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REVIEW ARTICLE

A review on metal-organic framework: Synthesis, properties and application

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ABSTRACT

Metal organic framework is a class of hybrid network of supramolecular solid materials comprised of a large number of inorganic and organic linkers all bounded to metal ions in a well-organized fashion. This type of compounds possess a greater surface area with an advantage of changing pore sizes, diversified and beautiful structure which withdrew an intense interest in this field. In the present review articles, the structural aspects, classification, methods of synthesis, various factors affecting the synthesis and stability, properties and applications have been discussed. Recent advances in the field and new directions to explore the future scope and applications of MOFs have been incorporated in this article to provide current status of the field.

Keywords: Metal Organic Framework; Nanoporous Material; Drug Delivery; Gas Sensor; Secondary Building Unit

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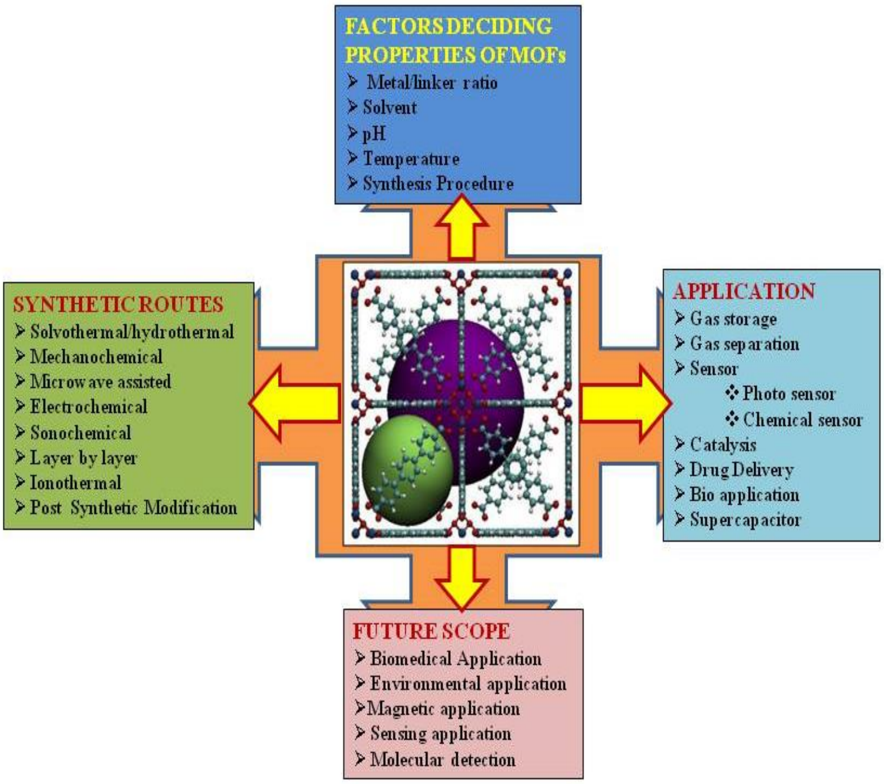

Framework of this paper

1. Introduction

Metal-organic framework (MOF) is a promising class of materials composed of metal centres or clusters and organic linkers. These are porous crystalline materials in which metal is locked into a position to produce rigid and porous geometry and connected through different organic groups. Due to structural flexibility, large surface area and tailorable pore size, MOFs have wide applications in field of gas adsorption and storage, separation, catalysis, sensing, molecular recognition, drug delivery, non-linear optics, luminescence etc.[1-12]. Due to three dimensional tuneable porous channels, MOFs are useful materials for storage, separation or conversion of molecules on the basis of dimension. Generally, MOFs are related to the general class of co-ordination polymers. However, MOFs are more specific than co-ordination polymers for 2D or 3D crystallized networks with porous structure. Thus these are also termed as porous coordination polymer (PCP)[13,14]. Although, several review articles on metal-organic frameworks have been published previously, however, recent advances including the contributions of some Indian research groups, such as Banerjee *et al*., Ghosh *et al*., and Kumar etc. necessitates further review on this topic. The present paper comprehensively reviewed the methods of synthesis, properties and applications of MOFs based on reported literature. Recent advances and new foundations, direction for further exploring MOFs for their applications as well as critical analysis of the research have been incorporated in this paper so as to provide the current status of the field.

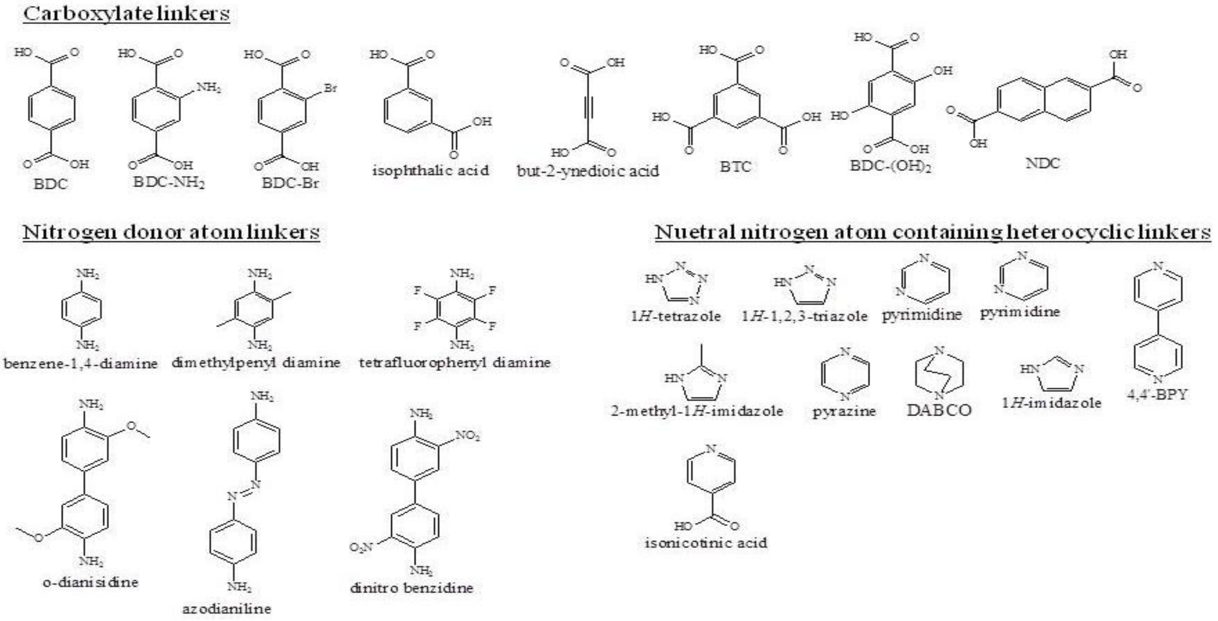

Figure 1. Some Linkers used in synthesis of MOFs.

2. Structural aspects

2.1 Primary building units

The metal ions (connectors) connecting the organic polymers which are linkers are basic primary units that result in porous three dimension structure MOFs. Thus, the metal ions and organic compounds used in the formation of metal-organic frameworks are the "Primary Building Units". Commonly, metal ions of first row transition series such as Cr^{3+}, Fe^{3+}, Co^{2+}, Zn^{2+} are used as connectors in the formation of MOFs[15-17]. Some alkali metal ions[18,19], alkaline-earth metal ions[20-22] and rare earth metal ions[23-27] are also used as a metal connector in the synthesis of MOFs. Nitrate, acetate, sulphate, chloride and oxide of metals are used as precursor for preparing MOFs in most of the synthesis routes. However, in electrochemical synthesis of MOFs metal rods are used.

Organic linkers, through which the metal ions or nodes are connected, generally contain functional groups that are capable of forming coordination bonds such as carboxylate, phosphate, sulfonate, amine, nitrile etc. some examples of organic linkers are shown in **Figure 1**.

2.2 Secondary building units (SBUs)

In MOFs, organic linkers are connected through metal-oxygen-carbon clusters, instead of metal ions alone. These metal-oxygen-carbon clusters are referred as “Secondary Building Units” (SBUs). SBUs have intrinsic geometric properties, which facilitate MOF’s topology[28]. Some SBUs are shown in **Figure 2**.

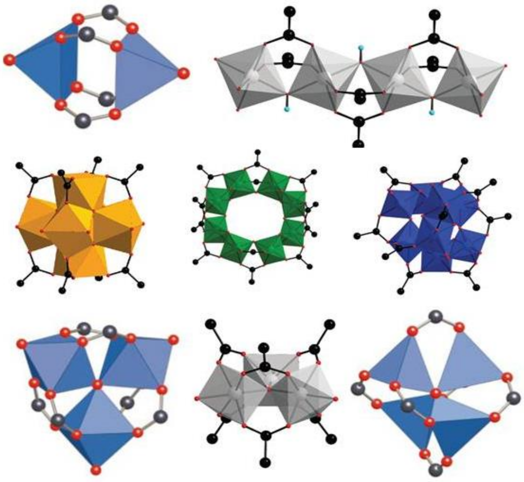

Figure 2. Some secondary building units (SBUs).

2.3 Classification of metal-organic frameworks

On the basis of structural features, MOFs have been classified[29] in following groups.

(a) Rigid frameworks: These are stable and robust porous frameworks and retain their porous framework on adsorption or desorption of guest molecules. These MOFs are applicable in molecular sieving[30].

(b) Flexible/dynamic frameworks: Flexible frameworks show an utmost change in shape on insertion or removal of guest particles and also affected by external factors such as pressure, temperature. Dynamic MOFs show a change in framework on removal of solvent molecules but retain their porous structure on adsorption of gas molecules at high pressure[4]. MIL-5[31,32], MIL-8[33] and SNU-M10[34] are some MOFs that exhibit breathing effect during adsorption and desorption. In breathing MOFs[35], there is a severe change in unit cell volume (pore volume) on adsorption/desorption of guest molecules. Different types of flexibility modes are identified and reviewed as shown in **Figure 3**.

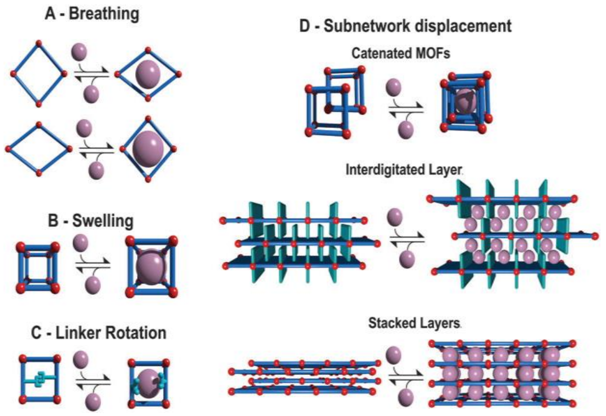

Figure 3. Classification of different flexibility modes of MOFs.

(c) Open metal site: Performance of MOFs can be enhanced by the presence of open metal site. Presence of water in open metal site MOFs enhances the CO_2 capture ability of the MOFs. For example, HKUST-1 $[(Cu)_3(btc)_2]$ which has an open metal site structure and consists of paddlewheel units $Cu_2(COO^-)$ connected through btc^{3-} ligands, exhibits a significant increase in CO_2 adsorption when it contains 4 wt.% water[36].

(d) Surface functionalized framework: Adsorption ability of MOFs can be enhanced by grafting functional groups onto the surface of the MOFs. Functional groups with a high affinity for CO_2 (e.g. arylamine[37], alkylamine[38], hydroxyl[39]) have been reported to enhance the capacity and selectivity of MOFs for CO_2 adsorption when these functional groups are grafted onto the surface of the porous framework through either ligand modification or coordination to unsaturated metal centre.

3. Synthesis of MOFs

As discussed earlier, MOFs consists of two major components, metal ion and organic linkers or bridging ligands. Conventionally, MOFs are prepared by combining metal ions and organic linkers under mild conditions in order to get a crystalline and porous network. This is termed as “Modular Synthesis”[40].

Metal ions + organic linkers → MOF

During the last two decades, different synthesis methods have been developed and applied to synthesize these materials. In general, these can be classified as conventional solvothermal method and unconventional method.

3.1 Conventional solvothermal/hydrothermal and non-solvothermal method

In conventional solvothermal synthesis, a mixture of metal ions and organic linkers in solvent is heated in glass vials (for lower temperature) or in Teflon lined autoclaves or bomb reactor (for temperature higher than ≈400 K)[41]. If water is used as solvent, this method is termed as hydrothermal method. The synthesis parameters that are controlled for specific structure are pressure, temperature, solvent composition, reagent concentration etc. Temperature of reaction mixture is an important parameter in the synthesis of MOFs. When the temperature of the reaction is higher than the boiling point of solvent, then the reaction is referred as solvothermal reaction and when the temperature is lower than the boiling point of solvent, it is referred as nonisothermal reaction. Some MOFs, such as MOF-5, MOF-74, MOF-177, HKUST-1 ZIF-8, have been reported to synthesize at ambient condition[42-44]. This method is also known as direct precipitation reaction. Morphology of the crystals produced is highly affected by the reaction temperature[45].

3.2 Unconventional methods

A mixture of metal salt and organic linker is grinded in a mortar pestle or in a ball mill without using solvent after grinding the mixture is heated gently to evaporate water or other volatile molecules which are formed as by products in the reaction mixture[46]. This method is termed as mechanochemical method. In this method, breaking of intramolecular bonds by mechanical force takes place followed by a chemical transformation. The method is known to be environmentally friendly because of no use of any solvent and can give high yield of products[47,48]. Quantitative yields of small MOF particles can be obtained in short reactions times, normally in the range of 10-60 min. In many cases, metal oxides were preferred over metal salts as starting material, which results in water as the only byproduct[49]. Synthesis of porous framework using mechanochemical method is first reported by Pichon *et al.*[50] in 2006. Comparative study of a bipyridene-based covalent organic framework (COF) has been reported using solvothermal and mechanochemical methods and it is revealed that proton conducting property[51] is revealed by mechanochemically synthesized COF only. When solvent is added in a small amount, the mechanochemical process is termed as liquid-assisted grinding (LAG). Addition of small amount of solvents in reaction mixture accelerates the mechanochemical reactions by increasing the mobility of the reactants[52].

3.3 Alternative synthesis methods

Alternative routes have also been attempted in addition to these methods. Alternative routes can lead to different crystallization rate, particle size, size distribution and adsorption properties as well as morphologies that can have an influence on the properties of material. For example, diffusion of guest molecules in porous materials with different particle size can exhibit a direct effect on catalytic activity, adsorption and separation capacity of molecules. Important alternate routes can be categorised as:

3.3.1 Microwave-assisted synthesis

In this method, energy for reaction is provided in the form of microwave (MW) radiation. It is generally used in organic syntheses, but it has wide application in rapid synthesis of nanoporous materials. Apart from fast crystallization, phase selectivity[53,54], narrow particle size distribution[55] and morphological controls[56,57] are some of the advantages of this method. Several MOFs containing

Fe^{3+}, Al^{3+}, Cr^{3+}, V^{3+}, Ce^{3+} have been synthesised using MW assisted method. Cr-MIL-100[58] is the first MOF which has been synthesized via MW method.

Formation of MOFs has been reported to carry out under MW radiation at a temperature over 100˚C with reaction time exceeding 1 hour. Generally, MOFs can be formed quickly via MW irradiation with respect to conventional electrical heating process. By applying MW synthesis route two MOFs, named IRMOF-1 and HKUST-1, are studied widely. IRMOF-1 reveals crystals of higher quality and better CO_2 adsorption when it is synthesized via MW assisted route[59]. Highly pure and micropore with high volume (0.79 cm^2 gm^{-1}) HKUST-1 is prepared by MW synthesis in a short time of 30 minutes[60].

3.3.2 Electrochemical synthesis

Researchers at BASF first reported the synthesis of MOF using electrochemical route[61]. They developed new synthesis procedures for some MOFs using Zn, Cu, Mg, Co as cathode material and 1,3,5-H_3BTC and 1,2,3-H_3BTC, H_2BDC and $H_2BDC\text{-}(OH)_2$ as linkers. Electrochemical synthesis of MOF uses metal ions continuously supplied through anodic dissolution as a metal source instead of metals salts, which react with the dissolved linker molecules and a conducting salt in the reaction medium. Protic solvents are used to avoid deposition of metal on cathode, but H_2 is generated in this process[62]. The electrochemical route is also possible to run normal batch reactions[49]. MOFs containing ionic liquids as linker e.g. $[Zn(MIm)_2]$ and $[Zn(BIm)_2]$ are also synthesized via electrochemical route[63].

Schlesinger *et al.*[60] synthesized HKUST-1 using solvothermal, ambient pressure and electrochemical routes and compared the effect of synthesis procedures on its properties. It has been pointed out that the product obtained via electrochemical route reveals inferior quality due to incorporation of linker molecules and/or conducting salt in the pores during crystallization.

3.3.3 Sonochemical synthesis

This is a rapid and environmental-friendly method in which ultra-sonic radiation (20 kHz-10 MHz) is used for MOFs synthesis. This method, via homogenous and accelerated nucleation, can also achieve a reduction in crystallization time and significantly smaller particles size than those by the conventional solvothermal synthesis[64,65]. When high energy ultrasound interacts with liquid, cavitation (process of bubble formation, growth and collapse under altering pressure) takes place and provides energy with high temperature of ≈5000K and pressure of ≈1000 bar[66].

In case of solids, microjets are formed as a result of cavitation process and these microjets clean, erode or activate the surface. Dispersion of agglomerated smaller particles takes place. A chemical reaction can take place when ultrasonic radiation is applied to homogenous liquid. Qiu *et al.*[67] were the first who reported a MOF $[Zn_3(BTC)_2]$ synthesized sonochemically in ethanol which reveals selective sensing towards organoamine. Effect of reaction time on particle size is also investigated in sonochemical synthesis of MOFs. Partial decomposition of crystals at long reaction time is obtained in the sonochemical synthesis of HKUST-1[68].

3.3.4 Layer by layer synthesis

Layer by layer method is used for the preparation of MOF thin films. The method is based on surface chemistry in which functionalized organic surface is immersed sequentially into the solutions of metal ion and organic linker. It was observed that orientation of thin film depends on that sequence through which the reactants are added[69]. The kinetics for stepwise formation in this method has been studied using Surface Plasmon Resonance (SPR) spectroscopy. Metal source and surface termination are the two major factors that affect the rate of growth MOF film[70,71]. Highly oriented growth was observed for substrates functionalized with different functional groups such as COOH, OH[72].

Besides these synthesis routes, other routes such as chemical solution deposition[73-75] (for the preparation of thin film MOFs), post syntheis modification[49] (when functional groups cannot be incorporated during MOF synthesis), and ionothermal method[76, 77] (ionic liquids are used as solvent) have also been implemented for MOF synthesis. Banerjee and coworkers have reported Fe-based MOF which is prepared by Fe-metallogels via gel degradation[78]. However, other MOF has not been reported by this method so far.

4. Factors affecting the synthesis of MOFs

4.1 Solvents

Solvent system plays an important role in MOF synthesis as well as in deciding the morphology of MOFs. Solvents may coordinate with metal ion and or may act as space filling molecules[79,80]. Instead, they also act as a structure directing agent[49]. Solvents used in MOF synthesis should have high boiling point and polar nature. Usually, dimethyl formamide (DMF), diethyl formamide (DEF), dimethyl sulphoxide (DMSO), dimethyl acetamie (DMA), alcohols, acetone, acetonitrile etc. are used as solvent as is shown in **Figure 4**. Sometimes a mixture of solvents is also used, which depends on the solubility of starting materials.

MOF synthesis process is affected by the reaction medium because of polarity of solvent used and solubility and protolysis property of organic linker. It is also reported that different solvent systems in same reaction condition provide MOF of different morphology. This may happen because of difference in degree of deprotonation of organic linker in different solvent system. Banerjee *et al.*[81] reported MOFs containing magnesium and PDC (3, 5–pyridine dicarboxylic acid) have different crystal structure prepared under same condition using different solvent system (**Figure 5**). They found that coordination ability of solvent with metal determines the dimensionality of MOF network. Among DMF, H_2O, EtOH and MeOH, H_2O has the highest affinity towards Mg while EtOH and MeOH do not having any affinity to coordinate with metal centres when DMF/MeOH and EtOH/H_2O are used as solvent.

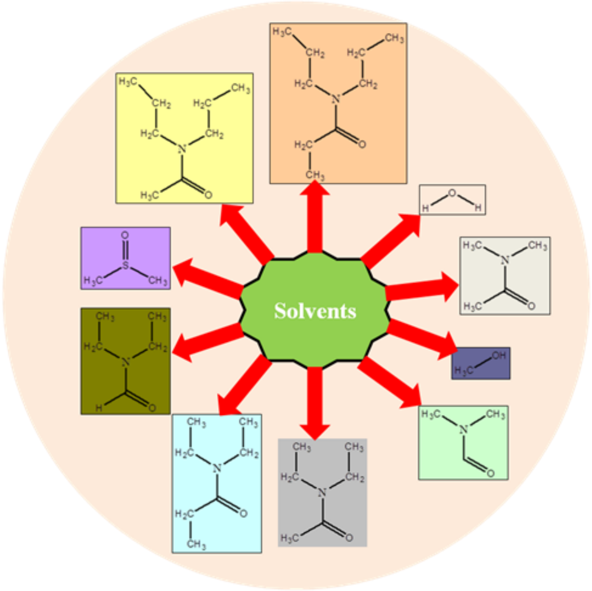

Figure 4. Solvents used in Synthesis of MOFs**.**

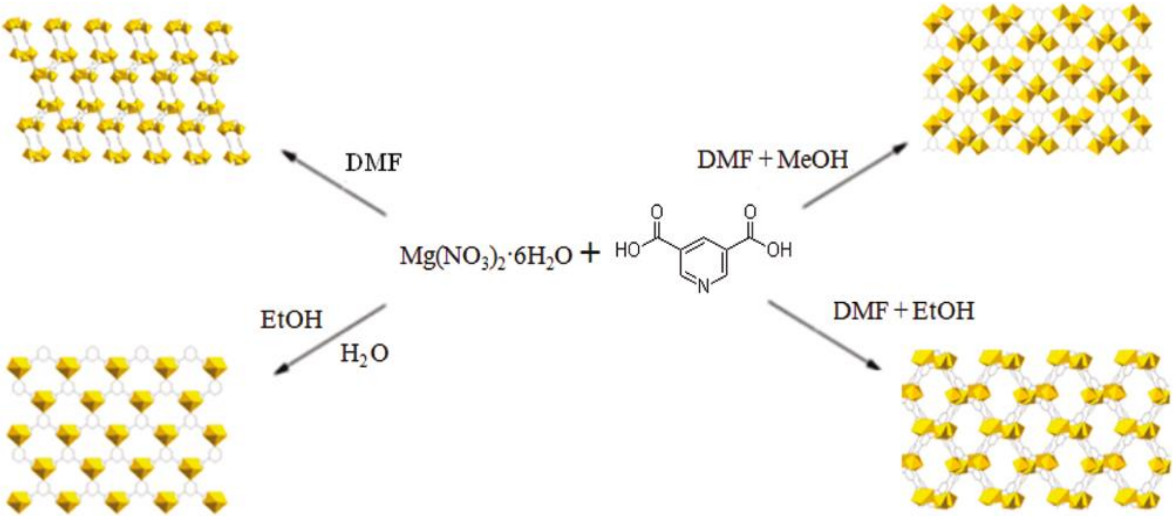

Figure 5. Effect of solvent systems on morphology of MOF**.**

In addition to structure, different solvent systems result in synthesis of MOFs having difference in pore size. MOFs of cobalt and 4,4'-((5-carboxy-1,3-phenylene bis(oxy)) dibenzoic acid (H_3CPBDA) were synthesized using three different solvents viz. DMP, DMA and DMF under the similar conditions resulting into pore sizes of 76.84 Å, 74.37 Å and 72.76 Å respectively. The change in pore size due to different solvents has been correlated with the size of the solvent molecule. Among the three solvents used the size of the molecules varies as DMP > DMA > DMF. The pore size also reduces in the same order[82]. Similar correlations are reported by other researchers[83].

4.2 Effect of temperature and pH on synthesis of MOFs

Temperature and pH of reaction medium have remarkable influence on synthesis of MOFs. Different coordination modes can be adopted by linkers at different pH ranges[84]. Further, the degree of deprotonation of linker increases on increasing the pH value. For example, Al^{3+} ion is coordinated with four, six and eight carboxyl O-atoms with increasing pH resulting into MIL-121 (pH = 1.4), MIL-118 (pH = 2) and MIL-120 (pH = 12.2) respectively[85]. Interpenetrated network has been reported to be formed at higher pH value and uninterpenetrated at lower pH[86]. Colour of MOF compounds also depend on pH of reaction medium. Luo *et al*[87], through their experimental work, explored three Co-MOF complexes, viz. $[Co_2(L)(HB\text{-}TC)_2(\mu_2\text{-}H_2O)(H_2O)_2].3H_2O$ (1), $[Co_3(L)_2(BTC)_2].4H_2O$ (2), $[Co_2(L)(BTC)(\mu_2\text{-}OH)(H_2O)_2].2H_2O$ (3), (L = 3,3',5,5'-tetra(1H-imidazol-1-yl)1,1'-biphenyl and BTC = 1,3,5-benzenetricarboxylate) exhibit different structure and colour, by altering the pH value. Along with structure and colour, these three MOFs exhibited different adsorption capability. It is also revealed that compounds of higher dimension are formed at higher pH[88]. The effect of pH on various properties of MOFs is summarized in **Table 1** as reported in the study of Chu *et al*.[88]

Table 1. Effect of pH on MOFs

S. No.	**Properties of Co-MOFs**	**Complex-1**	**Complex-2**	**Complex-3**
1	Chemical Formula	$[Co_2(L)(HBTC)_2(\mu_2\text{-}H_2O)(H_2O)_2].3H_2O$	$[Co_3(L)_2(BTC)_2].4H_2O$	$[Co_2(L)(BTC)(\mu_2\text{-}OH)(H_2O)_2].2H_2O$
2	Morphology	Monoclinic	Monoclinic	Orthorhombic
3	Space group	P2/c	C2/c	Pccn
4	pH	5	7	9
5	Colour	Pink	Purple	Brown

Temperature of the reaction is another important factor which affects the properties of synthesized MOFs. High temperature favours higher crystallization due to high solubility of reactants and results in formation of large crystals of high quality[89-91]. Nucleation and crystal growth rates were affected by temperature of reaction mixture. Morphology of synthesized MOFs can also be altered by varying the temperature of reaction medium. MOFs of Tm-succinate[92], are synthesized at different temperatures with same empirical formula but different morphology i.e. monoclinic and triclinic. Bernini *et al*. prepared two Ho-succinate MOFs and reported that the MOFs prepared via hydrothermal method at higher temperature is thermally more stable as compared to the other prepared at room temperature[93]. Along with thermal stability, hydrothermal methods also provide denser, less hydrated and higher dimensional solids[94].

5. Factors affecting the stability of MOFs

5.1 Surface engineering

Crystal growth of MOFs can be altered via "coordination modulation"[95] which involves introduction of monodentate ligands known as "modulators" with same functional group as to the existing multidentate organic ligand. Modulators can increase or decrease the crystal growth by controlling the nucleation leading to the formation of MOFs crystals of different size. When modulators decrease the crystal growth they can be used as “capping agents”. Sodium acetate[96-99], sodium formate[99-101], acetic acid[102-104], benzoic acid[103], n-dodecanoic acid[105], trifluoroacetic acid (TFA)[106], pyridine[104], n-butyl amine[101], 1-methyl imidazole[101], polymers such as PVP[107], PEG[108], chitosan[108] have been used as modulators/capping agents in synthesis of MOF. It is also reported that the concentration of modulator can influence the crystal size and morphology of MOF crystals. In microwave synthesis[109] of HKUST-1, when lauric acid is used as modulator, the crystal sizes change from nano to micro scale range. However, when capping agent is used in large amount formation of a new phase is induced[99]. Stability and specific properties of MOF crystals such as molecule sensing[107,110], drug delivery[108] etc. can be enhanced by using modulators. MOF[111] coated with liposomes lipid has been explored for imaging and anticancer property. Effect of some modulators or capping agents on the properties of MOFs has been summarized in the **Table 2**.

Table 2. Effect of capping agents/modulators on MOF properties

S. No.	Modulator/caping agent	MOF	Change in MOF’s property	Ref
1	Sodium formate	HKUST-1	Reduction in crystal size, phase change	100
2	Sodium Acetate	MIL-68(In)	Decrease in length and diameter of hexagonal nanorods	97
3	n-dodecanoic acid	HKUST-1	Change in morphology	105
4	Acetic acid	NH_2-MIL-53 (Al)	Selective capping of crystal faces	102
5	Benzoic acid, acetic acid	UiO-66, UiO-66(NH_2), UiO-67, UiO-68	Improve crystallinity, formation of single crystal	103
6	TFA	UiO-66	Induce defects	106
7	Sodium Acetate	$[Ln(1,3,5\text{-btc})(H_2O)]_n$ (Ln = Dy^{3+}, Tb^{3+})	2D nano sheet	98
8	PVP/silica	$[Mn(1,4\text{-bdc})(H_2O)]_n$	Selective uptake in human cancer cell, Enhance imaging	110
9	PEG	MIL-88, MIL-100	Improve aggregation, neutral zeta potential	108

MOFs are also modified via exchanging a terminal ligand by a bridging ligand of different functionality (**Figure 6**). Research group of Kitagava successfully exchanged the surface ligands of Zn-based MOFs $[Zn_2(1,4\text{-ndc})_2\text{ (dabco)}]_n$ and $[Zn_2(1,4\text{-bdc})_2\text{(dabco)}]_n$ with a fluorescent dye boron dipyromethene (BODIPY). In these MOFs, only surface carboxylate ligands were exchanged and surface dabco ligands remained unmodified. Further, due to bulkier nature of BODIPY in comparison to original carboxylate ligand, it gets attached to surface only[112]. Liu *et al.*[113] demonstrated the effect of surface modification on properties of ZIF–8. It shows greater stability towards hydrolysis when its surface ligand 2-methylim-idazole has been exchanged with more hydrophobic ligand 5, 6-dimethylbenzimidazol (DMBIM).

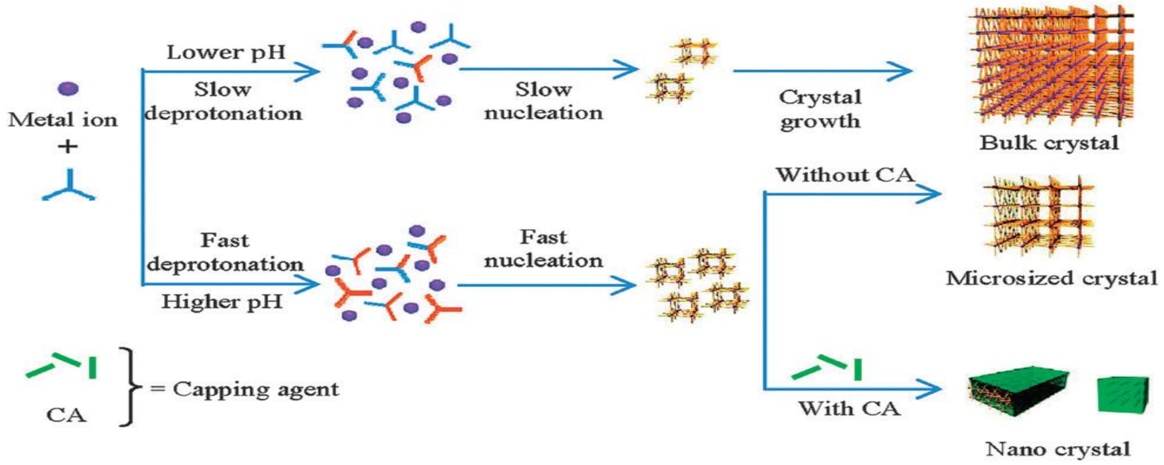

Figure 6. Effect of pH control and crystal capping during coordination modulation**.**

Unlike linker ligand exchange, it has been difficult to control metal cation exchange in MOFs, as it can lead to the formation of Core-shell structure[114]. Kitagawa and group reported the core shell hybrid of Cu-MOF $[Cu_2(1,4\text{-}ndc)_2(dabco)]_n$ synthesized on Zn analogous $[Zn_2(1,4\text{-}ndc)_2(dabco)]_n$ by adding Zn crystals to the solution of $CuSO_4.5H_2O$, 1,4-ndc and dabco. Formation of green crystals confirms the formation of Cu-MOF on Zn framework surface[115].

6. Major applications of MOFs

In MOFs, there is a simultaneous appearance of three characteristics, viz. crystallinity, porosity and existence of strong metal-ligand interaction. The unique combination of these properties makes MOFs a very special class of materials[116]. MOFs show application in catalysis, drug delivery, gas storage, nanoparticle precursor, luminescence, electrochemistry and as sensor in technology.

6.1 Gas storage and separation

There are several methods for storing gas effectively but these require high pressure tank and multistage compressor. These methods are highly expensive for practical uses and there is a need of simpler and cheaper solution. To overcome these issues and to find safer storage methods, several materials, like Zeolite or activated porous carbons, have been studied for gas storage. In this context, MOFs have provided edge over other materials. This is due to easy preparative methods, high surface area, wide opportunities for functionalization and tuneable pore structure which makes MOFs preferable compared to other porous materials.

More than 300 MOFs have been tested for H_2 storage. One of the promising MOFs for this purpose is MOF-177 which consists of $[Zn_4O]$ clusters and 4,4’,4’’-benzene-1,3,5–triyltribenzoate (BTB) to form (6,3) net[117]. Due to its high surface area (~5000 m^2g^{-1}) and large pore volume, it shows a gravimetric H_2 uptake of 7.5 wt.% at 70 bar and 77 K. MOF-5 (IRMOF-1), which is constructed from $[Zn(OAc)_2]$ and terepthalic acid, possesses a BET surface area of 3800 m^2g^{-1} and takes up 7.1 wt.% at 40 bar and 77 K. Apart from these two, MOF-210, MIL-101, HKUST-1, NU-100, PCN-12, NOTT-102 and MOF-205 are also known for H_2 storage[118-121]. Generally MOFs with open metal sites provide high surface area facilitating stronger interaction between the metal ion and H_2 molecule. This is the principal reason behind the high H_2 uptake in MOFs. NU-100[120] has the highest excess H_2 storage capacity i.e., 99.5 mgg^{-1} at 56 bar and 77 K. MOF-210[121] has been reported as highest total H_2 storage capacity of value 176 mgg^{-1} at 80 bar and 77 K. In addition experimentally, it is reported that doping MOFs with metal ions could enhance the H_2 uptake capacity[46,122]. As compared to other H_2 storage systems such as transition metal hydrides, MOFs require little energy to release adsorbed hydrogen. This released hydrogen can be used in automobile and fuel cell industries[123].

MOFs are reported to be useful for reducing CO_2 level in atmosphere. For example, MOF-210 is the highest surface area (10450 m^2 g^{-1}) MOF known to date, synthesized from 4,4’,4’’-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)] tribenzoate (H_3BTE), biphenyl-4,4’-dicarboxylat (H_2BPDC), and zinc (II) nitrate hexahydrate[121] and has an uptake of CO_2 2400 mg g^{-1} (74.2 wt.%, 50 bar at 298 K) which exceeds that of any other porous material. MOF-200 has a similar CO_2 uptake as MOF-210 under similar experimental conditions[121]. Other well-known MOFs, such as NU-100 (69.8 wt.%, 40 bar at 298 K), Mg-MOF-74 (68.9 wt.%, 36 bar at 278 K), MOF-5 (58 wt.%, 10 bar at 273 K), and HKUST-1 (19.8 wt.%, 1 bar at 298 K) also show considerable CO_2 uptake. It has also been proved experimentally and theoretically that the presence of polar groups such as — NH_2 or free N containing organic heterocyclic residues on the pores is helpful for high CO_2 uptake compared with unfunctionalized analogues. One of the best examples, Bio-MOF-11, exhibited the effects of an N-heterocycle and its CO_2 uptake of 15.2 wt.% (at 1 bar and 298 K) exceeds any other MOF in the same category[124].

Noro *et al*. studied the first methane sorption study on MOFs[125]. Zhou and co-workers showed methane uptake of 16 wt.% (35 bar) in PCN-14 [Cu_2(adip), Adip = 5,5'-(9,10-anthracenediyl)di-isophthalate] MOF, having BET surface area 1753 m2 g-1[126]. Other MOFs such as HKUST-1 (15.7 wt.% at 150 bar), MIL-101 (14.2 wt.% at 125 bar), IRMOF-1 [228 cm3 (STP) g-1 at 298 K and ~36 bar], and MOF-210 (264 mg g^{-1})[121] also show considerably high methane uptake capacity. In the case of Ni-MOF-74 [190 cm^3 (STP) g^{-1} (298 K, 35 bar)], open metal sites are the dominating factor responsible for the high methane capacity[15]. Other important hydrocarbons like benzene, toluene, xylene and linear hydrocarbons have also been effectively separated from liquid mixtures by trapping inside MOFs.

Hazardous gases like CO and NO can also be separated from gas mixtures by using MOFs. Though separation of CO in MOFs could not be achieved experimentally, it is believed that interaction between CO dipole and open metal sites in MOFs are the dominating factor for the sorption performance. On the other hand, MOFs have been used for capturing NO gas, e. g. Cu-SIP-3[127] and Zn (TCNQ-TCNQ) (bpy) [TCNQ = 7,7,8,8-tetracya-no-p-quino dimethane, bpy = 4,4'-bipyridyl][128]. Usually these two MOFs are nonporous in nature and they do not absorb gases like Ar, N_2, CO_2 etc., however, these are reported for uptake of NO gas (~9 molecules per formula unit at 1 bar) above gate–opening pressure. Reducing the pressure, the desorption path is not like adsorption. In 2010, Allen and co-workers reported the reason for this performance of the above two MOFs. The strong coordination to coordinatively unsaturated metal sites (CUMs) in case of Cu-SIP-3, while for [Zn (TCNQ-TCNQ)(bpy)], charge transfer plays a crucial role for high NO capture[127]. Ni- and Co-MOF-74 also exhibited very high NO uptake (~7.0 mmol NO per g of activated material) at room temperature[129].

In 2014, Yan *et al*. synthesized and characterized a new organic linker 1,2,4,5-tetrakis(3-carboxyphenyl)-benzene (m-H_4TCPB) and its first metal-organic framework Cu-m-TCPB. This compound can uptake 24.4 cm^3g^{-1} H_2 and 2.3 cm^3g^{-1} N_2 at 77K and 1 atm. It has been reported to possess uptake capacity 23.3 cm^3g^{-1} acetylene, 23.0 cm^3g^{-1} CO_2 and 7.3 cm^3g^{-1} at 273 K and 1 atm[130].

Instead of gaseous molecule uptake, some MOFs have also been prepared which are capable of adsorption of water molecule. In this direction, R. Banerjee and his research group demonstrated the water adsorption ability of chemically stable keto-enamine COFs[131].

6.2 Magnetism and its application

Metal organic framework materials show magnetism when paramagnetic 3d transition metal nodes are used along with suitable diamagnetic organic linkers and MOFs with magnetic properties are named as magnetic metal organic frameworks (MMOFs). The MOFs consist of first-row transition metals (V, Cr, Mn, Fe, Co, Ni and Cu) have contributed significantly to develop porous molecular magnets[132-137]. Close-shell ligands[138] such as oxo, cyano, azido bridges and polycarboxylic ligands, which give weak magnetic interaction, are good candidates for this purpose.

Another reason for magnetic behaviour of MOFs is the framework structure, which may involve layered geometry with a shorter conjugated distance between metal clusters. Organic linkers have also been used for synthesis of MMOFs, where radicals present in organic linker are responsible for magnetic properties. This metal-radical combined approach has also been used for synthesizing a variety of MMOFs[139-141].

A Ni-Glutarate based MOF [$Ni_{20}(H_2O)_8(C_5H_6O_4)_{20}.40H_2O$][142] showed ferromagnetic behaviour with a curie temperature of 4K due to weak ferromagnetic interactions of Ni-O-Ni angle. HKUST-1 is antiferromagnetic at high temperature and below 65K shows weak ferromagnetism[143]. MIL-9[144] [$Co_5(OH)_2(C_4H_4O_4)_4$] is reported to possess ferrimagnetic properties. Jain *et al.* [145] reported four MOFs of general formula [$(CH_3)_2NH_2$] $M(HCOO)_3$ (M = Mn, Fe, Co, Ni) as multiferroics.

Instead of 3d transition metals, lanthanides also produce magnetic metal-organic frameworks. Two magnetic lanthanide-organic frameworks[146]

(LnOF), having formula $[Dy_2(bpa)_2(H_2O)_3]$ and $[Er_4(bpa)_4(H_2O)_6](H_2O)$, consist a 3D frameworks built by the 1D rod shaped metal carboxylate SBUs and 3,5-bis (4-carboxyphenoxy) benzoate (bpa^{3-}) ligands.

Magnetic MOFs can also be explored for the environmental application in removal of arsenic. Magnetic nanoclusters have been reported for applications in arsenic removal[147,148].

6.3 Sensing

A large number of MOFs have been reported to be photoluminescent because aromatic units of linkers in most of the MOFs lead to excitation by absorbing UV-visible light and provide luminescence. MOFs as luminescent materials or phosphors can find application in cathode ray tubes, projection television, fluorescent tubes and X-ray detectors[149], small-molecule sensors[150,151], pH sensors[152], light concentrators for photovoltaic devices, antennae in photo-sensitive bioinorganic compounds and high-technology optics. Trivalent lanthanide metal ions are widely used for synthesis of luminescent MOFs due to their electronic transition from d- to f-shell, with accompanying photon emission. Lanthanides like Eu, Tb, Dy, Sm, Nd, Gd, Er and Yb are used as luminescent metal ions. Naphthalene, anthracene, pyrene, perylene and stilbene types of ligands are most commonly used for synthesis of luminescent MOFs. Both the metal and the linker can be used to give rise to luminescence, and can furthermore interact (via antenna effect) to increase the brightness and the quantum yield. 4,4-[(2,5-Dimetoxy-1,4-phenylene)-di-2,1-ethenediyl] bisben toxy-1,4-phenylene)-di-2,1-ethenediyl] bisbenzoic acid (H_2pvdc) was used to efficiently sensitise the NIR emission of the Yb^{3+} ions at ca. 1000 nm in an extended $[Yb_2(pvdc)_3(H_2O)_2].6DMF.8.5H_2O$ porous network[153]. The LnMOFs co-doped with multiple Ln^{3+} ions can be used as bimodal (or multicoloured) light emitters. Bimodal (or multicoloured) emission may be applied in multiplexed detection and imaging of therapeutic cells[154]. Ln-MOFs are used in cation sensing, anion sensing as well as molecule sensing. A visible colour change of material is one of the simplest, most powerful sensing strategies. For example, a nanotubular MOF, $\{[(WS_4Cu_4)I_2(dptz)_3].DMF\}n$ (dptz = 3,6-di-(pyrid-in-4-yl)-1,2,4,5-tetrazine, DMF = N,N-dimethylformamide) was reported for sensing small solvent molecules. When accommodating different solvent molecules as guests, the resulting inclusion compounds exhibited different colours depending on the solvent guests, showing a new way of signal transduction as a new kind of sensor[150]. Recently, water stable cationic MOF[155] has been reported which can adsorb oxoanionic pollutents such as MnO_4^-, $Cr_2O_7^{2-}$. Recently, MOFs have been demonstrated as chemical sensor for selective fluorescence quenching of an explosive TNP (2,4,6-tri nitro phenol) in water using urotropin-based metal-organic framework (Ur-MOF)[156].

Nano MOFs (NMOFs) have experirnced another exciting development and NMOFs are used for sensing pesticides. Akash Deep *et al.*[157] were the first who demonstrated biosensing application of Nano MOF $[Cd(atc)(H_2O)_2]_n$ (atc = 2-amino terepthalic acid) impedimetrically for the detection of organo-phospate pestiside by developing an anti-paration/NMOF/2-ABA/ITO (ABA = 2-amino benzyl amine, ITO = Indium Tin oxide) sensing platform.

A novel approach to develop an inkless and erasable printing medium using MOFs has been demonstrated by synthesizing photochromic MOF containing 1,4,5,8-naphthalenediimide (NDI) and Ca, Mg, Sr and revealed their inkless printing property[158]. The print content was self-erased after 24 hours. This may be useful for reducing paper wastage.

6.4 Catalysis

The presence of strong metal–ligand interaction in MOFs can provide permanent porosity to the material, i.e., it is possible to remove solvent molecules completely without structure collapse. MOFs have shown great potential as heterogeneous catalyst. The MOFs, in which metal centres are not completely blocked by organic ligands or unsaturated, i.e., labile ligands are introduced, and are good catalysts because when labile ligands are generally solvent molecules and when they are removed leave a free coordination position on the metal. For example, $[Cu_3(btc)_2]$ (btc = 1,3,5-benzenetricarboxylate) material HKUST-1, in which coordinated water molecule leaves a coordination vacancy on Cu upon thermal activation[159]. A number of organic reactions have been catalyzed by using nanoporous MOFs. For example, Knoevenagel condensation reaction catalyzed by using either $[Cd(4\text{-}btapa)_2(NO_3)_2]$ (btapa = 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide])[160] or $[Cr_3F(H_2O)_2O(bdc)_3]$ (bdc = 1,4-benzenedicarboxylate) [161]. Xu *et al*. synthesized a novel bimetal complex $[Zn_4Ru_2(bpdc)_4.4C_2NH_8.9DMF]_n$ (H2bpd = 4,4'-biphenyldicarboxylic acid), which can adsorb Ru(II) photosensitizer $[Ru(bpy)3]^{2+}$ and cobalamin derivative such as heptmethyl cobyrinate perchlorate (B_{12}) to form a complex B_{12}-Ru@MOF. This complex has been reported to catalyse dechlorination reaction and 1, 2-migration reaction in solid state. This is the first example of B_{12} catalysis using MOF system[162].

6.5 Biomedical application

MOFs offer extremely high drug loading capacity and very long release time. As compared to mesoporous silica materials, MOFs can load four times greater drug, i.e., ibuprofen adsorption (upto 1.4 gm per gram of MOFs) with longer release time (upto 21 days)[108]. Non-toxic MOFs are applicable in targeted drug delivery. MIL family of metal-organic frameworks has a good candidature for storage and controlled release of biologically important molecules due to their enhanced stability, enormous porosity and large pore volume[10,163]. Serrey and Férey *et al.*[8] demonstrated encapsulating drug molecules (Ibuprofen) in chromium carboxylate MOFs, MIL-100 and MIL-101, exhibiting drug storage capacities of 35 wt.% and 140 wt.% respectively and controlled drug release behaviour of 5 to 6 days under physiological conditions. Iron (III) carboxylate MOFs such as MIL-88A, MIL-8, MIL-100 and MIL-101 are able to entrap anticancer[163], antitumor and antiretroviral drugs as well as cosmetic agents[8]. Férey *et al.*[164] reported first group of synthesized MOFs using trivalent metal centers with carboxylic acid bridging for drug delivery application. A novel type of magnetic MOF composite $Fe_3O_4/Cu_3(BTC)_2$, fabricated by incorporation of Fe_3O_4 nanorods with nanocrystals of $Cu_3(BTC)_2$ (HKUST-1), adsorbed upto 0.2 gm of Nimesulide (an anticancer drug for pancreatic cancer treatment) per gram of composite and it took as long as 11 days for the complete drug release in physiological saline at 37°C[165]. Zhuang *et al*. demonstrated ZIF-8 as pH responsive drug delivery system with high cellular uptake efficiency by incorporating camptothecin into ZIF-8 nanospheres. This encapsulated ZIF-8 exhibited enhanced cell death[11].

Bernini *et al*. demonstrated the ability of GCMC (Grand canonical monte carlo) simulation to predict the microscopic performance of new porous MOFs in drug delivery application and validated their simulation, with the available experimental data reported for the adsorption-release of ibuprofen in MIL-53(Fe), MIL-100(Fe) and MIL-101(Cr)[166]. Their simulation predicted an outstanding ibuprofen adsorption capacity of 1969 mg g^{-1} for mesoporous BioMOF-100 which is six times higher than the values reported for mesoporous silica. The presence of strong electrostatic interactions due to existence of charge compensating ions in MOFs enhances the adsorbate-adsorbent interaction which leads to higher drug loading at low pressure. In BioMOF-100, dimethylammonium cations present in the pores reinforce the attractive interaction with ibuprofen molecules. Monte carlo simulation was also used for comparing the drug uptake capacity of two different mesoporous MOFs, viz. MIL-101 and UMCM-1 computationally[9].

Anti-bacterial activity of novel MOF STAM-1[138] has been compared with that of the HKUST-1 against the growth of some bacteria such as Clostridium difficle, Staphylococcus aureus and Pseudomonas aeruginosa. It is found that both the MOFs have significant effect against the growth of these pathogens. Antimicrobial activity of these MOFs has been enhanced when they are impregnated with NO.

6.6 Electrical property and its application

MOFs have been demonstrated as useful device material for energy storage. Electrical storage capacity of MOFs in Co-doped MOF-5, i.e., Co8-MOF-5[167] as electrode for supercapacitors has been reported by Diaz *et al*. However, this MOF has much lower capacitance than the commercially activated carbon. Lee *et al*. introduced Cobalt based MOF film[168] which has pseudocapacitor behavior with specific capacitance upto 206.76 F g^{-1} and energy density of 7.18 Wh kg^{-1} at 0.6 A g^{-1}. Zn-doped Ni-based MOF[169] with a flowerlike microsphere exhibited high specific capacitance (1620 F g^{-1} and 860 F g^{-1} at 0.25 and 10 A g^{-1} respectively), good rate capability and good cycling stability (91% for the MOF with Zn/Ni of 0.26). In 2014, a series of 23 different nanocrystalline MOFs (nMOFs) were reported for their electrochemical energy storage capacity. Among these nMOFs, a zirconium based MOF, i.e. nMOF-867 exhibited high capacitance. nMOF-867 has the stack and areal capacitance of 0.64 and 5.09 mF cm^{-2} which is about six times higher than that of the supercapacitors made from activated carbon[170]. Recently, a Mn-based MOF is employed as the active coating material to enhance the capacity of Li-rich layered Li ($Li_{0.17}Ni_{0.20}Co_{0.05}$-$Mn_{0.58}$)$O_2$ oxide as cathode for Li-ion batteries. This surface modified oxide material showed a large discharge capacity, good thermal stability without harming the cycle stability, high initial coulombic efficiency and high rate capability[171]. Researches in this direction are needed to further explore the applications of MOFs.

7. Future scope

The knowledge about metal organic frameworks is growing rapidly during recent few years but there are still significant gaps in the completeness of our understanding of their structure, stability and properties. Detailed investigations on factors responsible for destruction of crystal structure of certain MOFs with time stability and decomposition mechanism have still not been carried out systematically.

There are some reports on applications of MOFs in drug loading and delivery for some anticancer and antiviral molecules. MOFs can be explored for such application for other drug molecules too. Detailed toxicological investigation should be carried out commercialization of such products.

8. Conclusion

In this review article, we have discussed various synthetic methods of MOFs along with their applications. Different methods lead to the MOFs having different properties. MOFs introduced a huge number of applications including gas storage and separation, catalysis, magnetism, sensors, electrical energy storage systems etc. Several applications of MOFs have not been explored yet, for instance, magnetic MOFs can be explored for removal of arsenic from environmental sample same as magnetic nano clusters have been demonstrated. Research work should be carried out to study degradation mechanism of unstable MOF. Studies can also be carried out to evaluate the toxicity of degradation products. These studies will be helpful to explore the biomedical application of nontoxic MOFs. Nontoxic MOFs can be explored for application as solid support for natural bioactive molecules to increase their shelf life and effectiveness.

MOFs should be evaluated for antibacterial and antifungal activities to explore their clinical and biological applications as solid support, UV-screens and synergist.

Abbreviations used

1. Adip — 5,5’-(9,10-anthracenediyl)di-isophthalate
2. BDC — benzene dicarboxylate
3. BODIPY — boron dipyromethene
4. BTC — benzene tricarboxylate
5. COF — covalent organic framework
6. DABCO — diazabicyclooctane
7. HKUST — Hong Kong University of Science and Technology
8. IRMOF — isoreticular metal organic framework
9. MIL — Materials of Institute Lavoisier
10. MOF — metal organic framework

11. MW — microwave
12. NDC — naphthalene dicarboxylate
13. NU — North Western University
14. PCN — porous coordination network
15. PCP — porous coordination polymer
16. SBU — secondary building unit
17. SIP — 5-sulfoisophthalic acid
18. SNU — Seoul National University
19. STAM — St. Andrews Material
20. TCPB — tetra kis (carboxyphenyl) benzene
21. TFA — trifluoro acetic acid
22. ZIF — zeolitic imidazolate framework

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