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Catalytic Applications of Metal-Organic Frameworks

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<http://dx.doi.org/10.5772/61865>

Abstract

In recent years, metal organic frameworks (MOF) have received considerable interest due to their physicochemical properties, such as structures' flexibility, high surface area, tunable pore size, and topologies, among others, which have lead to promising applications, particularly in the area of catalysis. In this chapter, we present the most important results of research conducted with MOF in catalytic applications; mainly in the design of its structure, synthesis, characterization, and possible limitations.

Keywords: Metal-organic frameworks, Heterogeneous catalysis, Porous materials

1. Introduction

MOFs and the related researches have become more and more important not only in chemistry but also in general science and technology. MOFs are a class of porous materials composed of metal-containing nodes connected by organic linkers through strong chemical bonds. The union of these two building units produces different coordination modes, depending on the symmetry of the linker and the coordination number of the metal center. The flexibility or rigidity of the added linker can allow the articulation of the clusters into a highly crystalline three-dimensional framework, which can exhibit higher surface area and pore volume than most porous zeolites [1]. Depending on the architecture of the obtained MOFs, they can be synthesized with high purity and also, they can be engineered to have a high skeletal density but constructed from relatively light elements. Therefore, most of the important related work is aimed at designing compounds possessing very large pores and high surface areas in order to load these materials with atoms, molecules, or even biomolecules. Due to these loading possibilities, wide applications of MOFs have emerged in different fields, such as in catalysis [2–4], guest adsorption (molecular recognition) [5], drug delivery [6, 7], gas storage [8–13], optical applications [14–16], composites [17], water treatment [18, 19], and sensor technologies [20], among others [21–26].

Some materials as metals in solution (transition metal complexes or metal salts) have been used in catalysis with excellent results. These materials are able to catalyze a variety of organic reactions, in many cases, reaching high yields and regenerating the material after the reaction. However, in many cases the metals are hardly recovered and/or decompose during the reaction due to the conditions. To achieve control these limitations, researchers have developed methods using porous materials as carriers, to achieve well-isolated, uniform single sites that don't interact between them, preventing the decomposition [2, 27]. Active sites on MOFs are located at the metal nodes on the crystalline structure; when the reaction occurs, the framework protects their active sites and increases the efficiency and resistance of catalyst [28].

Given the variety of metallic nodes and organic linkers, it is possible to control the synthesis of MOFs to design them with modular properties, functionalized with specific sites or specific assets to catalyze organic reactions. In this chapter, we present the main results of research with MOFs in the field of catalysis, with special focus on design, relationship between structure and activity, formation of active sites and limitations of these materials.

2. Design of MOFs

2.1. Crystal engineering of MOF

The term of metal organic framework was introduced by Yaghi in 1995 [29, 30], however, such structures were known until 1964 when Bailer first reported them [31]. The resurgence of the structures has been accompanied by the application of these materials in various areas, including: catalysis [2–4], guest adsorption (molecular recognition) [5], drug delivery [6, 7], gas storage [8–13], optical applications [14–16], composites [17], water treatment [18, 19] and sensor technologies [20], among others [21–26].

The structural characteristics of the MOFs are mainly determined by the nature of the metal center and the organic linker, yet, during the synthesis of these materials, solvents and/or counterions are typically used [32] and they also play an important role. The counterions change the environment of the metal ion and may generate overlaps with the structure resulting in weak interactions with the MOF. Meanwhile, solvent molecules with the MOF generally crystallize during synthesis, modifying the pore size.

Generally, the transition metal ions used can generate a wide range of structures. The properties of these metals, including the oxidation state and coordination number (typically varies from 2 to 7), produce a linear, trigonal, square planar, tetrahedral, trigonal pyramidal, trigonalbipyramidal, octahedral, and pentagonal bipyramidal geometries as well as some other distorted forms [32]. The lanthanoid ions, whose coordination number varies between 7 and 10, have polyhedral geometries and can generate MOFs with particular topologies [33].

In the formation of MOFs, the organic linkers must meet certain requirements to form coordination bonds, mainly being multidentate having at least two donor atoms (N-, O- or S-) and being neutral or anionic. The structure of MOF is also affected by the shape, length, and functional groups present in the organic linker. The linkers commonly used in the MOFs

synthesis are piperazine [34], 4,4'-bipyridine [34–37] (neutral ligands), and polycarboxylates (anionic ligands). Polycarboxylates may be di- [38–43], tri- [38, 40–43], tetra- [44, 45], or hexacarboxylates [46, 47].

The binding of a linker to the metal center may generate a one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) arrangement, which depends on the metal center (Figure 1) [48]. In a 1D network, two ligand molecules are coordinated to the metal center to generate a chain, while in a 2D network, three or four molecules of the organic linker are coordinated to generate a plane, and it grows in two dimensions. In a 3D MOF, the metal center, with high coordination number, joins three more linker molecules, along the three spatial dimensions, generating a three-dimensional structure with pores and cavities defined.

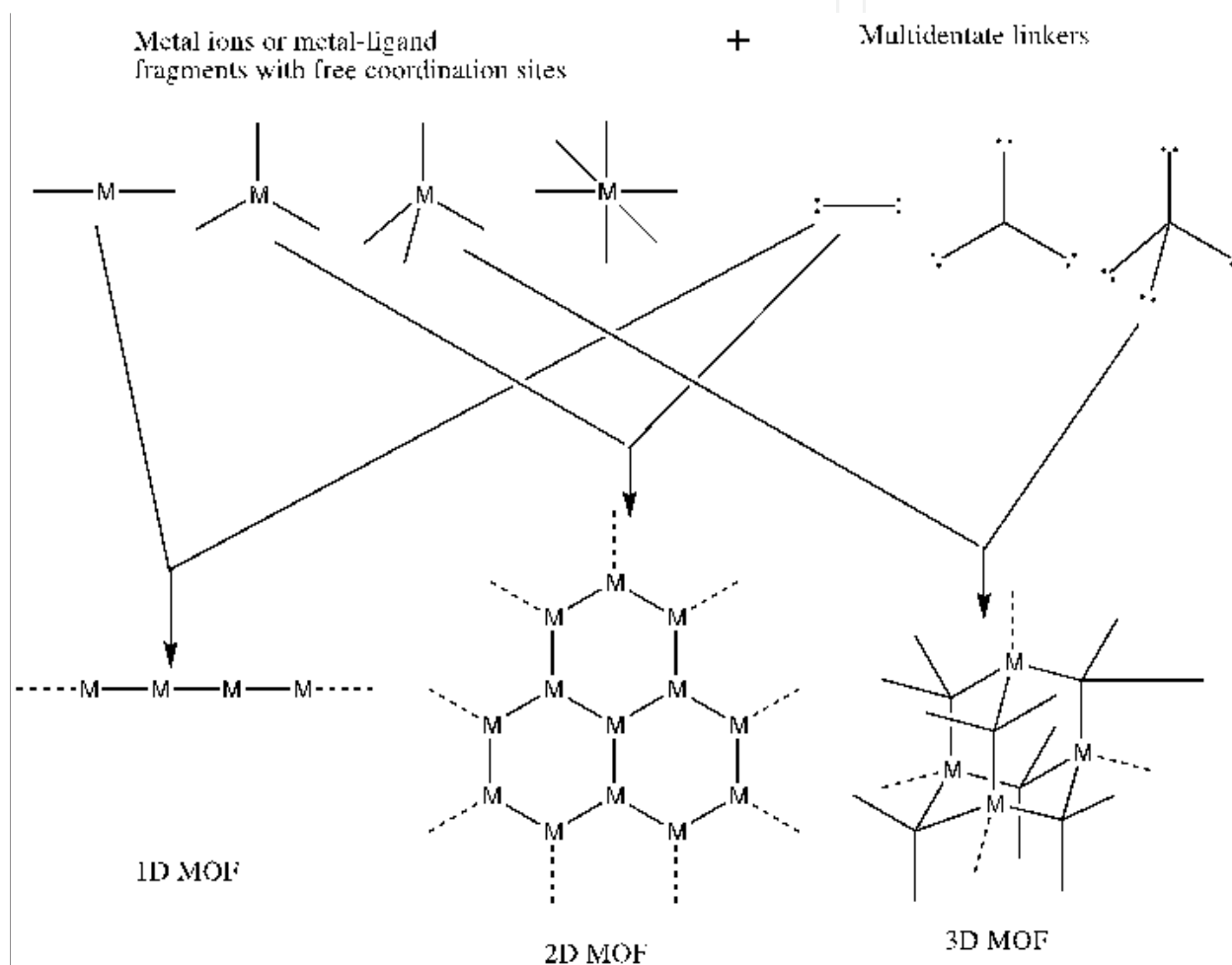


Figure 1. Basic building units of one-, two-, and three-dimensional MOFs [48].

Figure 2 shows examples of MOF with different dimensionalities. The helix (1D) is constituted by distorted tetrahedrons mercury (II), formed by the union of two nitrogen atoms (from two different linkers) and two terminal bromine atoms [49].

The 2D structures with grid shape are generally synthesized with a molar ratio between the ligand and the metal center of 1:2. An example of such structures is shown in Figure 3, the MOF is constituted by cobalt metal centers and ligands *N*-(3-pyridyl) nicotinamide [50]. The

metal ions are coordinated with four molecules of ligand, which result in a two-dimensional flat-shaped structure.

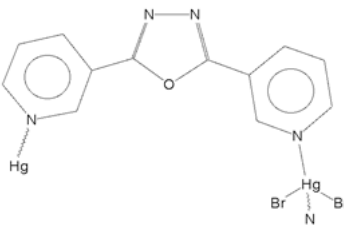
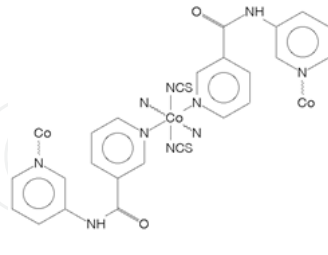
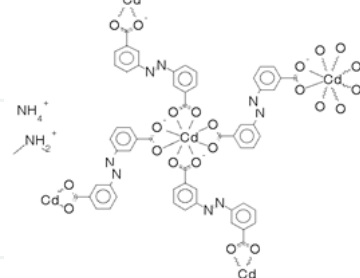
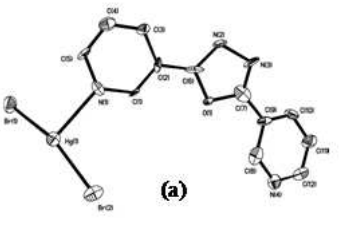
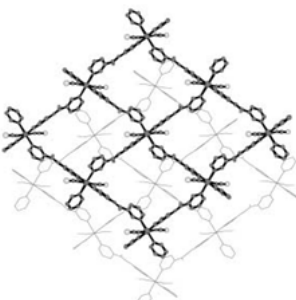
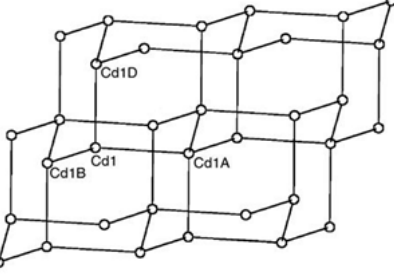
1D	2D	3D
		
		
HgBr ₂ (2,5-bis(3-pyridil)-1,3,4-oxadiazole) [49]	Co(SCN) ₂ (3-pna) ₂] _∞ (SCN = tiocyanate), (3-pna = N-(3-pyridil) nicotinamide) [50]	[Cd(3,3'-AZDB) ₂](H ₂ NMe) ₂ (NH ₄)(3,3'-AZDB = 3,3'-azodibenzoate) [51]

Figure 2. Examples of MOF structures 1D, 2D, and 3D.

The three-dimensional MOFs are formed by the interaction of one-dimensional chains in all three directions. Connectivity of the construction nodes depends on the metal center, and the formed structures are usually tetrahedral or octahedral. An example of such structures, wherein the metal is cadmium center and has an octahedral coordination, is given in Figure 3. The bidentate linker forms connections, where the four terminals of each linker involves oxygen atoms. The three-dimensional growth of the framework generates cavities; generally occupied by solvent molecules [51].

2.2. Synthesis of MOF

The physicochemical characteristics of MOFs can be modulated and it is clear that all these properties can be modified in the material from the synthesis process. The solvothermal synthesis is the most common way of obtaining MOFs. However, other recently studied methods of synthesis, which may cause significant changes in the MOF's properties, include (i) mechanochemical, (ii) electrochemistry, (iii) assisted synthesis (by ultrasound or microwave), and (iv) subcritical water.

2.2.1. Solvothermal synthesis

The solvothermal synthesis comprises the reaction of the metal salt and the organic ligand in the presence of organic solvents or solvent mixtures typically involving formamide [52–55], alcohols [56, 57], or pyrrolidones [58]. The reaction temperature is usually considerably less than 523 K, but depends on the boiling point of the solvent used, for example, in the case of methanol, the synthesis temperature is 338 K. Upon heating, the blends in sealed containers such as teflon or glass pressure tubes produced compounds incorporating solvent molecules in the pores of the material. These organic solvents are often toxic, carcinogenic, and/or dangerous to the environment. For example, dimethylformamide (DMF), one of the most commonly used solvents in the synthesis of MOFs is contaminant, mutagenic, and toxic [59]. Additionally, DMF decomposes when heated at high temperatures for long periods and therefore cannot be reused [60].

The concern about the use of these organic solvents has increased due to their negative impact on the environment [61]. Therefore, the replacement of polluting solvents in the synthesis of MOFs with solvents that do not pose a risk to the environment has been established as a primary objective, committing to the principles of Green Chemistry [62]. When the solvent is water, the main problem encountered during synthesis is the low or nonsolubility of the reactants and organic ligands, which generally prevents the formation of coordination polymer.

Other important parameters in the solvothermal synthesis are: temperature, concentration of reactants (which can be varied over a wide range) and the pH of the solution.

One of the advantages of this synthesis are the yields ranging from 60% to 95%; however, removing solvent molecules occluded in the pores of the MOF is not a simple process, the solids must be washed several times, which can take several days and considerably reduce performance.

2.2.2. Mechanochemical synthesis

The mechanochemical synthesis is named due to the chemical reaction that occurs as a consequence of mechanical energy supplied to the system [63]. In the mechanical grinding process, several phenomena occur, such as

- a. Fragmentation of grains
- b. Generation of new surfaces
- c. Formation of dislocations and defects in the crystal structure
- d. Polymorphic phase transformation material, and
- e. Chemical reactions (decomposition, ion exchange, oxidation-reduction, complexation, etc.).

In the synthesis of MOFs, the metal salt and the organic linker are ground together in the absence of solvents. In 2002, Belcher et al. [64] reported the synthesis of a 1D copper coordination polymer, using mechanochemical synthesis (Figure 3).

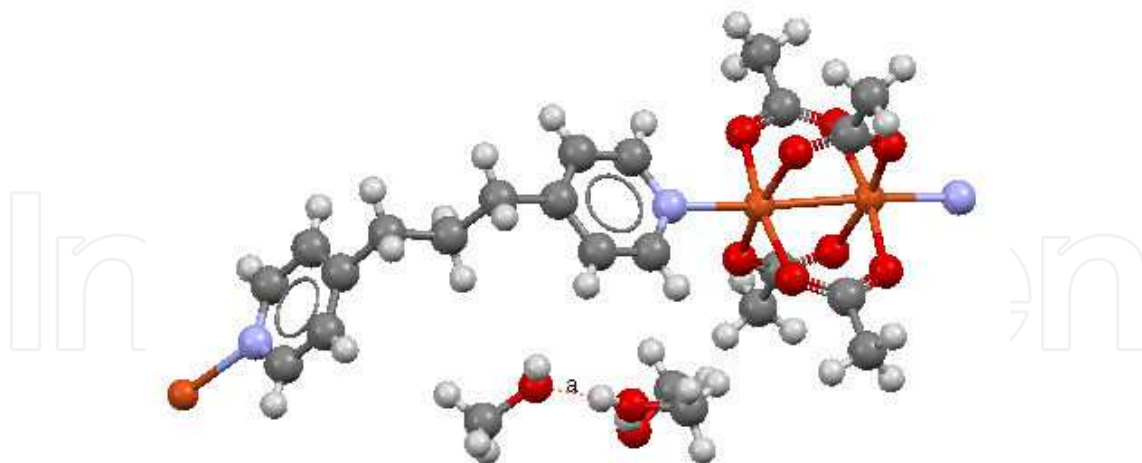


Figure 3. Basic unit of construction of coordination polymer $[\text{Cu}(\text{O}_2\text{C-Me})_2]_2(\mu\text{-dpp})$ dpp = 2,3-bis(2-pyridyl)pyrazine. Gray, red, white, violet, and orange spheres correspond to atoms of C, H, N, O and Cu, respectively.

In other recent studies [65], MOFs were synthesized using 12 metal salts and 5 organic linkers to obtain 60 different solids. As a result, 38 microcrystalline MOFs were identified using X-ray diffraction techniques. Their structure patterns are found on the CSD database (Cambridge Structure Database), including microporous MOFs $[\text{Cu}(\text{INA})_2]_n$ (INA = isonicotinate) and $\text{Cu}_3(\text{BTC})_2$.

2.2.3. Electrochemical synthesis

Electrochemical synthesis of MOFs was reported by BASF in 2005 [66], in order to eliminate the use of anions such as nitrate, perchlorate, and chloride, which act as counterions or as impurities in the network. In this synthesis method, the metal salts are replaced by metal ions produced from the anodic dissolution in the reaction medium. The dissolution also contained organic linkers; in cathodes, metal deposition occurred. In particular, for the synthesis of $\text{Cu}_3(\text{BTC})_2$, copper metal bars that function as electrodes (anode and cathode) were employed in the electrochemical cell with organic linker (BTC = benzene-1,3,5-tricarboxylic), dissolved in methanol [67], with an applied voltage between 12 and 19 V and a current of 1.3 A for 150 min. The result was the oxidation of the copper bar acting as the anode to form Cu^{2+} , which reacts with the organic linker. Furthermore, in cathode, water reduction took place to produce hydrogen. At the end of the reaction, a greenish-blue precipitate was formed, which was filtered and dried to obtain $\text{Cu}_3(\text{BTC})_2$. Using these synthesis pathways, materials can be produced with high purity and ease of being industrially scalable.

Other studies on the electrochemical synthesis of MOFs are presented in Table 1.

2.2.4. Microwave or ultrasound-assisted synthesis

Synthesis assisted by ultrasound or microwave is an alternative to the solvothermal synthesis. In microwave-assisted synthesis, the reaction mixture is subjected to nonionizing radiation,

MOF	Type of synthesis	Reference
Zn and Cu-carboxylates	Systematic study of Zn, Cu, Co and Mg as anode 1,2,3-H ₃ BTC, 1,2,5-H ₃ BTC, H ₂ BCD y H ₂ BCD-(OH) ₂	[66]
Zn-Imidazoles	Synthesis of Zn(MeIm) ₂ and Zn(BIm) ₂	[68]
Cu ₃ (BTC) ₂	Synthesis and y growth of galvanic displacement layered	[67]

H₃BTC = benzene-1,3,5-tricarboxylic acid; H₂BCD = terephthalic acid; MeIm = 2-methyl-1H-imidazole; BIm = benzimidazole.

Table 1. MOFs synthesized electrochemically.

which does not change the electronic structure of the material. The energy supplied to the material by electromagnetic waves through interactions of molecular type offers a number of advantages, such as a uniform controlled heating as well as a great speed with which energy is generated [69]. The characteristic frequency of this radiation is between 300 MHz and 300 GHz (wavelengths between 0.01 and 1 m). This synthetic method has been applied to organic molecules [70] and inorganic materials [71].

Generally, the microwave synthesis is carried out in minutes and offers a better method to control the morphology of the material and the selectivity of the phases. For example, MOF-5 (Figure 4) was synthesized using microwave at 368 K for 9 min, with a yield of 27% [72], while using the solvothermal synthesis, a yield of 60% was achieved after 7 days.

Table 2 shows the conditions of microwave-assisted synthesis of MOFs.

MOF	Time (min)	Temperature (K)
IRMOF1, IRMOF2, IRMOF3	0.42	
(EMIm) ₂ [Ni ₃ (TMA) ₂ (OAc) ₂](EMIm) ₂ [Co ₃ (TMA) ₂ (OAc) ₂]	50	473
[Ni ₂₀ (C ₅ H ₆ O ₄) ₂₀ (H ₂ O) ₈]·40H ₂ O	1	423–493
MIL(Cr)-101	1–40	483
[Cu ₂ (pyz) ₂ (SO ₄)(H ₂ O) ₂] _n	20, 360	453
[Cu ₂ (oba) ₂ (DMF) ₂].5.25(DMF)	1–150	433
[Mn ₃ (BTC) ₂ (H ₂ O)] ₆	10	393
[Cd(H ₃ IDC)(bbi) _{0.5}]	20	
MOF-5	9–60	368–408
[Cu ₃ (BTC) ₂ (H ₂ O) ₃] [Cu ₂ (OH)(BTC)(H ₂ O)]·2nH ₂ O	60	413
[Cu(H ₂ BTC) ₂ (H ₂ O) ₂].3H ₂ O	10	443
[Zn ₂ (NDC) ₂ (DPNI)]	60	393
[Co ₃ (NDC) ₃ (DMF) ₄] y [Mn ₃ (NDC) ₃ (DMF) ₄]	30	383

EMIm = 1-ethyl-3-methylimidazolium; TMA = trimesate; pyz = pyrazine; oba = 4,4'-oxydibenzoic acid; BTC = benzene-1,3,5-tricarboxylic; H₃IDC = 4,5-imidazoledicarboxylic acid; bbi = 1,1'-(1,4-butanediyl)bis(imidazole); NDC = 2,7-naphthalene dicarboxylate; DPNI = N,N di(4-pyridyl)-1,4,8-naphthalenetetracarboxydiimide.

Table 2. Conditions of microwave-assisted synthesis of MOFs [73].

Ultrasound-assisted synthesis is another route for obtaining materials, where you can get MOFs with small crystal size in a short reaction time. In this synthesis, the reaction mixture is subjected to ultrasound (part of the spectrum of the sound whose frequency is approximately 19 kHz) to generate high temperatures (above 5000 K) and pressures at specific locations within the mixture. Such increases in temperature and pressure are due to the phenomenon of "cavitation", which involves the creation, expansion, and destruction of small bubbles that appear when the reaction mixture is treated with ultrasound [74]. In this case, acoustic radiation mechanical energy is converted into thermal energy. Among the MOFs synthesized by this method are MOF-5, MOF-177, Cu_3BTC_2 , Zn-2,2'-bipyridina-5,5'-dicarboxilato, $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ [Zn (1,4-bencendicarboxilato) (H_2O)] $_n$ [75].

2.2.5. Synthesis of MOFs using near supercritical water conditions

Motivated by the resolution of the problem that exists with the use of solvents (1.3.1), Schröder and Poliakoff [76] developed a new methodology for the synthesis of MOFs, building for its acronym high-temperature water (HTW). Due to these properties, the HTW has been studied as a means of organic reactions [77, 78], destruction of contaminants [79] and formation of nanoparticles [80, 81]. Water properties change dramatically as it approaches its critical point (647 K, 220 bar) [82]. For example, the dielectric constant decreases to values of typical nonpolar solvents, and therefore, organic compounds, such as organic ligands of MOFs, can be dissolved.

Water can potentially be reused after the reaction has been completed and, if necessary, ion exchange may be employed in order to remove any traces of unreacted organic ligand and metal ions. HTW presents some technical difficulties due to the high pressures and accelerated corrosion of the reactors. However, Schröder and Poliakoff [76], in 2012, first reported the possibility of using HTW (573 K) as solvent for the synthesis of a MOF with high performance. The new MOF, $\{[\text{Zn}_2(\text{L})] (\text{H}_2\text{O})_3\}_\infty$; (L = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene) (Figure 4), is synthesized using only water as reaction medium at 573 K and 80 bar.

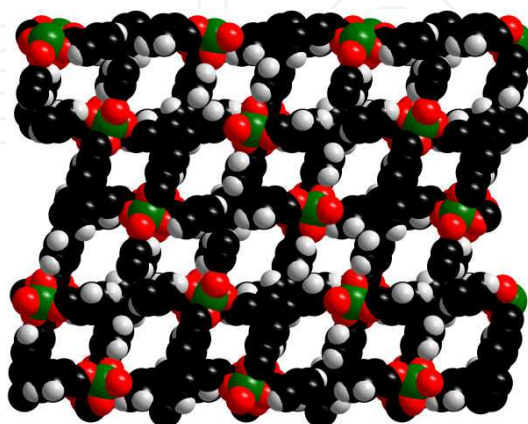


Figure 4. View of the crystal structure of the structure $\{[\text{Zn}_2(\text{L})] (\text{H}_2\text{O})_3\}_\infty$. Green, red, black and gray represent Zn atoms, O, C, and H, respectively [76].

2.3. Characterization and evaluation methods of MOFs

The different methods of synthesis of MOFs can generate homogeneous solids that allow carrying out processes of heterogeneous catalysis. Once the reaction finished, it is desirable that the physicochemical characteristics of material prevail. There are different characterization techniques for determining the homogeneity of the material, structural characteristics, and stability of the MOF. Analytical methods that are useful and applicable are listed below. However, others characterizations may exist which are also useful in the evaluation of MOFs, such as heterogeneous catalysis.

Powder X-ray diffraction (XRD) is used in determining the crystallographic MOFs by comparing the diffractogram of MOF before and after the catalytic process. In certain processes, the stability of the structure is also determined. Additionally, it is possible to determine the purity of the catalyst and some crystallographic parameters as red parameter, size of lattice, and crystal size.

Fourier transform infrared spectroscopy (FTIR) provides information about functional groups present in the network of the MOF. It is possible to make a comparison to determine the changes once the network has carried out the catalytic reaction.

Nuclear magnetic resonance (NMR) is a widely used technique in the characterization of products, by-products, and intermediates of the catalysed reaction. It is possible to determine the chemical environment inside the catalyst using probe molecules.

Nitrogen physisorption. The texture parameters such as surface area, pore volume, and average pore size are determined by this technique. The shape of the isotherm provides information about the homogeneity of the solid.

Ultraviolet-visible diffuse reflectance spectrum provides information about the environment metal coordination before and after carrying out a catalysed reaction.

Thermogravimetric analysis (TGA) is useful to determine the thermal stability of the MOF. In some processes, it is necessary to conduct a heat treatment prior to the catalysed reaction and treatment parameters are determined by TGA. It is possible to obtain a model which is highly suitable for the process reaction desired.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are able to show the morphology, defects, grain boundaries, mixtures of crystalline phases, and grain size, among others. In some solids, even the crystallinity and porosity can be determined by these techniques.

Energy-dispersive X-ray (EDX) is used to determine the elemental materials analysis. The MOF is studied before and after the catalytic process for identifying the presence of new elements and their percentage.

Gas absorption analyser can be used to analyze the adsorption capacity for MOF for a particular gas or vapour.

Gas/liquid chromatography-mass spectrometry (GC/LC-MS) is a powerful technique to analyse the catalytic reaction and determine the amount and type of products.

Raman spectroscopy is widely used in the characterization of noncrystalline or low-crystalline catalysts. Comparing the spectra before and after the reaction provides information about the incorporation of new components into the MOF network.

Temperature-programmed reduction (TPR) is used in determining redox reaction parameters. The catalytic activity in redox conditions can be determined by this technique.

3. MOF's structure using catalytic reaction

The active sites of MOFs can be designed depending on the type of catalytic process. The Rosseinsky group reported the methanolysis of rac-propylene oxide and expected to yield 2-methoxy-1-propanol and 1-methoxy-2-propanol reaction. They used the postsynthesis modification of a porous homochiral Ni(L-asp)bipy 0.5, 1 (L-asp = L-aspartate, bipy = 4,4-dipyridyl), leading to a functional Brønsted acidic material. These compounds are amino acids (L- or D-aspartate) together with dipyridyls as struts. The coordination chemistry is such that the amine group of the aspartate cannot be protonated by added HCl, but one of the aspartate carboxylates can. Thus, the framework-incorporated amino acid can exist in a form that is not accessible for the free amino acid. While the nickel-based compounds are marginally porous, on account of tiny channel dimensions, the copper versions are clearly porous [83].

The results showed that the carboxylic acids behave as Brønsted acidic catalysts, facilitating (in the copper cases) the ring-opening methanolysis of a small, cavity-accessible epoxide at up to 65% yield. These researchers pointed out that the superior homogeneous catalysts existed, but emphasized that the catalyst formed here is unique to the MOF environment, thus representing an interesting proof of concept [84].

Lewis acid solids are commonly used in selective oxidation. An example of this type of catalysts is trinuclear networks containing Cu^{2+} , which have shown a high activity and selectivity for the peroxidative oxidation process of cyclohexane into the corresponding alcohols and ketones ($\text{MeCN}/\text{H}_2\text{O}/\text{HNO}_3$ media) [85]. The structure of such MOFs is composed of the secondary building unit of $\{\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pyrazole})\}$ with tetracoordinate metal centers in axial positions of easy access.

Other structures with these types of catalytic sites on the $\text{Cu}_3(\text{BTC})_2$ coordinated network are made of copper links. It is feasible to prepare this MOF with modulated amounts of physisorbed (molecules placed into the channels) or chemisorbed (molecules occupying CuX coordination sites) water molecules with high surface area straight from the reaction vessel without any postsynthetic steps [8]. Different reaction models have been tested in this MOF including: citronellal cyclization [86], benzaldehydecyanosilylation [87], rearrangement of ethylene acetal of 2-bromopropiophenone, isomerization of alpha-pinene oxide [86], among others [28].

Another example of MOF with high concentration of Lewis acidic sites is $\text{Mn}_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{CH}_3\text{OH})_{10}]_2$; H_3BTT = 1,3,5-benzene-tristetrazol-5-yl. Mn^{2+} ions that are exposed on the surface of the framework might serve as potent Lewis acids, and catalyze the

cyanosilylation of aromatic aldehydes and ketones, as well as the more demanding Mukaiyama-aldol reaction. Moreover, in each case, a pronounced size-selectivity effect consistent with the pore dimensions is observed [88].

Different types of MOF have been used in catalytic process as base catalysis, Brønsted acid catalysis, Lewis acid catalysis, C–C bond formation and polymerization, enantio selective catalysis, and catalysis by organometallic complex supported on MOFs, among others. Table 3 summarizes the MOF structures used in some catalytic processes reported so far. The most common ions catalysis are: Ag^+ , Al^{3+} , Bi^{3+} , Ce^{4+} , Cr^{3+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Mg^{2+} , Pd^{2+} , Sc^{3+} , V^{4+} , Zn^{2+} , and Zr^{4+} .

MOF	Catalysed reaction	Reference
$\text{Al}_2(\text{bdc})_3(\text{MIL-53}(\text{Al}))$	Reduction of carbon–carbon multiple bonds	[89]
$[\text{Ag}_3(\text{tpha})_2] 3\text{BF}_4$ (Ag-tpha)	1,3-Dipolar cycloaddition	[90]
Bi(btbt)	Hydroxymethylation of 2-methylfuran	[91]
Ce-mdip1	Cyanosilylation of aldehydes	[92]
$\text{Cd}(4\text{-btapa})_2(\text{NO}_3)_2$	Knoevenagel condensation	[93]
$[\text{Cd}(\text{bpy})_2](\text{NO}_3)_2$	Cyanosilylation of aldehyde	[94]
$\text{Cd}_3\text{Cl}_6\text{L13}$	Alkylation of aldehyde	[95]
Co(BPB)	Oxidation of olefin	[96]
$\text{Co}_2(\text{dhbdc})(\text{H}_2\text{O})$ (Co-MOF-74)	Cycloaddition of CO_2 and epoxides	[97]
$[\text{Co}(\text{DMA})_6]_3[(\text{Co}_4\text{Cl})_3 \cdot (\text{btt})_8(\text{H}_2\text{O})_{12}]_2(\text{Co-btt})$	Ring opening of epoxides; oxidation of hydrocarbons	[98]
$\text{Cr}_3\text{X}(\text{H}_2\text{O})_2\text{O}(\text{bdc})_3$ $\text{X} = \text{F}, \text{OH}, (\text{MIL101}(\text{Cr}))$	Knoevenagel condensation; Heck coupling; Cyanosilylation of aldehydes Oxidation of hydrocarbons Oxidation of sulfides Cycloaddition of CO_2 and epoxides	[99–103]
$[\text{PW}_{11}\text{TiO}_{40}]^{5-} @ [\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{bdc})_3]$, and $[\text{PW}_{11}\text{CoO}_{39}]^{5-} @ [\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{bdc})_3]$	Oxidation of olefin	[104]
$\text{Cu}(2\text{-pymo})_2$ and $[\text{Co}(\text{PhIM})_2]$	Aerobic oxidation of olefin	[105]
$\text{Cu}(\text{bpy})(\text{H}_2\text{O})_2(\text{BF}_4)_2(\text{bpy})$	Ring-opening of epoxide	[106]
$\text{Cu}(\text{D-asp})\text{bpe}_{0.5}$ and $\text{Cu}(\text{L-asp})\text{bpe}_{0.5}$	Methanolysis of epoxide	[83]
$\text{Cu}(\text{L}_2)_2(\text{H}_2\text{O})_2$, $\text{Cu}(\text{L}_3)_2(\text{H}_2\text{O})(\text{Py})_2$, $\text{Cu}(\text{L}_3)_3(\text{H}_2\text{O})\text{Cl}$ and $\text{Co}(\text{sal})(\text{H}_2\text{O})(\text{Py})_3$	Epoxidation of olefin	[107]
$\text{Cu}(\text{SO}_4)(\text{pbbm})$ and $(\text{Cu}(\text{Ac})_2(\text{pbbm}))\text{CH}_3\text{OH}$	Oxidative self-coupling	[108]

MOF	Catalysed reaction	Reference
$\text{Cu}_3(\text{btc})_2$	Isomerization; cyclization; rearrangement Oxidation of polyphenol Cyanosilylation of aldehyde	[86, 87, 109–113]
$\text{Cu}_2(\text{papa})_2\text{Cl}_2$	Biginelli reaction; 1,2-addition of a,b-unsaturated ketones	[115]
$\text{Cu}_3(\text{pdtc})(\text{pvba})_2(\text{H}_2\text{O})_3$	Henry reaction	[115]
$\text{Cu}(2\text{-pymo})_2$	Click reaction	
	Three-component couplings of amines, aldehydes and alkynes	[116, 117]
$\text{Cu}(\text{tcba})(\text{DMA})$	Epoxidation of olefins	[118]
$\text{Cu}_2(\text{bpdc})_2(\text{bpy})$	Cross-dehydrogenative coupling reaction	[119]
$\text{Cu}_2\text{I}_2(\text{bttp4})$	Three-component coupling of azides, alkynes, and amines	[120, 121]
Cu-MOF-SiF_6 and Cu-MOF-NO_3	Oxidation of benzylic compounds	[122]
CuPhos-Br and CuPhos-Cl and CuPhos-PF_6	Ketalization reaction	[123]
$\text{Fe}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{btc})_2$ (MIL-100(Fe))	Friedel–Crafts benzylation Oxidation of hydrocarbons Ring-opening of epoxides Claisen Schmidt condensation Oxidation of thiophenol to diphenyldisulfide Isomerization of a-pinene oxide	[124–129]
$\text{In}(\text{OH})(\text{hippb})$	Acetalization of aldehyde	[130]
$\text{In}_2(\text{OH})_3(\text{bdc})_{1.5}$	Reduction of nitroaromatic; oxidation of sulfide	[131]
$\text{Mg}_3(\text{pdc1})(\text{OH})_3(\text{H}_2\text{O})_2$	Aldol condensation reactions	[132]
$\text{Mg}(\text{pdc2})(\text{H}_2\text{O})$	Aldol condensation reactions	[133]
$\text{Mn}(\text{porphyrin})@[\text{In}_{48}(\text{HImDC})_{96}]$	Oxidation of alkane	[134]
$\text{Ln}(\text{OH})(1,5\text{-NDS})\text{H}_2\text{O}$	Epoxidation of olefin	[135]
$(\text{Mn}(\text{TpCPP})\text{Mn}_{1.5})(\text{C}_3\text{H}_7\text{NO})_5\text{C}_3\text{H}_7\text{NO}$	Epoxidation of olefin; oxidation of alkane	[136]
$[\text{Mn}_3((\text{Mn}_4\text{Cl})_3\text{BTT}_8(\text{CH}_3\text{OH})_{10})_2]$	Cyanosilylation of aldehyde; Mukaiyama-aldol	[88]
$\text{Mn}_2(\text{pvia})_2(\text{H}_2\text{O})_2$	Alcohol oxidation	[137]
$(\text{Na}_{20}(\text{Ni}_8\text{L4}_{12})(\text{H}_2\text{O})_{28})(\text{H}_2\text{O})_{13}(\text{CH}_3\text{OH})_2$	Oxidation to CO_2	[138]
$\text{Sc}_3(\text{OH})(\text{H}_2\text{O})_2\text{O}(\text{btc})_2$ (MIL-100(Sc))	Intermolecular carbonyl ene reaction; Michael addition reaction; ketimine and aldimine formation	[139]

MOF	Catalysed reaction	Reference
Pd(2-pymo) ₂	Oxidation of alcohol; Suzuki–Miyaura coupling; hydrogenation of olefin	[140–142]
Tb[V ₆ O ₁₃ {(OCH ₂) ₃ C(NH ₂ CH ₂ C ₆ H ₄ -4-CO ₂)}{(OCH ₂) ₃ C-(NHCH ₂ C ₆ H ₄ -4-CO ₂)} ₂] ⁴⁺	Oxidation of sulfide	[143]
V ^{IV} O(bdc) (MIL-47(V))	Oxidation of hydrocarbons	[144, 145]
Zn ₂ (bpdc) ₂ L5	Epoxidation of olefins	[146]
Zn ₂ (Py ₂ (PhF ₅) ₂ PorZn)(TCPB)	Intermolecular transfer of acyl	[147]
[Zn ₃ (m ₃ -O)(O ₂ CR) ₆ (H ₂ O) ₃] ⁿ⁺	Transesterification	[148]
Zn ₄ O(bdc) ₃] and [Zn ₄ O(ndc) ₃	Friedel–Crafts alkylation	[149]
[(Zn ₄ O)(bdc-NH ₂) ₃]Vsal _{0.4}	Oxidation of olefin	[150]
Zn ₂ (bdc)(L-lac)(dmf)	Oxidation of thioethers	[151]
Zn ₃ (chirbtb-1) ₂	Mukaiyama aldol reaction	[152]
Zn ₃ (chirbtb-2) ₂	Mukaiyama aldol reaction	[152]
Zn(Meim) ₂ (ZIF-8)	Cycloaddition of CO ₂ and epoxides	[153]
Zr ₆ O ₄ (OH) ₄ (bdc) ₆ (UiO-66)	Aldol condensation reactions Cyclization of citronellal	[154–156]]

Ac = acetyl; bdc = 1,4-benzenedicarboxylate; BPB = 1,4-bis(4'-pyrazolyl)benzene; bpdb = 1,4-bis(3,5-dimethyl-1H-pyrazol-4-yl)benzene; bpdc = biphenyldicarboxylate; bpe = trans-1,2-bis(4-pyridyl)ethylene; bpy = 4,4'-bipyridine; btc = benzene-1,3,5-tricarboxylate; btapa = 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide]; btb = 5-(4-carboxyphenyl)-[1,1':3',1''-terphenyl]-4,4'-dicarboxylate; btt = 1,3,5-benzenetris(tetrazol-5-yl); btp4 = benzene-1,3,5-triyl triisonicotinate; ChirBTB-1 = 5'-(4-carboxy-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)phenyl)-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-3'-(3-isopropyl-5-oxooxazolidin-4-yl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate; ChirBTB-2 = 3,3''-bis((S)-4-benzyl-2-oxooxazolidin-3-yl)-5'-(3-(3-benzyl-5-oxooxazolidin-4-yl)-4-carboxyphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic; D-aspartate; bdc = benzene-1,4-dicarboxylate; dhbdc = 2,5-dihydroxyisophthalic; ImDC = 4,5-imidazole dicarboxylate; ippb = 4,4'-(hexafluoroisopropylidene)bis(benzoate); L1 = (R)-6,6'-dichloro-2,2-dihydroxy-1,1'-binaphthyl-4,4'-bipyridine; L2 = (4-formylphenoxy)acetic acid; L3 = 2-[2-[(2-aminoethyl)imino]methyl]phenoxy]acetic acid; L4 = 4,5-imidazoledicarboxylic acid; L5 = (R,R)-(-)-1,2-cyclohexanediamino-N,N-bis(3-tert-butyl-5-(4-pyridyl)salicylidene)Mn^{III}Cl; L-lac = L-lactic acid; mdip = 5,50-methylenediisophthalic; meim = 2-methyl-1H-imidazole; nds = naphthalenedisulfonic acid; papa = (S)-3-hydroxy-2-((pyridin-4-ylmethyl)amino)propanoic; pbbm = 1,1'-(1,5-pentanediy)bis(1H-benzimidazole); pdc-1 = pyrazole-3,5-dicarboxylate; pdc-2 = pyridine-2,5-dicarboxylate; PhIM = phenyl imidazolate; ptdc = pyridine-2,3,5,6-tetracarboxylic; pymo = 2-hydroxypyrimidinolate; Py₂(PhF₅)₂Por = 5,15-dipyridyl-1',2'-bis(pentafluorophenyl)porphyrin; pvia = (E)-5-(2-(pyridin-4-yl)vinyl)isophthalic; pvba = (E)-4-(2-(pyridin-4-yl)vinyl)benzoic; sal = salicylidene moiety; tcba = 4,4'',4'''-nitrotris([1,10-biphenyl]-4-carboxylic); TCPB = 1,2,4,5-tetrakis(4-carboxyphenyl)benzene; TpCPP = tetra-(p-carboxyphenyl)porphyrin; tpha = tris(4-((E)-1-(2-(pyridin-2-yl)hydrazono)ethyl)phenyl)amine.

Table 3. MOF structure used for catalytic reaction.

4. Limitation of MOF structures

MOFs are excellent candidates for certain catalytic processes because: (1) they can be designed on a rational basis according to specific requirements; (2) their well-defined

structure allows the assessment of structure–activity relationships; (3) the uniform catalytic sites; and (4) the intrinsic nature of their pores.

However, the synthesis of MOF requires a series of steps to allow an activation network free of solvent molecules and to expose the active sites, which can often require coordinating solvents that may be toxic, carcinogenic, and/or dangerous to the environment [59]. In some processes, the structure collapses, and activation prevents further use in catalysis.

Furthermore, when washed with solvent, they typically require energy, which increases the time synthesis process and drastically affects the efficiency. For example, with MOF-5 synthesized using solvothermal processes, a yield of 60% was achieved after 7 days [72].

The use of coordinating solvents during the synthesis of MOF such as dimethylformamide (DMF) or diethylformamide (DEF) may interfere with the availability of molecules to interact with the active sites. DMF and DEF decompose when heated at high temperatures for long periods and therefore cannot be reused [60]. The study of local defects is also crucial since catalytic processes can be favoured with the appearance of the same or conversely the process is catalysed not by excess thereof.

The MOF's purity can be affected by the formation of other crystalline compounds or the presence of reagents in the network. However, characterization of MOFs' purity and homogeneity can seldom be found in scientific papers about catalysis.

The thermal and chemical stability of MOFs is also a limitation for use in some catalytic process. The zirconium MOF reported by Hafizovic Cavka et al. [157], which has a thermal resistance above 500°C, resistance to most chemicals, and they remain crystalline even after exposure to 10 tons/cm² of external pressure, whereas other MOFs have a lower thermal and chemical stability.

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