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Methods for the synthesis of Metal Organic Frameworks (MOFs)

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Abstract

MOFs were a kind of porous substance made up of naturally occurring ligands & metallic ions or oligo-nuclear metal complexes. These may be expanded into one, two, or three dimensions and are regarded as a subgroup of coordinated polymers. MOFs are classified as nano-porous, meso-porous & macro-porous based on shape and size of pore spaces. Typically, the last two are amorphous. Because of the existence of coordinating bonds, MOFs exhibit great permeability, a significant area of specific surface, as well as significant thermal resistance. In accordance with the total charge of MOF, molecules of gas, & the biomolecules; these pores may include molecules that are neutral like solvent molecules, anion molecules, & cations as well. The synthetic techniques for creating MOFs and its related substances are included in this review, along with the variables influencing MOF synthesis.

Keywords: MOFs, Coordinated polymers, Thermal resistance, metallic ions, Permeability

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Review article

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1. Introduction

MOFs were group of solid porous-like substances composed of the polydentate ligands that are organic serving as linker within nodes and metallic ions / metallic clusters functioning as nodes. One-dimension, two-dimension, or three-dimension systems are generated by organic ligand connecting metallic center via coordinating bond as well as the nodes made of metal (metallic clusters or metal ions) serving as connecting points. Very important significant properties of Metal organic frameworks are their extremely porous nature, large volume of pores (up to 90 percent of crystallized volume or greater), a significant area of specific surface (a few thousands of $\text{m}^2 \cdot \text{g}^{-1}$), and significant heat resistance (250 to 500 °C) caused by existence of powerful interactions (for example, C–C, M–O, C–O and C–H). Isoreticular Metal-Based Organic Frameworks (IRMOFs) have been an important category of MOFs that were originally developed by Yaghi group [1]. The octagonal Zn–O–C networks and the 1,4-benzenedicarboxylic acid connected build network using pcu-topology acted as a foundation for the archetype IRMOF-1. That IRMOF series depends on various kinds of organic linking agents which generate variable pore volumes and surface dimensions while preserving an identical PCU topology. MOFs belong to a group of coordinating networks (such as coordination substances extending to two, three, or one dimensions by means of repeated coordination components), that are a

subclass of coordinating polymers (i.e., coordinated molecules with repeated coordinated structures extended in 1, 2, or 3 dimensions; however, that don't require to be considered crystalline), in accordance to the terminologies officially accepted by the IUPAC in the year 2013 [2]. MOFs are complex structures which might not be crystallized as well as susceptible to modifications in structure regarding to environmental factors like pressure and temperature. Chemical composition of Metal organic frameworks has evolved rapidly in recent years, so it has become possible to alter the area of the surface, network structure, as well as shape and size of their pores, thus permitting structure and features of Metal organic frameworks to be easily adjusted to meet demands of different functions. Knowing about the molecular or intermolecular connections among the three-dimensional structure is crucial to carry out the targeted synthesis of novel MOFs with intended chemical and physical characteristics on the basis of fundamental Crystal Engineering techniques. Coordination bonds among ionic metals and natural ligands are referred to as interactions between molecules, whereas weak interaction like hydrogen bonds as well as pi-pi interactions have been identified as intermolecular interactions. Numerous investigators have made the point that it can't be feasible to entirely regulate all aspects of chemical process, however intended manufacturing of Metal organic frameworks additionally

require complete control of elements or instruments being employed.

On the contrary, one can make a claim that the planned manufacturing of IRMOFs, which was depending on MOF-5, has generated significant array of solids. The variety of coordination configurations which the metallic ions adopt, such as the utilization of oligo-nuclear metallic cluster as terminals (SBU), geometrical properties as well as versatility of natural ligands, the role of the opposing ions, along with reaction solvent are all having a significant effect on structural characteristics of MOFs [3-4]. A number of coordination configurations that metallic nodes might adopt—that vary according to electronic makeup of metallic ion—are all strictly associated with overall network topology along with dimension of MOFs. Since they display an extensive variety of coordination numbers, configurations, as well as states of oxidation, transition-metal ions—particularly those from the initial row, the lanthanides, along with the alkaline earth metals—had been utilized, offering synthetic as well as diverse structures. While developing a MOF, the selection of flexible or rigid natural ligands is important since the flexible binding agents may result in unreliable structure of crystals or provides more number of independent variables compared to rigid one [5]. In the case of MOFs, molecules of organic matter with multiple nitrogen and oxygen-donating atoms were often used as natural binders in order to link metallic ion. The most frequently used binders involve carboxylates (which can be either aromatic or aliphatic having multiple ring structures), pyridyl derivatives (like 4,4'-bipyridyl derivatives as well as pyrazine), cyanide molecules, polyamines that are made from oxalic acid, imidazole, as well as benzene, sulfonates, phosphonates and crown-like ethers.

By either directly inhabiting the structure's porosity or interacting with metal ions, anions have ability to influence the supra molecular framework and balanced the positive charge associated with cationic MOFs [6]. As illustrated by the bio-MOF-1, which holds Me_2NH_2^+ cation or solvate particles as well as preserves crystal structure in solvent exchange investigations and also throughout preservation and dissolution of positively charged molecules of drugs, organic cations may also be trapped within the tiny pores of anion-based MOFs and replaced with other cations [7]. Although negatively charged metal clusters need huge permeable frameworks and, in some cases, may be changed with other cations for sensing purposes, metallic cations tend to be linked to the primary network, modifying its structural characteristics [8]. By steric effects, reaction's solvent may affect network topologies as well as crystallization processes. It may additionally fill metal-ion coordinating sites, complete the MOF's cavities, and participate in weaker interactions between molecules which maintain lattice's thermal durability or structural integrity. Effective coordination interactions among metallic ions & ligands that are organic provide MOFs in three-dimensional configuration. They consist of holes and interior surfaces that were occupied by opposite ions, host molecules or solvate molecule.

Long-term durability of MOFs may additionally influence by different type of interactions, like metal-metal bonds, hydrogen bond, as well as π - π interaction. Coordinating bonds, on the other hand, tend to be more powerful and generate long-lasting networks. MOFs are categorized as nanoporous compounds (pores that are smaller

than twenty Å in diameter), mesoporous compounds (pores that are between 20 and 500 Å in diameter), as well as macroporous compounds (pores that are greater than 500 Å in diameter) depending on shape or pore size. Amorphous substances comprise a vast majority of macroporous and mesoporous MOFs [9]. Although interpenetration precludes the occurrence of free unoccupied space in the system, expanding the diameter of the pore remains an issue. Organic binders experiencing ring structures that can form π - π interaction improve interpenetration. Poly-carboxylate and stiff alkyne-based binders, in addition to SBUs that come with vast dimensions that control dimensions of holes, being used to generate extremely porous MOFs [10]. Synthetic methods that generate MOFs of different dimensions and pore sizes are presented in this article (Figure 1).

2. Metal organic framework names and categories

Term "MOFs," that stand for "Metal Organic Frameworks," typically employed as general term for collection of chemicals; whenever it was accompanied by numerical ordinals, it refers to particular MOF. Developing framework geometries with required characteristics, like a group of Metal-organic frameworks with identical Crystallography, IRMOF-1–IRMOF-16 (isorecticular, MOFs) [11-12] could be made easier by investigating the characteristics and designs of MOFs. Russian [13-14] or Chinese [15-16] investigators frequently refer to "metal-organic coordinating polymers" with certain compositions. Several MOFs have been classified according to the location where they discovered, like MIL, UiO, LIC, HKUST etc. Another large class of MOFs is zeolite topography. Imidazole rings, which may be used for a variety of purposes, link metal ions like Co, Fe, Zn, Cu and others to tetrahedra composed of nitrogen-containing atoms. A variety of techniques plus zeolite imidazolate framework may be used to create these Molecular Organic Frameworks. The research organizations that manufactured MOFs were categorized using numerous additional designations, including CPL, F-MOF-1, MOP-1 and CPL among others (Table 1).

3. MOF Synthesis

A number of variables, including timing of reaction and temperature, kind of metallic ion or natural binder, size or structural properties of nodes involved, existence of opposing ion, as well as the process of precipitation, which at first will result in nucleation or development of crystals, regulate the formation of MOFs. MOFs are normally produced in the liquid phase through the combination of ligand molecules and metallic salt solutions. The solvent has been chosen according to its potential for redox, dissolution capacity, as well as reactivity. The thermodynamic parameters or energy of activation of reaction are significantly affected by solvent that is used. Solid-state manufacturing methods are being employed in various circumstances despite difficulties in developing single crystals. MOFs crystal has frequently synthesized by slowly evaporating the reaction solution. MOFs are often produced under extreme temperatures & high pressures using hydrothermal techniques. This is the traditional strategy for MOF preparation. Recent decades have seen the emergence of additional alternative manufacturing techniques, including mechanochemical, electrochemical, mechanochemical, sono-

chemical and microwave techniques. These methods are less costly, faster and provide cleaner items (Figure 2) [17-18].

3.1. Methods of Diffusion & Slow Evaporation

Both techniques don't require a source of energy and are conducted at normal temperatures. To promote polymerization and crystal development, the solution of reagents combined & permitted to dry slowly. Whenever a threshold concentration level is attained, crystal is created. To accelerate the procedure, low-temperature boiling solvent mixtures are commonly employed [19-20]. Diffusion approach involves stacking reagent solution placed one above the other separating them with multiple layers of the solvent or slowly diffusing them by sinking barriers of physical nature. Gels are sometimes used as diffusing & crystalline material. When precipitated solvent progressively diffuses into distinct layer, crystals develop in the space among the layers [5]. Particularly when products are not readily soluble, a diffusion approach is taken. In order to create IRMOF-1 and MOF-5, Et₃N was diffused within solution of H₂BDC and zinc nitrate in chlorobenzene/dmf solution, and just a little quantity of hydrogen peroxide were introduced so as to form O₂⁻ attach to middle of SBU [21].

3.2. Methods of Hydro-Thermal & Iono-Thermal

Solvo (hydro) thermal processes usually take place in sealed chambers with autonomous pressure beyond the point at which the solvent boils [22]. The largest number of MOFs that have been characterized until now were created under hydro(solvo) thermal processes [23-25]. The processes involved typically take several days or hours to completion & are conducted in sealed chambers (autoclaves) that utilize solvents that are polar at temperatures that range between 50 & 260 degrees Celsius. Autoclaves constructed accompanied by a Teflon coating were usually employed for reaction which take place more than 400 degrees Celsius. Whenever kinetically neutral ions have been employed, operating temperature of processes might be raised to encourage bond formation & guarantee appropriate precipitation. Physical appearance of these crystal also affected by temperature or extended reaction period may cause finished product to break down [26-27]. The development of crystals is impacted by the speed of cooling, which needs to be extremely gradual. Solvents having an extremely high boiling temperature have been most frequently utilized.

H₂O, Diethyl Formamide (DEF), Dimethyl Formamide (DMF), methanol, methyl cyanide, ethanol Me₂CO as well as any combination of them are substances most frequently employed. Original reagents might experience unpredictable modifications in chemical structure during hydrothermal processes that wouldn't be possible during moderate synthetic conditions, resulting in the production of novel ligands in situ. Ionized fluids are employed as precursors & solvents in iono-thermal process, which is a category of hydro (solvo) thermal techniques. Due to their extremely low pressure of vapor, excellent binding capacity for molecules of organic matter, excellent thermal resistance, as well as non-inflammability, ionized liquids serve as superior reagents during production of Molecular Organic Frameworks and other kinds of substances (such as chalcogenides along with zeolites) than traditional solvents made from organic molecules. Ionized fluids have been extensively investigated as alternative for the production of

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Metal-organic frameworks in recent years since they provide both the cation or anion molecules that work as opposing agents and precursors for building blocks of MOFs [28].

3.3. Method with Microwave Assistance

Nanoporous inorganic & Organic compounds are frequently synthesized using this technique [29]. The technique has been applied in past few decades in production of Metal-organic frameworks [30-31] as well as clusters of metal [32]. The technique's benefits are its cheap price, excellent yield, and quick response period need. Compared to its traditional hydrothermal method, microwave-assisted production of the HKUST-1 compound having formula [Cu₃(BTC)₂(H₂O)₃] produced crystal had better yield & physical attributes, demanding a much shorter time for reaction [33]. Microwaves used help molecules to move, that causes the nucleation as well as the development of crystals which have a specified size and shape by suitably controlling both the temperature and concentration of the process, even though this particular method cannot generate crystals [34].

3.4. The Mechanochemical Approach

The process grinds the substances by hand, particularly, in automated grinding mills used to form bonds of coordination at normal temperature using mechanical force instead of the solvent. Three dimension, one dimension and two dimension coordinated polymer might occasionally be manufactured through introducing tiny proportion of solvent in solid mixture from chemical process [35]. The mechanical-chemical technique accelerates the reaction's speed via promoting transfer of mass, decreasing the size of particles, heating, as well as locally melting the substances being used. It is an eco-friendly green chemistry technique that yields components with excellent efficiency or high quality at quick response times [36]. As a replacement to the extremely high pressure and temperature involved in hydrothermal synthesis, the role of mechanical chemistry in manufacturing of Metal-organic frameworks is also interesting. The technique's main disadvantage is separation of non-crystalline products, that makes it inappropriate for monocrystalline X-ray structure investigations.

3.5. The Electrochemical Approach

MOF powders can be produced via this method on industrial level. Anodic dissociation into mixture of reactions which include the natural ligands or the electrolytes supplies a metallic ion. In comparison to the solvent-based method, this technique's primary benefits are its much faster synthesis under less severe conditions or lower temperatures at which reactions occur. This technique has been employed to synthesize various Metal-organic frameworks in a cell with electrochemical activity, like HKUST-1, ZIF-8, MIL-53(Al), NH₂-MIL-53(Al), as well as MIL-100(Al), or impact of multiple reactions conditions on the resulting output or physical characteristics has been studied [37].

3.6. Sonochemical Approach

Sono-chemistry investigates how compounds undergo chemical reactions if exposed to high-energy electromagnetic radiations (Twenty kHz to Ten MHz). Whenever reaction mixture is exposed to electromagnetic radiation, cavities have been created. Such temporary, extreme temperatures and elevated pressure localized hot

areas encourage chemical processes as well as the rapid growth of crystallized nucleus [38-40]. Using the 1-methyl-2-pyrrolidone compound as the solvent, this sono-chemical technique generated excellent crystalline forms of MOF-177 & MOF-5 having sizes of 5 to 25 micrometer or 5 to 20 micrometer correspondingly, in a notably shorter reaction period [41-42].

3.7. Microemulsion Technique

Many people utilize this approach to make micron-sized particles, and it was most recently employed to make MOFs [43-44]. Nanometer-small sized drops of water are held in place by a compound called surfactant in the organic region of water micro-emulsions. The micelles that are found in small emulsions work like small reactors that regulate how fast crystals form and develop. The dimension as well as amounts of tiny particles in the micro emulsion can have modified by altering water content to surfactant proportion or surfactant type that is used. This technology is beneficial given that the shape and size of the nanoscale substances are easily monitored, whereas the main drawbacks are somewhat its high price or the realization that the majority of the surfactants that are employed are harmful to the environment.

3.8. Post Synthesis Modifications

Technique, that is basically a chemical modification of MOFs during their separation, includes adding the required functional group within the MOFs during their formation (also known as Post Synthesis Modifications). The technique was extensively utilized to create iso-structural metal oxide frameworks with various chemical as well as physical features [45-48]. For instance, IRMOF-3, a compound that contain 2-Amino-1,4-benzenedicarboxylic acid, might be chemically altered utilizing several kinds of anhydrous compound & isocyanate to generate iso-structural Metal-organic frameworks with multiple functional group [49]. The basic building blocks of MOFs (also known as BBR), include solvent-based ligand transfer (also called SALE) [50], non-bridged ligands, as well as metallic nodes, might be changed in the course of post-synthesis modifications. Throughout Solvent-assisted Linker Exchange process, natural ligands may totally change, giving metal organic framework additional features. By rupturing & reestablishing chemical connections inside initial MOF, Building Block Replacement processes include uneven transfer of ligand and metallic ions [51].

When direct production of required MOF is not possible, Building Block Replacement techniques are employed to activate pore spaces and terminals inside MOFs with goal of providing or improving desirable functional qualities like redox, conductivity of ions, catalytic activity, and selective gas adsorption. Only the exterior layer of crystals made from MOF exhibits BBR processes [52-54]. Errors on MOFs may result from post-synthesis modification processes that may replace or remove metal nodes and partially substitute naturally occurring linkers. These flaws may also arise during the traditional manufacturing of MOFs, as well as during the process of crystallization & crystal development procedures [55]. Mixed-metallic MOFs, which include a minimum of two metallic ions within the structure, may be made via post-synthesis techniques, single-pot techniques, or metalloligands. The addition of a second

metallic ion gives these MOFs new characteristics and functions [56]. Defective engineering had been successfully employed to alter or enhance MOFs for uses such as in catalytic activity, gas absorption, removal or preservation, as well as luminescence or magnetized substances because imperfections in structure as well as dissimilarities are frequently linked to significant properties of the material.

3.9. Template Techniques

Using molecular templates in mixture of reactions can result in new Molecular Organic Frameworks that are difficult to synthesize using traditional methods [57]. Tiny molecules of organic matter, such as solvents made from organic materials, carboxylic acids, organic amines, nitrogen- heteroaromatic substances, ionic solutions, chemical surfactants, or various natural compounds, were extensively employed as molecular templates. The manufacturing & precipitation of MOF are impacted differently by each member of this group of molecules that are organic. For instance, the polarization or dissolution of solvent influence the MOF's capacity for crystallization process; naturally occurring amines modify the pH levels of chemical reaction or aid in breakdown of naturally occurring ligands; carboxylate-containing compounds function as binding agents for the metal cores as well as may fill the MOF's cavities; heterocyclic aromatic substances function as weakened organic bases or opposing ions if protons are present; ionic liquids function as solvent or opposing ions; as well as surfactants can create pores in liquid solvents that control the MOFs' dimension or appearance. Coordinating compound (like $[\text{Ru}(2,20\text{-bipy})_3]^{2+}$), the polyoxo-metalates, blocking copolymer, metal-organic frameworks, polystyrene fragments, substrate like seldom bio-macromolecules and graphene oxide are additional substances that could serve as precursors. Complex molecules like enzymes or proteins can be accommodated in multilayered porous substances made with microporous & mesoporous channels utilizing a template synthetic technique. The reticular chemical approach, which uses binders of lengths that vary to create Molecular Organic Frameworks with identical geometry yet different sizes of pores, is the most popular synthesizing technique to produce complex molecular organic frameworks.

4. Factors influencing MOF synthesis

4.1. Solvents

Both the manufacturing of MOFs and their physical characteristics are highly affected by solvent's system. The solvent can function as space-filling compounds or interact with metallic ions [58-59]. Rather, they additionally act as a facilitator that directs the structure [23]. Diethyl Formamide, Dimethyl Formamide, Dimethyl Acetamide, Dimethyl Sulphoxide, Alcohol, Acetone, Acetonitrile, and other compounds were typical solvents utilized in the production of MOF that have an extremely high boiling temperature and are polarized in nature. Depending on how soluble raw materials are, a combination of solvents may also be used. In addition to the polar nature of solvent and the natural linking agent's dissolution or protolysis properties, reaction medium exhibits impact on metal-organic frameworks manufacturing procedure. Additionally, it has been observed that various solvent mixtures can produce MOF that have various morphologies under similar reaction parameters.

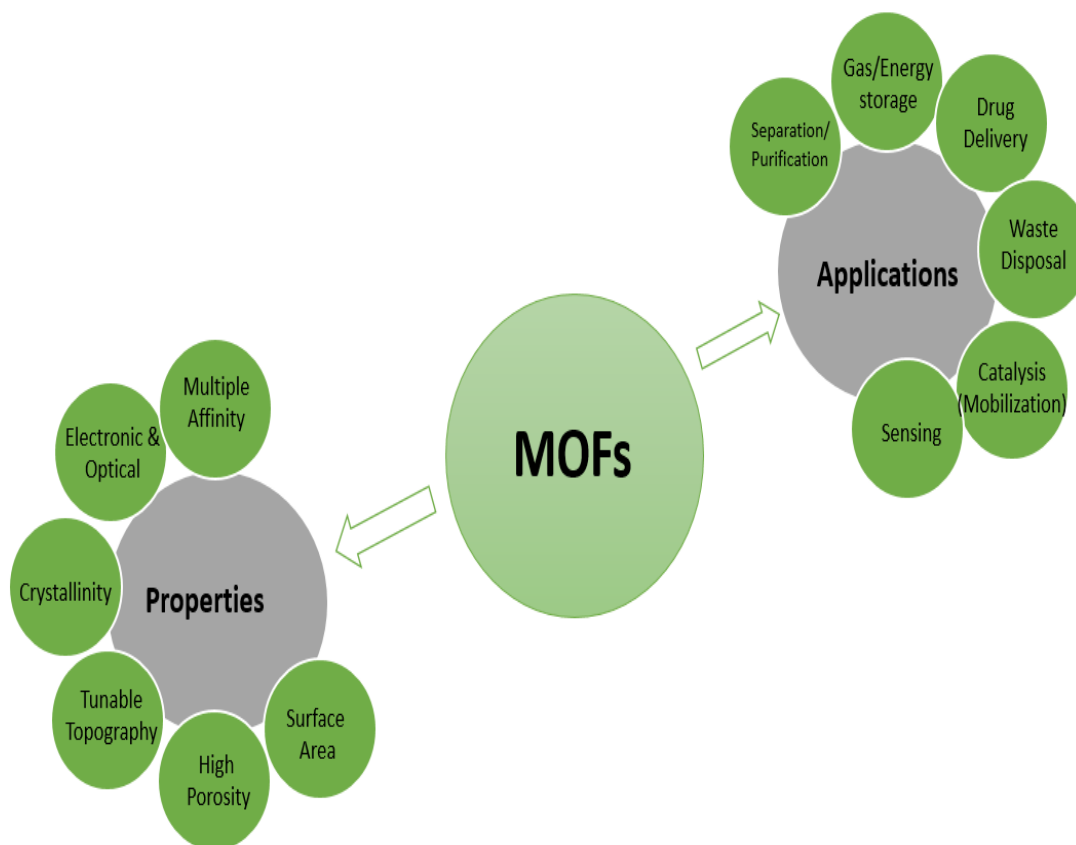


Figure 1. Properties and Applications of Metal Organic Framework (MOFs)

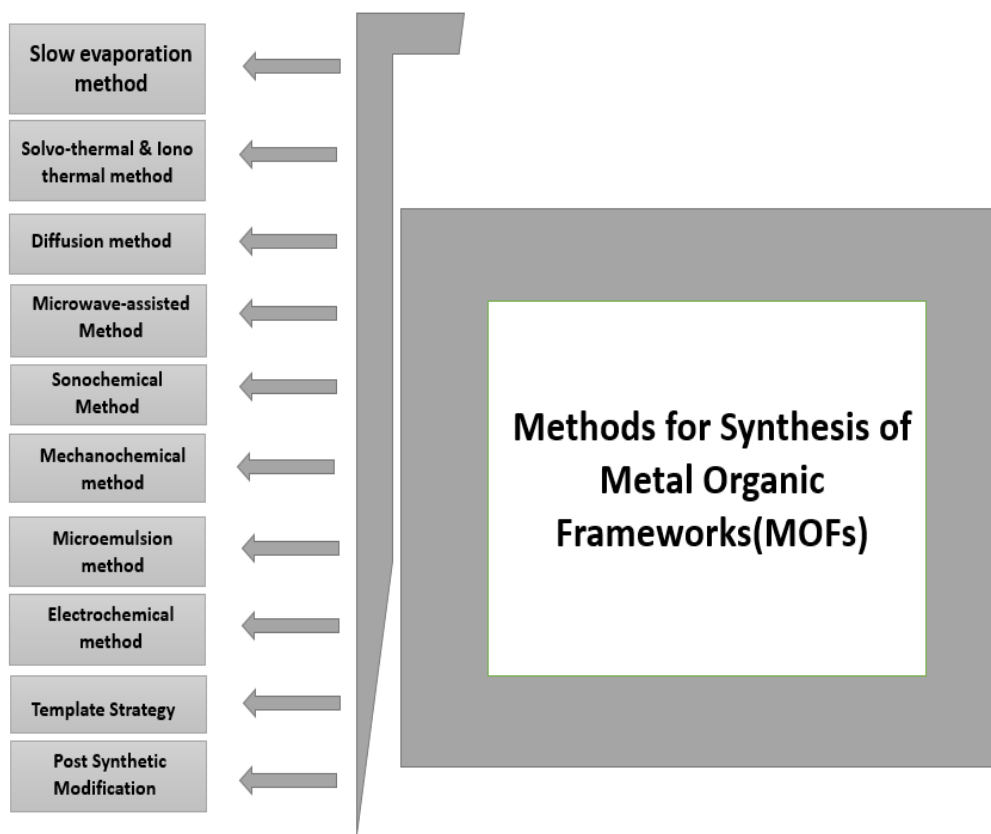


Figure 2. Methods for synthesis of Metal Organic Frameworks

Table 1: Examples of MOF names and their formulation

Sr.No	Designation	Chemical formula	Abbreviation interpretation
I	MOF-74	Zn ₂ DOT	Metal-Organic Frameworks
II	IRMOF-1 (MOF-5)	Zn ₄ O(BDC) ₃ . 7DEF.3H ₂ O	IsoReticular Metal-Organic Frameworks
III	UiO-66	Zr ₆ O ₆ (BDC) ₆	Universitetet i Oslo
IV	MIL-53	Al (OH)(BDC)	Materials of Institut Lavoisier
V	HKUST-1 (MOF-199)	Cu ₃ (BTC) ₂	Hong Kong University of Science and Technology
VI	LIC-1	Gd ₂ (BDC-NH ₂) ₃ (DMF) ₄	Leiden Institute of Chemistry
VII	ZIF-8	Zn (MIM) ₂	Zeolite Imidazolate Framework
VIII	CPL-2	Cu ₂ (PZDC)2(4,40 -BPY)	Coordination Polymer with pillared Layer structure
IX	F-MOF-1	[Cu(HFBBa)(phen) ₂](H ₂ HFBBa) ₂ (H ₂ O)(HCO ₂)	Fluorinated Metal-Organic Framework
X	MOP-1	Cu ₂₄ (m-BDC) ₂₄ (DMF) ₁₄ (H ₂ O) ₁₀	Metal-Organic Polyhedra

Table 2: Impact of PH value on Metal organic frameworks

Sr. No	Cobalt-MOFs properties	Complex-One	Complex-Two	Complex-Three
I	Chemical Formula	[Co ₂ (L)(HBTC) ₂ (μ ₂ -H ₂ O) (H ₂ O) ₂].3H ₂ O	[Co ₃ (L) ₂ (BTC) ₂].4H ₂ O	[Co ₂ (L)(BTC)(μ ₂ -OH) (H ₂ O) ₂].2H ₂ O
II	Space group	P ₂ /c	C ₂ /c	Pccn
III	Color	Pink	Purple	Brown
IV	Morphology	Monoclinic	Monoclinic	Orthorhombic
V	pH	5	7	9

This could occur due to variations in the organic linking agent's extent of deprotonation in various solvent mixtures. MOFs composed of magnesium (Mg) or a PDC with distinct crystalline forms have been created according to similar conditions utilizing an alternative solvent mixture, according to research of Banerjee and colleagues [60] (Fig 5). They discovered that dimensions of MOFs depend on the solvent's ability for coordinating with metal. If EtOH/H₂O as well as DMF/MeOH are employed as solvents, water had the strongest affinity for Mg within DMF, water, ethanol along with methanol, whereas ethanol & methanol have no binding capacity for coordinating with metallic centers. Multiple systems of solvent lead to production of Metal-organic frameworks with varying pore sizes in combination with structural differences. Three separate solvents, namely DMP, DMA or DMF, are used to create MOFs of Co along with 4,4'-(5-carboxy-1,3-phenylene bis(oxy)) dibenzoic acid (H₃CPBDA) below identical circumstances. The obtained sizes of the pores were 74.37Å, 76.84Å and 72.76Å. The dimension of the solvent molecules was linked to variations in size of pores because of multiple solvent. Dimensions of molecules vary within three distinct solvents used, with DMP > DMA > DMF. In a similar sequence, size of pores decreases as well [61]. Other investigators have identified similar associations [62].

4.2. Impact of pH as well as temperature on MOF synthesis

Production of MOFs is significantly influenced by reaction medium's pH as well as its temperature. At different pH levels, binders may adopt numerous interaction strategies [63]. Additionally, as the pH level rises, the linker's degree of reduction in protons rises. For instance, as pH increases, the aluminum ion interacts with a six, four or eight oxygen atoms from carboxyl group to produce MIL-121 (with a pH equal to

1.4), MIL-118 (a pH value of 2), or MIL-120 (pH equal to 12.2), respectively [64]. According to studies, un-interpenetrated structures form at less pH values or interpenetrated structures appear at greater pH levels [65]. PH level of chemical process additionally influences pigmentation of metal-organic frameworks substances. Luo and colleagues al [66], by means of their experimental investigations, examined three cobalt-MOF complexes such as [Co₃(L)₂(BTC)₂].4H₂O(i), [Co₂(L)(HBTC)₂(μ₂H₂O)(H₂O)₂].3H₂O (ii), [Co₂(L)(BTC)(μ₂ OH)(H₂O)₂].2H₂O (iii) show various configuration or color, by changing the pH values. In addition to configuration or color, these three distinct MOFs displayed various adhesion capacities. It is furthermore demonstrated that the molecules of greater dimensions are generated at greater pH value [67]. Impact of the pH value on multiple characteristics of Metal-organic frameworks is described in table 2.

Temperature of reaction is an additional significant component that influences the characteristics of generated MOFs. Higher temperature; promotes greater precipitation because of significant dissolution of the reactants or consequences in creation of big sized crystal of significant stability [68-70]. Reaction temperature had impact on the speeds of nucleation & crystal growth. Changing reaction medium's temperature may additionally affect the shape and size of produced MOFs. Metal-organic frameworks of Thulium-succinate [71] synthesized under varying temperatures have similar empirical formula yet distinct morphologies, such as triclinic & monoclinic. The two Holmium-succinate MOFs were synthesized by Bernini and colleagues, who found that the MOFs made using the hydrothermal technique at a greater temperature were more resistant to heat than the one made at the room temperature [72]. Hydrothermal techniques yield more dense, least

hydrated, & stronger dimensional materials in addition to their thermal resistance [73].

5. Conclusions

Unique structural features of Metal-organic frameworks like their spongy nature, greater particular area of surface or great thermal resistance, have drawn more attention. Metal-organic frameworks can be readily produced using environmentally friendly techniques like mechano-chemical, electro-chemical, and sono-chemical processes, as well as under ambient or harsh environments involving high temperature and significant pressure. Following the synthesis process, Molecular Organic Frameworks are frequently altered after their synthesis to add functional groups or provide the required chemical and physical characteristics. Metal-organic frameworks are synthesized in continuous-flow hydrothermal reactors for large-scale production. Uses in energy-related or environmental fields, such as gas absorption, preservation as well as separation of ions of metals or hazardous substances for analysis or detection applications, drug inclusion, along with biologically significant compounds as smart carrier molecules in cancer fighting or antibacterial treatments are highly promising due to the potential for modifying the dimension and form of the pore spaces. Metal organic frameworks may be altered with tiny particles, polymer chains, or cyclodextrins to create complex material composites. These materials are being tested to be smart substances for systems to deliver drugs, catalytic processes, as well as novel therapeutic substances; textiles during air purification, light hindering, or pollution reduction; detectors for gases; as well as charged particles for removal. The "core" of innovative materials required to advance fourth industrial era in this century is Metal organic frameworks & derivative compounds.

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