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Metal Organic Frameworks (MOFs) in Catalysis: A Comprehensive Review

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Abstract

Metal-organic frameworks (MOFs) have emerged as a promising category of crystalline porous materials with great potential in catalysis because of their high surface area, tunable pore structure and well-defined active sites. This review offers a comprehensive overview of the role of MOFs as catalysts depending on the type of active site, including coordinatively unsaturated metal nodes, functionalized organic bridges, and encapsulated guest species. Pristine MOFs acting as Lewis acid, Bronsted acid, and basic catalysts are addressed together along with advanced functionalization strategies, including post-synthetic functionalization, immobilization of metal complex, and the introduction of metal nanoparticles and polyoxometalates that greatly broaden the scope and efficacy of MOF-based systems. Special focus is placed on MOFs that can bridge the benefits of homogeneous and heterogeneous catalysis by combining high activity and selectivity as well as recyclability. Moreover, the multifunctional nature of MOFs allows them to be used in other areas beyond catalysis, such as efficient adsorbents to eliminate heavy metal ions and organic dyes from wastewater. Lastly, the current challenges including stability, scalability and practical implementation are critically addressed and future opportunities regarding the rational design of MOF-based catalysts for sustainable chemical processes are described.

Keywords: Metal-organic framework, Catalysis, Membranes, Adsorption, Wastewater treatment

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1. Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), represents a novel kind of porous solid, composed of metal ions/clusters and organic linkers [1]. They have gained widespread interest and rapid development in the last few decades. The MOFs are applicable in numerous applications, such as gas sorption, chemical sensing, proton conductivity, and biomedicine, mostly due to crystalline structure, structural diversity, flexibility and ultrahigh surface area [2]. Particularly, catalysis is among the earliest applications of MOFs that have proven effective and is emerging as one of their most promising uses in the past few years [3]. In their structure, MOFs resemble homogeneous catalysts, like transition metal complexes, and can be viewed as isolated units of the entire network of MOFs. The periodic structure of MOF provides uniform distribution of active sites across the structure as well as porosity enables accessibility to active sites and catalytic substrates and products movement [4]. Therefore, MOFs can function in a very similar manner to metal complex catalysts and have advantage of being a homogeneous catalyst. Conversely, MOFs being porous solids can be recycled very easily following their catalytic cycles which is a property of heterogeneous catalysts [5]. Thus, MOFs are extraordinary catalysts that bring together the benefits of homogeneous (e.g., metal complex) and heterogeneous catalysts, such as high reactivity and recyclability [6].

MOFs compared to traditional porous catalysts such as zeolite, activated carbon, etc. have much more diverse structure features with highly adaptable pore sizes (0-3 nm, up to 9.8 nm) [7]. This pore size and shape uniformity allows reaction substrates or products to enter the pores, which allows metal-organic frameworks (MOFs) to selectively catalyze. Moreover, they have a high surface area (BET, 1000 $m^2\ g^{-1}$ on average, up to 7000 $m^2\ g^{-1}$) that allows the adsorption and enrichment of substrates around active sites, enabling activation and catalytic transformation [8]. MOFs are therefore highly promising as unique solid catalysts especially in fundamental catalysis. Pure MOFs tend to have either coordinatively unsaturated metal centers (Lewis acid centers), or active centers on organic linkers (usually acid/base centers) [9]. As a matter of fact, this fact limits MOFs to a particular range of catalytic reactions. Fortunately, this problem can be solved at least in two ways: (a) functionalized modification (attachment of desired active sites to metal ions/clusters or organic linkers via a multivariate approach [10], or post synthetic modification); (b) pore confinement/encapsulation [11].

MOFs are capable of accommodating various active species, include organic molecules, inorganic nanoparticles, metal complexes and enzymes, and operate as a nanoreactor in catalyzing reactions (Fig.1) [12]. MOFs and MOF-based materials have also demonstrated promising results in photocatalysis and electrocatalysis to clean energy, in addition to their use in heterogeneous organic reactions and composites. Semiconductor like MOFs have been shown to be photocatalysts, especially in splitting water and CO_2 reduction [13]. The high porosity of MOFs would largely reduce classical volume recombination of electron-hole. Photocatalytic efficiency and charge separation can be improved by the addition of additional electron acceptors [14]. The present review is centered on recent advances in MOFs as a catalyst by classifying them in terms of reactive sites on the catalyst, and then focus on the recent progress in MOF-based catalysts in photocatalysis and electrocatalysis. Certain issues related to MOFs and material used in them, as well as possible possibilities of the study in the future development of catalysis are carefully discussed.

2. MOFs for Heterogeneous Catalysis

2.1. Pristine Framework Activity

2.1.1. Active Sites at Metal Nodes

MOFs are coordinated by organic ligands and solvent molecules, which can be eliminated by heating or evacuation, and leave coordinatively unsaturated metal sites (CUSs) in metal nodes [15]. The CUSs may be used as the Lewis acid center, where the electrons of the substrates are fed to these centers to create the products. The traditional HKUST-1 possesses a high Lewis acid activity in the cyanosilylation of benzaldehydes and the isomerization of terpene compounds and offers open Cu^{2+} sites with the removal of bound water molecules with heating [16]. Another classical MIL-101(Cr) consisting of trimeric chromium (III) octahedral clusters linked with 1, 4- benzene-dicarboxylate (BDC) anions is more active in the cyanosilylation of aldehydes than HKUST-1 because of enhanced Lewis acidity of Cr (III) compared to Cu (II) [17]. In addition to liquid-phase catalysis, MOFs with Lewis acidity able to be applied in gas-phase reactions too. Xu et al. prepared a MOF of Cu(mipt) (mipt = 5-methylisophthalate) having open Cu (II) sites [18]. They employed ^{13}CO and ^{12}CO probe molecules to demonstrate stable catalysis for CO oxidation to CO_2. Engineering structural defects in MOFs results in extra exposed metal centers that are catalytically active. De Vos and co employed trifluoroacetic acid (TFA) as a modulator to generate UiO-66 with the desired number of faults [19]. TFA substituted a part of the terephthalate linkers, and created additional Lewis acid sites, which made the Meerwein reduction of 4-tert-butylcyclohexanone (TCH) faster than in the parent MOF.

2.1.2. Active Sites at Organic Linkers

Heterogeneous catalysis can be performed by modification of functional groups on the organic linkers. Many functional groups such as amino, amide, pyridyl, sulfoxy, bipyridyl, and many others may serve as active sites catalytic activities [20]. The active functional groups may be attached to the MOF ligands to form a stable catalytic system. A sulfonic acid ($-SO_3H$) group was attached to the aromatic linker to make MOFs such as MIL-101(Cr). Kitagawa et al. prepared partially protonated SO_3Na group functionalized MIL-101(Cr) with 2 sulfoterephthalate in the presence of HCl [21]. This MOF was found to be remarkably active in catalytic cellulose hydrolysis as a result of high Bronsted acid site on the pore surface of the MOF. More recently, Jiang et al. have reported ≈100% sulfonic acid functionalized MOF, MIL-101-SO_3H, prepared by a post synthetic HCl treatment method which exhibited good catalysis in the ring opening of styrene oxide in methanol [22].It is possible to make MOF basic catalyst by incorporating basic functional groups in organic linkers, including pyridyl, amide, and amino [23]. These basic catalysts were MOF which were utilized in the Knoevenagel condensation and transesterification reaction (Fig.2). Kim and others prepared d-POST-1, a 1D channeled homochiral MOF, using an organic linker, functionalized by a pyridyl group [24]. The pyridine group structure revealed that half of the pyridine groups moved into the channel, which provides the basic sites required in catalyzing the transesterification of 2,4-dinitrophenyl acetate [25]. MOFs are a special heterogeneous catalytic system because a variety of catalytic sites, including acid and base sites, can be precisely incorporated into an individual MOF without affecting each other. De Vos and colleagues employed the amino-functionalized MOF, UiO-66-NH_2, which contains Lewis-acidic sites of Zr^{4+} and basic amino groups as a bifunctional acid-base catalyst to the one-pot tandem synthesis of benzaldehyde and heptanal [26].

2.2. Functionalized Modification

Synthetic chemical modification is an extremely efficient method to incorporate particular functionalities to MOF materials to facilitate demanding and specialized applications that are typically not possible with normal synthetic methods. This functionality to modify the physical environment of the pores and cavities of MOFs would affect their interaction with substrates, and consequently reactivity. Various synthetic methods can be used to functionally modify MOFs through their metal nodes and organic linkers, and by introducing a guest species to the pore space.

2.2.1. Functionalized Modification for Metal Nodes

MOFs have coordinatively unsaturated metal sites which can be modified with active species through chemical binding. Ferey and colleagues found that the dehydrated MIL-101(Cr) gave CUSs to coordinate different amines groups, and this was a base catalyst of Knoevenagel condensation reactions [27]. Banerjee et al. post-synthetically modified chiral MIL-101 with catalytically active chiral compounds. L-proline was taken as chiral catalytic unit to bind unsaturated metal sites in MIL-101 to produce chiral MOF with the same XRD pattern and N_2 adsorption isotherm. Chiral MIL-101 was more active in the asymmetric aldol reaction with aromatic aldehydes and ketones to give 60-90% yield and 55-80% enantioselectivity than with unmodified MIL-101 (0% enantioselectivity) and the homogeneous chiral molecule (29% enantioselectivity). The obtained chiral MOF is reusable up to three times with minimal variation in yield and enantioselectivity [28].

2.2.2. Functionalized Modification for Organic Linkers

It is also possible to incorporate functional species through functionalized modification approaches, such as organic molecules, metal complexes and chiral compounds into organic linkers of MOF. The MOF-253 [Al

(OH)(bpydc); bpydc = 2,2-bipyridine-5,5-dicarboxylate] was synthesized by Bloch et al. The 2,2 2 -bipyridine (bpy) moieties are used as a ligand where metal centers such as $PdCl_2$ are inserted [29]. Carson et al. used MOF-253 to immobilize the ruthenium complexes taking into consideration that the uncoordinated bidentate chelating centers leading to MOF-253-Ru effectively oxidized alcohols to aldehydes. By adding the activity of the Ir complex to IRMOF-3 and UiO-66-NH_2, the new hybrid catalysts IRMOF-3LIr and UiO-66-NH_2LIr (Ir = iridium; L = 6 ((diisopropylamino)methyl) picolinaldehyde were produced for the synthesis of N-alkyl amines by reductive amination of aldehydes with nitroarenes in the presence of hydrogen [30]. A high yield of N-alkyl amines was obtained in good to excellent yields with the newly obtained IRMOF-3LIr and UiO-66-NH_2LIr which had good thermal stability. Similarly, post-functionalization of a molecular nickel complex to mesoporous MOF (Ni@Fe-MIL-101) was carried out to form a highly active and reusable catalyst to liquid-phase ethylene dimerization, which selectively produced 1-butene. Ni@Fe-MIL-101 catalyst was more selective with 1-butene compared to molecular nickel diimino complexes (Table 1) [31].

2.3. Encapsulating Guest Species in MOFs

In spite of the above-mentioned advantages of MOFs as catalysts, the number of active sites in pure MOFs is mostly limited to the following two sources: unsaturated metal centers and organic ligands, giving rise to reactivity in a very limited number of reactions. Besides the two methods for introducing active sites as described above, MOFs, being porous materials, can host a guest species (e.g., metal complexes, enzymes, and metal NPs (MNPs)) into their pore space, as a result of a noncovalent interaction, and the resultant guest@MOFs can serve as a multifunctional platform that can be exploited to their synergistic effect in catalytic reactions, which means that the use of MOFs in catalysis can be extended significantly.

2.3.1. Metal Complexes/Macromolecules

Eddaoudi et al. employed 4,5-imidazole dicarboxylic acid as an organic linker to construct rho-ZMOF, an anionic zeolite-like MOF with large cavities that have the ability to trap cation porphyrins through electrostatic interaction in the synthesis process. The confinement effect causes the porphyrins not to cross freely through small pore opening [32]. The obtained Mn-porphyrin-encapsulated rho-ZMOF gave an excellent yield of cyclohexane oxidation to cyclohexanol & cyclohexanone. A similar synthetic strategy used to absorb metalloporphyrin into HKUST-1 resembling heme enzymes in terms of structure and reactivity [33].

2.3.2. Polyoxometalates (POMs)

There are many applications of POMs such as acid and oxidation catalysis. Their disadvantages, however, are relatively low surface area (<10 m^2 g^{-1}), low stability in catalytic conditions, and high solubility in aqueous solution and these limit their potential application significantly [34]. Immobilization of POMs into MOFs is one of the interesting ways of stabilizing them and improving their catalytic efficiency. Liu, Su, and others came up with an easier one pot hydrothermal method of loading $H_nXM_{12}O_{40}$ (X = Si, Ge, P, As; M = W, Mo) into the porous MOF to form POM@HKUST-1 composites [35]. HPWing HKUST-1 composite, which is a strong Bronsted acid of the H3PW12O40 (HPW) species, demonstrated better catalytic ability and stability in the deprotonation of ethyl acetate than other inorganic solid acids [36]. It is also worth mentioning that HPW@HKUST-1 also demonstrated significant potential in the elimination of nerve gas. HPW at HKUST-1 composites is also capable of hydrolyzing dimethyl methylphosphonate (DMMP) in a simple hydrolysis reaction since they adsorb the nerve gas simulant well (Fig. 3) [37].

2.3.3. Metal Nanoparticles

The crystalline porous structure of MOFs offers inherent properties of confining small MNPs, preventing them from aggregating and thus have better catalytic activity and stability [38]. MOFs have two simple methods of immobilizing MNPs. The former technique is known as the ship-in-a-bottle pathway, whereby metal precursors are loaded into pre-existing MOF pores by solution infiltration, vapor deposition or solid grinding. The precursors are then reduced to MNPs by use of reducing agents such as hydrogen, ammonia borane, $NaBH_4$ etc. [39]. Ship-in-a-bottle strategy has been demonstrated to be a useful procedure of synthesizing ultrafine MNPs in MOFs. Fischer et al. used chemical vapor deposition (CVD) to load organometallics as metal precursors in the form of gas phase. The most common synthesis method is the exposure of the chosen MOF to vapor of gas-phase organometallic precursors in atmosphere of vacuum [40]. The volatile precursors are diffused into the MOF pores, followed by the subsequent addition of hydrogen to reduce organometallics, or high temperatures are employed in order to thermally decompose the precursors to form MNPs in the nanopores [41]. Given the quite difficult situation of CVD process, a straightforward solid grinding approach to fill metal precursors into MOFs has been further developed. Volatile organometallic dimethyl Au(III) acetylacetonate may be incorporated into most varieties of MOFs such as MIL-53, MOF-5, HKUST-1, ZIF-8, and others through solid grinding in air when used as a metal precursor [42].

On the one hand, the reduction of H_2 atmosphere at high temperature can result in the formation of Au NPs/MOF composites. Surprisingly, the product of this straightforward method were MNPs (approximately 2 nm) which exhibited significant catalysis during oxidation reactions [43]. The other approach, termed as bottle-around-ship or templated synthetic approach where the MNPs are initially synthesized and then reacted with the right reactants to form the MOF around MNPs [44]. Unlike the former method, this method will not allow MNPs to accumulate on the outer surface of MOF. Furthermore, the size, composition and shape of MNPs can be modified easily. Lu et al. reported a controlled coating methodology of encapsulation of NPs of different sizes, shapes, & compositions of polyvinylpyrrolidone (PVP)-stabilized ZIF-8 [45]. It has been further shown that the spatial distribution of integrated NPs in ZIF-8 crystals is also regulated by their sequence of addition. The same method of assembling was successfully applied to other nanostructured materials with PVP modified surfaces. The hydrogenation process was performed with the Pt/PVP/ZIF-8 sample, which indicated that it partially hydrogenated n-hexene but was totally inactive on trans-2-hexene, showing the size selectivity of MOFs and total encapsulation of Pt NPs [46].

3. MOFs as adsorbent in wastewater treatment

Due to its cheap cost, operating technology, simple design, and numerous uses, adsorption technology is considered better than other decontamination processes. Metal-Organic Frameworks (MOFs) are one of the several porous adsorbents that are of interest. MOF is important in the adsorption and removal of many toxic compounds in wastewater because of its diverse pore structures, large surface area, easy functionalization, and controlled porosity [47]. This diversity of central metals as well as coordinated unsaturated metal sites within the framework of MOF provides a new approach for the adsorption of different toxic substances. Therefore, MOFs can become the best adsorbent to use in purifying wastewater in future studies.

3.1. Heavy metal ions

The heavy metal ions are non-biodegradable and extremely harmful to the life even at low levels. Thus, the efficient elimination of the highly toxic heavy metal in water quality is of high significance to safeguard human lives and health and ensure green ecological environment [48]. MOF has been used extensively as an adsorbent to cleanse numerous heavy metals in wastewater.

3.1.1. Mercury ions

3.1.1.1. Sulfur-functionalized MOFs

MOFs can be functionalized with sulfur atoms and other functional groups to allow the elimination of heavy metals, especially Hg, since they strongly interact with metal ions. In order to prepare a pre-sulfurized MOF substance, vulcanize the ligand and then prepare. This enhances adsorption of heavy metals by MOFs and increases their potential applications [49]. A number of thiolated and thioetherified MOFs have been investigated to extract Hg^{2+} from wastewater. The sulfur content of the thiol-functionalized $[Co(NCS)_2 (pyz)_2]_n$ (pyz = pyrazine) (2D-NCS) nanosheets was 19.1% and mercury ions adsorption capacity was excellent at 1698 mg g^{-1} [50]. A high concentration of active sites in the 2D-NCS nanosheets enables rapid adsorption, where the level of mercury ions in 10 ppm was reduced to 1 ppb within approximately 15 minutes. What is even more interesting is that despite the mercury ion strength being high as 100 mM, 2D-NCS nanosheets are able to retain an excellent adsorption capacity and reusability within a broad pH range. Additionally, sulfhydryl groups were added at positions 2 and 5 of 1,4-terephthalic acid in a creative manner and yielded a Zr based MOF(Zr-DMBD), which effectively adsorbed Hg^{2+} [51]. Zr-DMBDMOF which is produced through the coordination of high-valent metal ions is highly stable.

Furthermore, Zr-DMBD is highly water resistant, and Sulphur lies near Zr-O cluster, which provides Zr-DMBDMOF with the foundation of adsorbing Hg^{2+} [52]. The Zr-DMBDMOF produced has an exceptionally high rate of Hg elimination of over 99.9% and the ability to lower the mercury ion concentration in wastewater to below 0.01ppm. Ding et al. thoroughly investigated the mechanism of adsorption of this material [53]. In their experiments, they showed that Hg^{2+} bonded with sulfur by substituting the hydrogen atom in the sulfhydryl group. The hydrogen that was substituted found its way into the solution forming hydrogen ions, which is capable of altering the pH of the solution. Also, pH variation on adsorption of Hg^{2+} was investigated. The findings reveal that mildly acidic conditions are the best adsorption environment of mercury ions. Hg^{2+} has the highest adsorptive capacity of 171.5 mg g^{-1} at pH of 6 [54]. More importantly, Zr-MSA synthesis method involves the use of clean environmentally friendly solvent water instead of the damaging organic solvents, making Zr-MSA materials more suitable in mercury removal applications.

3.1.1.2. Ammonia-functionalized MOFs

Besides mixing with sulfur, Hg^{2+} also forms very strong interactions with nitrogen. Therefore, ammonia functionalized MOFs are useful adsorbents in the removal of heavy metals. TMU-40 MOF ligands generated In situ has free amine functional groups, which may serve as Hg^{2+} receptors during Hg removal [55]. It was indicated that TMU-40 possesses the best adsorptive capacity of Hg^{2+}, of 269 mg g^{-1}. It is also noted that TMU-40 is helpful in reducing 40 ppm wastewater to safe drinking water of 2 ppb within a relatively short period of time [56]. TMU-40 has a great deal of application in practice due to its high adsorption performance. Moreover, the ammoniated MOF that was obtained after the post-synthesis modification has a high adsorptive capability with Hg^{2+}. MOF 808-EDTA has a high adsorption capacity (592 mg g^{-1}) and interception rate (99 %) of mercury ions, and can also decrease the solution concentrations in ppm down to ppb. It is remarkable that MOF-808-EDTA has the ability to efficiently adsorb 22 different kinds of heavy metals, including sharp and hard ones, besides soft acid ions such as mercury [57]. Moreover, the ammoniated MOF may serve as a fluorescence sensor to identity Hg^{2+} in addition to possessing capacity to adsorb it.

3.2. Dyes

The leftover dyes in the water may result in cancer in the human being as well as the aquatic life. Thus, the problem of synthetic dye pollution in water is a pressing issue and needs to be resolved. The use of adsorption technique has also been common in recovering dyes in wastewater. MOFs are much more favorable compared with traditional adsorbents in the extraction of dyes in wastewater [58].

3.2.1. Methylene blue

Methylene blue (MB) is a typical hazardous cationic dye which on exposure to human beings can lead to various negative effects including vomiting, dyspnea and gastritis [59]. Consequently, MB dye should be eliminated out of the actual aqueous solution. A variety of MOFs adsorbents have been observed to perform excellently as regards to removing MB in wastewater. As an example, one of the most studied MOFs, HKUST-1, was discovered rather early and exhibited a variety of properties. The characterizations and experiment results (including the Langmuir isotherm and Gibbs free energy function) demonstrated potential application value of HKUST-1 in managing wastewater that contained MB (Fig.4) [60]. The author found out that the most important driving force of this material adsorption reaction on MB is the enthalpy change. It is also notable that HKUST-1 can regenerate easily and retain its absorptiveness capacity once it is washed with ethanol [61]. Therefore, HKUST-1 could be regarded as best potential solutions to dye removal.

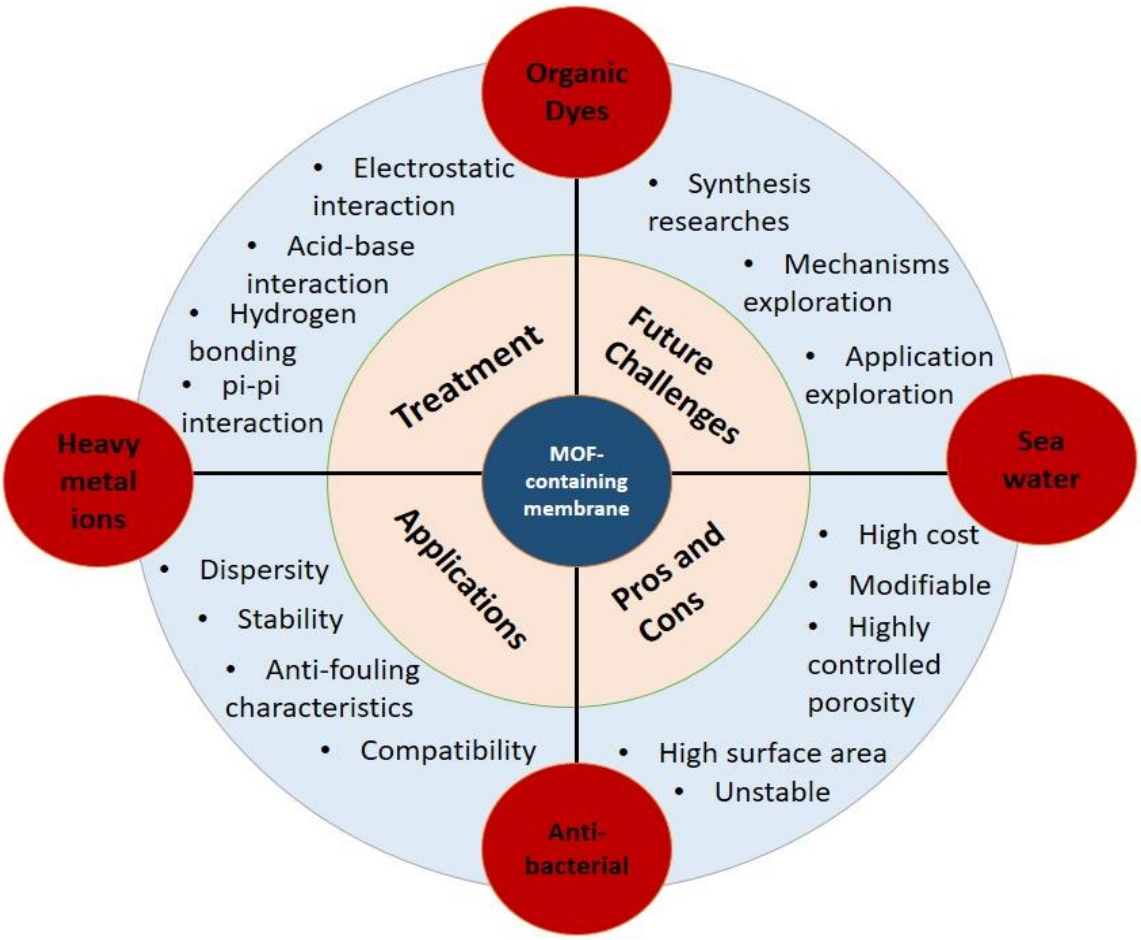

Figure 1. MOF membrane for wastewater treatment.

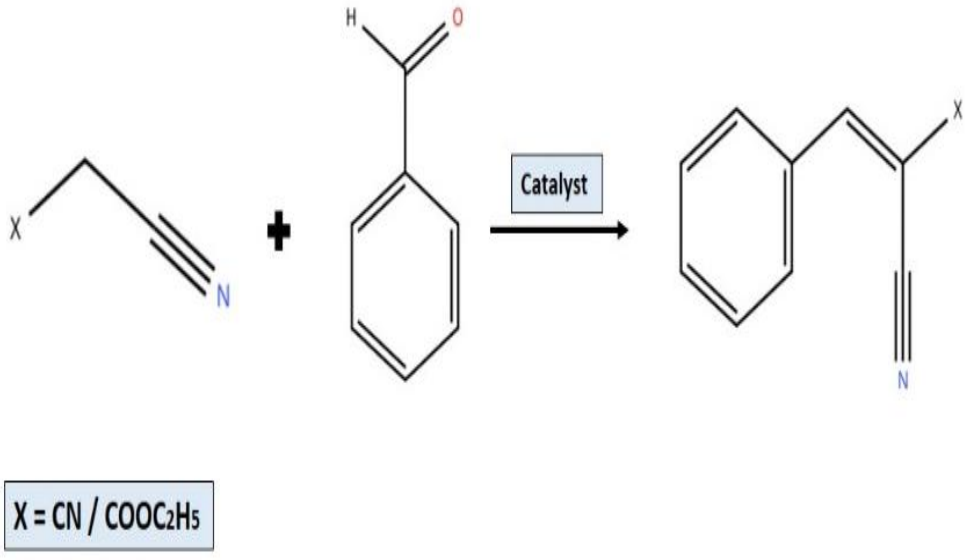

Figure 2. Knoevenagel condensation reaction between benzaldehyde and malononitrile or ethyl cyanoacetate catalyzed by MOFs.

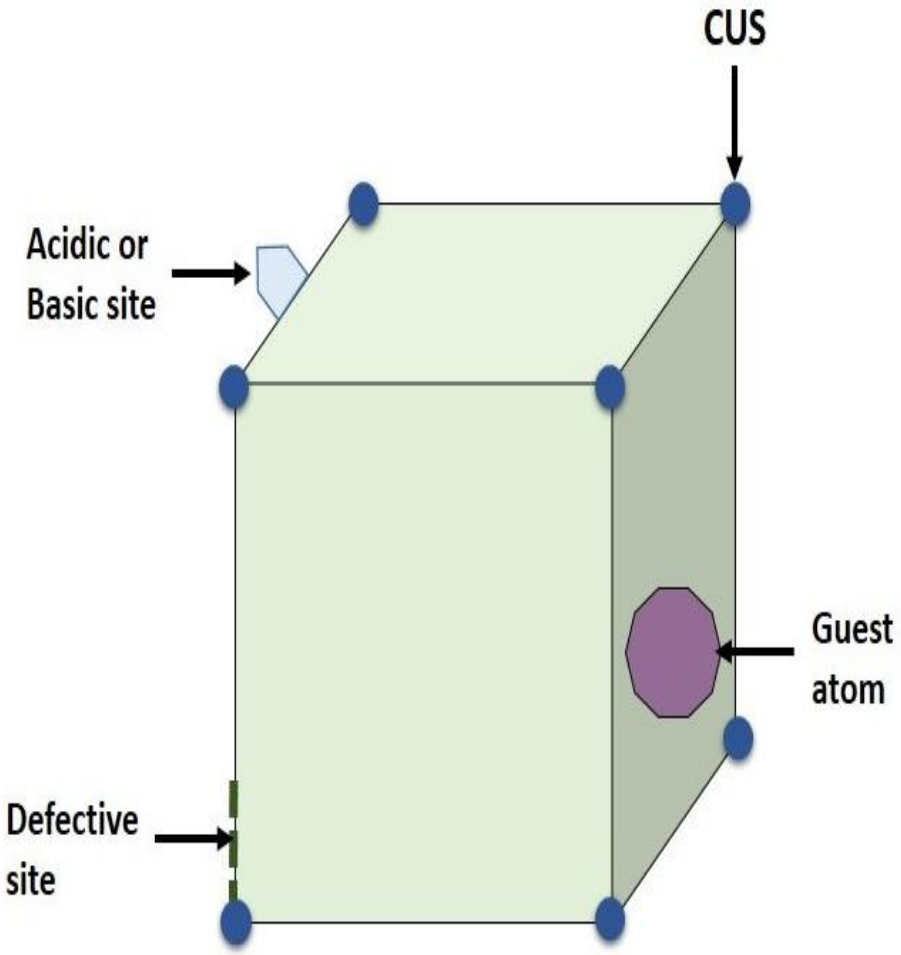

Figure 3. Various possibilities that MOFs offer to locate active sites for catalysis.

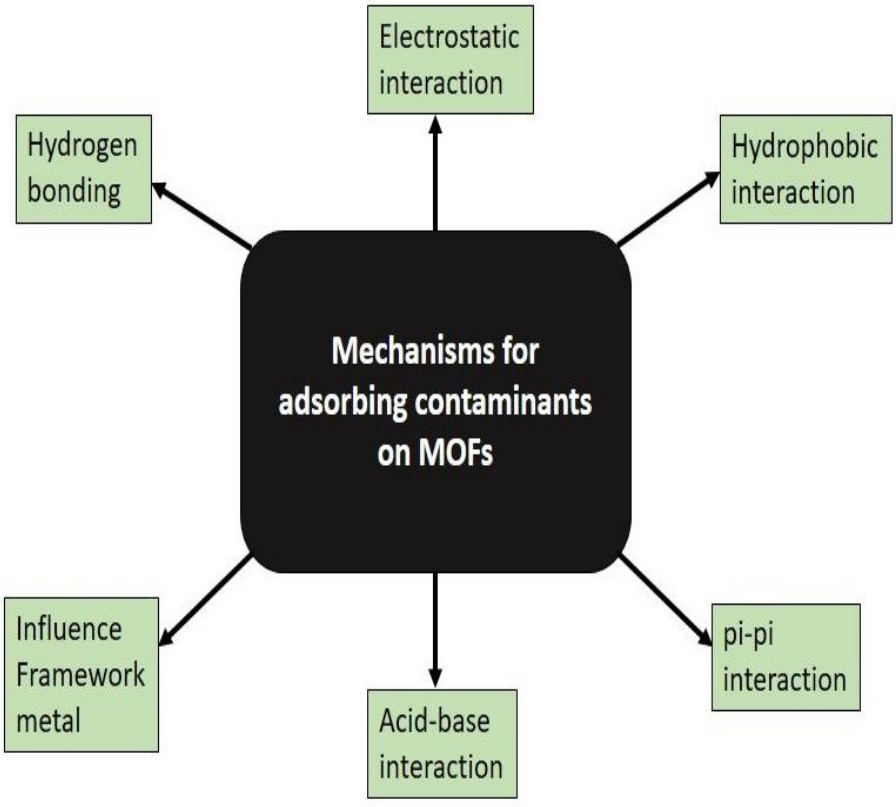

Figure 4. Diagrammatic sketch of probable mechanisms for adsorbing contaminants on MOFs

Table 1. Information about the water-stable MOFs to manufacture membranes for wastewater treatment.

MOF	Metal Centre	Ligands	Application in water treatment	Refs.
ZIF-300	Zn	5(6)-Bromobenzimidazole, 2-Methylimidazole	Nanofiltration	[63]
ZIF-8	Zn	2-Methylimidazole	Microfiltration, Ultrafiltration, Reverse osmosis, Pervaporation, Membrane distillation	[64], [65]
ZIF-8-NH_2	Zn	2-Methylimidazole, Ethanediamine	Pervaporation	[66]
UiO-66	Zr	1,4-Benzenedicarboxylate	Nanofiltration, Forward osmosis, Reverse osmosis	[67], [68]
UiO-66-NH_2	Zr	1,4-Benzenedicarboxylate, ethanediamine	Nanofiltration, Ultrafiltration, Reverse osmosis	[69]
MIL-101	Cr	Terephthalic acid	Nanofiltration, Reverse osmosis	[70]
CuBDC-NS	Cu	1,4-Benzenedicarboxylate	Forward osmosis	[71]

Table 2. Employment of different MOF membranes in dye removal.

Targets	Membranes	Key Performance		Refs.
		Permeability (L/m^2.h.bar)	Rejection (%)	
MB	ZIF-300	>24.0	99.3	[72]
MB	ZIF-8/PEI	33.1	99.1	[73]
MB	UiO-66-$(COOH)_2$/prGO	13.8–11.9	95.9	[74]
MB	MOF-808	4.71	>99.8	[75]
MB	UiO-66-rGO-1	-	98.4	[76]
MO	CMFP/ZIF-8	-	98	[77]
MO	CMFP/ZIF-67	-	96	[78]
MO	UiO-66/PVDF	-	85	[79]
MO	ZIF-300	>24.9	99.9	[63]

Removal of MO in wastewater together with adsorption is thus necessary. MIL-101 and MIL-53 are the two types of MOFs that have been widely used to remove MO by adsorption in the last decade. The study found that MIL-101 possessed a superior adsorption kinetic constant in comparison with adsorptive capacity compared to MIL-53 [80]. This work brought out the importance of pore size and porosity in adsorptive process. In addition, the adsorption capacity of MIL-101 declined as pH increased. On this basis, we found out that the major driving force of adsorption is electrostatic interaction. This study indicates that high porosity cationic adsorbents might be useful in the removal of anionic dyes [81]. Recently, a water-stable MOF constructed using zirconium called UiO-66 was created to eliminate and adsorb MO and MB. Experimental results suggest that UiO-66 can adsorb MO than MB, especially in neutral and acidic conditions. The reason is that MO and UiO-66 possess a higher level of electrostatic contact and p-p stacking [82]. It is interesting since UiO-66 retained its original structure and adsorption capacity over four consecutive adsorption desorption studies, which indicated a high reusability (Table 2).

4. Future Perspectives

In the past two decades, MOFs showcase impressive physio-chemical characteristics with immense potential and unique benefits in catalytic applications. The future studies on MOF-based catalysts are to enhance the structural stability of the catalysts under the extreme reaction conditions and especially in aqueous, acidic or high temperature conditions to allow real life industrial applications. The synthesis of water-stable and defective engineered MOFs containing active sites with a controllable precision will be essential to enhance catalytic stability and reproducibility. Advanced post-synthetic modification methods and multivariate MOF design strategies are expected to be important in tailoring catalytic selectivity and multifunctionality in a single system. Furthermore, to achieve rational optimization of catalysts, a more mechanistic understanding of charge transfer, mass transport and host-guest interactions is needed. There is also a need to develop scalable and cost-effective synthesis routes to facilitate the production at large scale. Lastly, dual functionality of MOFs as catalysts and adsorbents could be extended to provide integrated systems that can remove pollutants and convert biomass simultaneously, which can be a promising solution to green chemistry and the environmental sustainability.

5. Conclusion

Metal-organic frameworks (MOFs) have proven to be a very versatile type of porous material with enormous potential in catalysis due to their crystalline structure, high surface area, tunable pore environment, and highly specific active sites. This review has summarized the catalytic roles of MOFs by grouping them based on the origin of their activity, such as coordinatively unsaturated metal nodes, functionalized organic linkers, and encapsulated guest species, such as metal complexes, polyoxometalates, and metal nanoparticles. With rational structural design and post-synthetic modification, MOFs have been able to combine the benefits of homogeneous catalysts, including high activity and selectivity, with those of heterogeneous systems, including recyclability and stability. In addition to conventional organic transformations, MOF-based materials have also shown potential success in photocatalysis and electrocatalysis. This confinement effect, homogeneous distribution of active sites and synergistic interactions between host structures and guest species are an important factor in improving catalytic efficiency and selectivity. In addition to catalysis, the multifunctionality of MOFs allows them to be actively used as adsorbents in wastewater purification, in particular, the removal of toxic heavy metal ions and organic dyes, and this aspect also indicates their environmental applicability. Regardless of these advantages, challenges related to long-term stability, scalability, sensitivity to moisture and industrial applications are all barriers to practical applications. Overall, the developments summarized in this review demonstrates that MOFs are a versatile and potent catalytic science platform. The further development of material designs, functionalization approaches, and mechanistic insights is likely to strengthen the role of MOFs in sustainable chemical processes and environmental remediation.

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