazardous gases like CO and NO can be separated by using MOFs. The interaction between CO dipole and metal sites in MOFs are the main factor for preferential sorption. On the other hand, MOFs have been used for capturing NO gas.

4.2 Magnetism and its application:

MOFs show magnetism when paramagnetic transition metal are used along with suitable diamagnetic organic linkers. The MOFs having magnetic properties are termed as magnetic metal organic frameworks (MMOFs). Magnetic MOFs explored for the environmental application in removal of arsenic. Magnetic nanoclusters are applications in arsenic removal [29].

4.3 Sensing application:

When the ligands like naphthalene, anthracene, pyrene, perylene and stilbene are used for synthesis of luminescent MOFs are formed. Trivalent lanthanide metal ions like Eu, Tb, Dy, Sm, Nd, Gd, Er and Yb are widely used for synthesis of luminescent. Both the organic linker metal ions may rise to luminescence. MOFs (with aromatic unit) as luminescent

materials or phosphors are applied in cathode ray tubes, projection television, pH sensors [30], fluorescent tubes and X-ray detectors [31], small-molecule sensors [32,33], light concentrators for photovoltaic devices and high-efficient optics.

4,4-[(2,5-Dimethoxy-1,4-phenylene)-di-2,1-ethenediyl] bisbenzoic acid (H_2pvdc) and $[Yb_2(pvdc)_3(H_2O)_2] \cdot 6DMF \cdot 8.5H_2O$ with porous MOF network give sensitise emission in NIR range of the Yb^{3+} ions. [34]. The LnMOFs co-doped with multiple Ln^{3+} ions can be used as multicoloured light emitters.

4.4 Catalytic application:

MOFs have potential as heterogeneous catalyst. The MOFs, where metal centres are connected with labile organic ligands are good catalysts because labile ligands generally solvent molecules are removed leaving a free coordination position on the metal easily. In $[Cu_3(btc)_2]$ ($btc = 1,3,5$ -benzenetricarboxylate) material HKUST- coordinated water molecule leaves a coordination site on Cu upon thermal activation [35]. Nanoporous MOFs have been used catalyst in a good number of organic reactions. In Knoevenagel condensation reaction, MOFs like $[Cr_3F(H_2O)_2O(bdc)_3]$ [36] ($bdc = 1,4$ -benzenedicarboxylate) catalysed by using or $[Cd(4-btapa)_2(NO_3)_2]$ ($btapa = 1,3,5$ -benzene tricarboxylic acid tris[N-(4-pyridyl) amide]) have been used as catalyst [37].

4.5 Biomedical application:

MOFs are applicable in targeted drug delivery for high drug loading capacity and long release time. MOFs can load four times greater drug like ibuprofen adsorption (~ 1.4 gm / gm MOFs) with longer release time (21 days) [38]. Due to high stability, enormous porosity and large pore size; MIL class of metal-organic frameworks are good candidates for storing and controlled release of biologically active molecules. Fe(III) carboxylate MOFs such as MIL-8, MIL-88A, MIL-100 and MIL-101 have potential application in anticancer [39], antitumor and antiretroviral drugs delivery.

5. Conclusion

This report has covered the classification, synthesis methods and potential applications, of the metal-organic framework. Different methods including conventional solvothermal, unconventional and new methods like microwave-assisted, electrochemical, sonochemical, mechanochemical methods have been discussed. Potential applications including gas storage and separation, catalysis, magnetism, sensors, and drug delivery of MOFs have been explored in this study. Further research work should be carried out on toxicity and degradation mechanism of unstable MOF. It also should be explored the antibacterial and antifungal activities for better

clinical and biological applications. There are lot of scope of study about fascinating nano-MOF in the near future.

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