

AN OVERVIEW OF THE METAL-ORGANIC FRAMEWORK

Abstract

Metal-organic frameworks (MOFs), a special type of porous hybrid organic-inorganic materials, have attracted a lot of research in the last decade. Due to their benefits, including their high porosity, structure, and flexibility. MOFs and their imitations have been widely used to enhance catalysis and energy storage efficiency. They have also been used to solve water and electromagnetic pollution. This present article discusses structural exposure; types (MOF-5, HKUST-1, UiO, Zeoliticimidazolate framework (ZIF), MOF-76), methods of synthesis, and applications have been discussed. MOFs are created by swapping out conventional organic linkers for biomolecules to strengthen the stability connecting metal ions/clusters and ligands and reduce the production of hazardous by-products. Additionally, they have special benefits such as optimal reusability and stability, mechanical strength, and biocompatibility. To give the future development of MOFs as methodical tribunes for illness diagnosis and drug delivery systems, the provocation and perspectives are presented in the last section.

Keywords: MOFs, ZIF, drug delivery, biocompatibility, disease diagnosis.

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I. INTRODUCTION

Metal-organic frameworks (MOFs), a specific class of coordination polymers, have captivated attention in different areas of science. Metal-organic frameworks (MOFs) are composed of chemical bonds between inorganic metal clusters and organic ligands as linkers [1]. In terms of their potential for diversity, this puts them ahead of other manmade materials like zeolites [2], which benefits from their well-defined structure, high porosity, modularity, high surface area, a wide range of pore shapes, relatively low toxicity, and easy chemical functionalization [3]. MOFs can be quickly converted into metal oxides, metal sulfides, and porous carbon (PC) electroactive materials for energy storage devices, and that have potential applications in various fields such as ultra-strong applicability in adsorption, gas storage, catalysis, and electrochemical energy conservation [4]. Metal-organic porous materials based on copper, such as HKUST-1 and CuAdeAce, as well as metal-organic aerogels of CuDTA and CuZnDTA, are used to hydrogenate CO₂ with the saturated electrolyte of KHCO₃ [5]. A rapidly evolving field of biological material sciences, MOF is one of the most promising areas of human health care in generating safer and more effective drug carriers [6]. Recent years have seen a significant increase in interest in biological metal-organic frameworks (bio-MOFs), which have high biocompatibility and a variety of functionalities [7]. The four fundamental MOF capabilities that can be exploited in application development are known. These characteristics include composition, pore size, shape, and pairing with various nanomaterials [8].

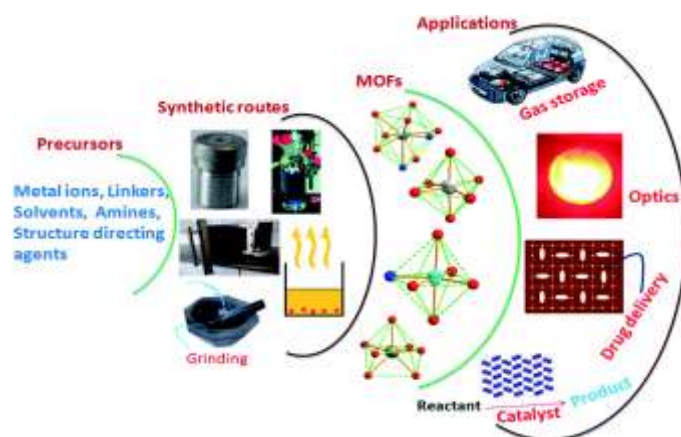


Figure 1: Schematic Representation of MOF Synthetic Routes and Probable Application

II. TYPES OF METAL-ORGANIC FRAMEWORKS

We might mention the following MOF-5, HKUST-1, UiO, Zeoliticimidazolate framework (ZIF), and MOF-76 as examples of the most popular types of MOFs alternatively used in sensing.

- 1. MOF-5:** A Cubic metal-organic framework substance MOF-5 or IRMOF-1 has the formula $Zn_4O(BDC)_3$, Where $BDC=1,4$ azodicarboxylate (MOF-5) with a surface area to volume ratio of $2200\text{m}^2/\text{cm}^3$. MOF-5 stands out among metal-organic frameworks as having one of the highest surface area-to-volume ratios [9]. It was also the first metal-organic framework that was investigated for hydrogen gas storage. Due to its massive and secondary construction unit and benzene linkages, MOFs' structure has a very high

porosity and thermal stability. [10]. The major methods used to synthesize MOF-5 were hydrothermal, solvothermal, microwave-based, and sonochemical processes. The solvothermal approach, which may produce a large amount of product in a single batch, is the most straightforward and effective of the procedures discussed. A MOF derivative produced by replacing Zn^{2+} with Mn^{2+} revealed selective catalytic epoxidation of olefins in which the SBU of MOF-5 played a significant catalytic role [11].

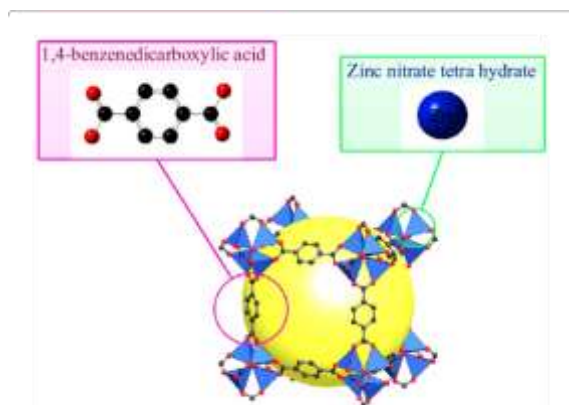


Figure 2: The Schematic Illustration of the Construction of Metal-Organic Framework Material (MOF-5)

- 2. HKUST-1:** A cubic lattice (fm-3m) of benzene dicarboxylate (BTC) ligands that coordinate copper ions. Cu (II) ions form dimers in the HKUST-1 Framework, with each copper atom being coordinated by four oxygen atoms from BTC linkers as well as a water molecule [12]. The creation of composites based on HKUST-1 is a popular and active research area and as a result, fresh and noteworthy instances have demonstrated intriguing applications (e.g. H_2 storage, catalysis, chromatography, CO_2 capture, and lithium-sulfur batteries) [13]. Another method of functionalization is the production of composites (hybrid functionalized materials) using MOF materials and other crystalline structures, such as graphene or multi-walled carbon nanotubes. [14]. When HKUST-1 and GO are combined the former's ability to decompose in water is prevented and the latter's adsorptive, photochemical, and electrical capabilities are enhanced [15]. HKUST-1 is a copper-based metal-organic framework (MOF) that exhibits high electrical conductivity as a result of the copper ions it contains. It can be employed in hydrogels as an antibacterial agent [16].
- 3. UiO:** The UiO MOF family consists of three primary classes: UiO-66, UiO-67, and UiO-68. Particularly boring versions of these MOFs have been made by attaching functional groups to the linkers, including amines, halogens, hydroxyls, or nitrous. Two commonly used Zr-based frameworks are UiO-66 and UiO-67. [17]. Especially, UiO-67 is a MOF procured by coordinating the $Zr_6O_4(OH)_4$ metal unit with the 4,4'-biphenyl dicarboxylate organic linker. On the other side, UiO-66 and UiO-68 prevailed by coordinating the same metal building block but with different linkers such as 1,4-benzene-dicarboxylate and 4,4',4''-triphenyl dicarboxylate, respectively [18]. We demonstrate that in pertinent lung tests, UiO-66 NPs exhibit good biocompatibility and negligible cytotoxicity both in vitro and in vivo. Our study shows that UiO-66 offers a novel strategy to control lung penetration and particle deposition with potential uses in inhaled immunotherapies, nano vaccines, medication delivery, and COVID-19 [19].

4. ZIF-8 and ZIF-67: A subfamily of MOFs with a cage resembling sodalite is known as zeoliticimidazolate frameworks (ZIFs), which are based on imidazole bridging with metallic nodes (such as Zn and Co).and Using a pyrolysis-oxidation-phosphorization method, a CoP/NCNHP nanostructure can be created using the ZIF-8@ZIF-67 framework as a precursor. Li et al. developed Zn/Co-ZIF with a regulated hollow structure using a template that was similar to ZIF-8@ZIF-67. This structure-based Pd@H-Zn/Co-ZIF exhibits better activity and selectivity in the semi-hydrogenation of acetylene [20]. Due to the high porosity of the framework, ZIF-8 and ZIF-67 have a relatively large surface area (1970 m² g). These compounds also have stable chemical and thermal characteristics. ZIF-8/ZIF-67 is made up of two MIM or Zn/Co ions and has a sodalite-like structure. They have an opening with a diameter of 3.4 nm in the center, which leads to a micropore with a diameter of 11.6 nm [21].

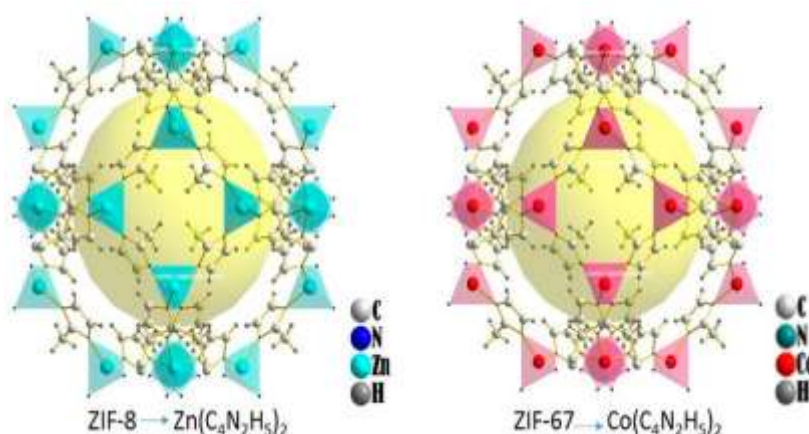


Figure 3: Representative Crystal Structures of ZIFs under Study.

MOF-76: The gadolinium(III) version of the MOF-76 family was selected because it is simple to make, has a high reaction yield, and works well in our investigations as a magnetic refrigerator, a humidity sensor, and an adsorbent of carbon dioxide, methane, and hydrogen [22].The terbium(III) and benzene-1,3,5-tricarboxylate(-III) ions, one coordinated aqua ligand, and one crystallization N, N'-dimethylformamide molecule make up the MOF-76(Tb) crystal structure. Biological imaging, light interactive devices, and sensing investigations can all take advantage of MOF-76.

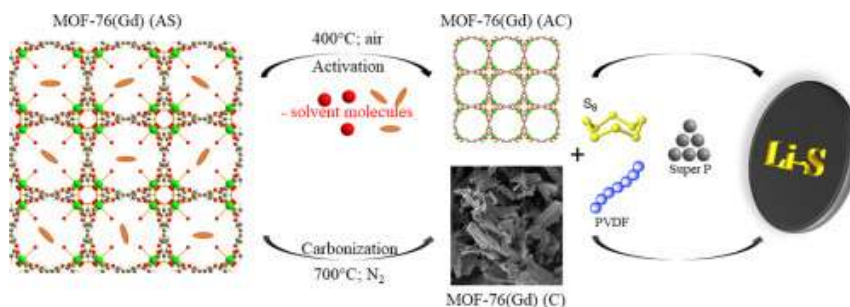


Figure 4: Structures of MOF -76

III. SYNTHESIS METHODS OF METAL-ORGANIC FRAMEWORK

The synthesis of MOFs is influenced by several factors, such as reaction time, temperature, solvent, type of organic ligands and metal ions, size of nodes, structural traits, presence of counter ions, and crystallization kinetics, which should lead to nucleation and crystal development. [23]. Oxalatotitanates and titanophosphates were first made using hydrothermal processes.

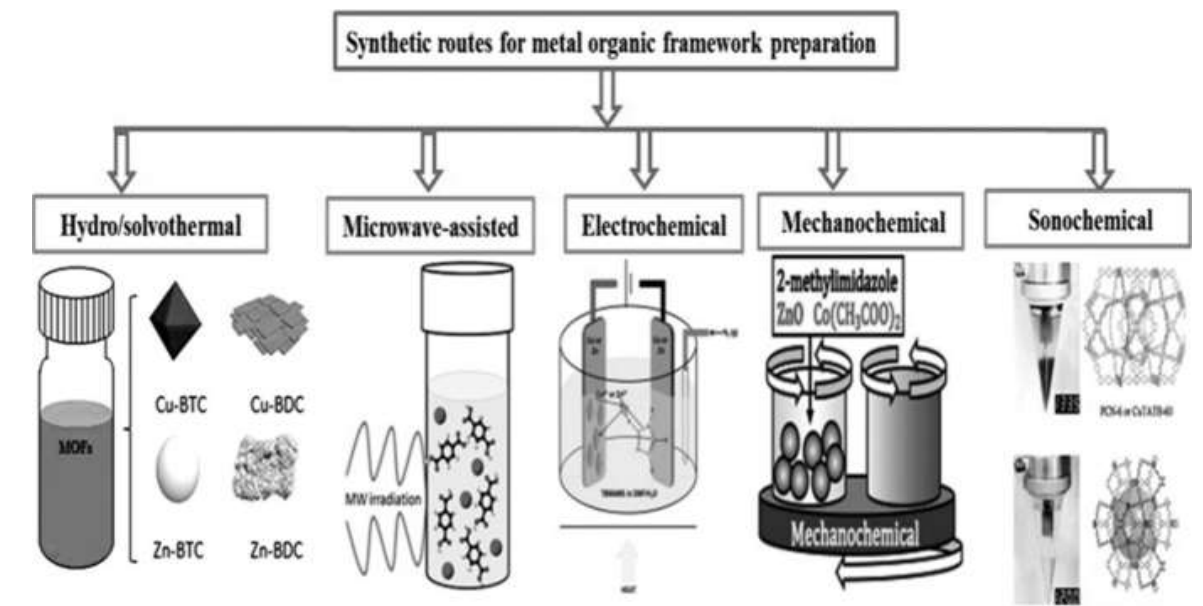


Figure 5: Overview of Synthesis Methods for the Preparation of MOFs

Metal extraction has historically been done using the hydrothermal method. It has also been mentioned that enormous crystals may be made using this technology. It depends on the temperature in an experiment with a controlled environment. The synthesis medium must be under extremely high pressure and temperature conditions. MW radiation has been developed for the production of inorganic or organic solid-state molecules and has the benefits of controlling phase and microstructure, particle size distribution, and shortening crystallization times [24].

The electrochemical approach can be used in batch mode or continuous flow operation. Compared to traditional microwave and hydrothermal synthesis, this one has the advantage of functioning under more favorable conditions. The sonochemical method stimulates homogenous nucleation and rapid kinetics, which is enabled by the acoustic cavitation of the ultrasound waves, leading to a significant reduction in particle size. This synthesis has the benefit of operating under more hospitable settings than conventional microwave and hydrothermal synthesis. A notable reduction in particle size results from the sonochemical strategy's stimulation of homogenous nucleation and quick kinetics, which is made possible by the ultrasound waves' acoustic cavitation [25].

IV. APPLICATIONS

Applications of modified MOFs are primarily unique in sectors relating to medicine, including illness diagnostics and drug delivery. (e.g., diabetes, cancer, anti-diabetic agents, wound healing, neurological diseases, ocular diseases, and factorial infections). then energy-related fields like hydrogen production, overall water splittings, and environmental-related fields that dye degradation and water pollution[26].

The most potential alternative energy source to combat the current issue of fossil fuel use is hydrogen energy. MOFs can also play a significant part in the generation of hydrogen. In photocatalytic and electrocatalytic production methods, MOFs are used to produce hydrogen[27].

- 1. Drug Delivery:** Due to their huge surface area, highly customizable pore size, and tailoring of the metal ion or organic linker, MOFs are a potential prospect for drug delivery. Nano-MOFs, which were made by shrinking the size of MOF particles, work well as drug delivery vectors.[28]. The cavity of MOF and/or the framework structures might be filled with a range of hydrophobic, hydrophilic, and amphiphilic therapeutic compounds[29]. The MOF nanocarriers provide targeted drug delivery, higher cellular uptake, and regulated drug release, making MOFs a viable family of DDSs for drug delivery. These medications include hormones, antiglaucoma therapies, anticancer treatments, and antibacterial compounds [30]. The continuous drug release capability of the external stimuli-responsive devices is increased, and they have a greater potential for biological use.
- 2. Disease Diagnosis:** There are numerous examples, including target-specific anticancer drugs, gold-incorporated MOFs for MRI and PTT, and more. With no negative impact on healthy cells, ZIF-8/enzyme hybrid MOFs, Fe₃O₄@bio-MOF-folic-acid-chitosan combine (FC) hybrid structures, and Zr-MOF@glucose-6-phosphate appeal in the therapy of kidney cancer [31].

Acetone was detected using MOFs made from ZnO@MoS₂ nanosheet core/shell heterojunctions. Making highly luminous frameworks from non-luminescent MOFs with a strong selectivity to acetone will enable the creation of fluorometric sensors for the detection and monitoring of diabetes [32].

V. CONCLUSION

We have examined the various MOF families and probable synthesis methods in this chapter. MOFs are characterized by large surface areas, high porosity, and flexible pore diameters. Therefore, We conclude that the discovery of MOF has shown to be advantageous to every part of our life today and that it still piques the curiosity of scientists. To make MOFs more applicable across a variety of sectors, a lot more studies must be conducted in this field.

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