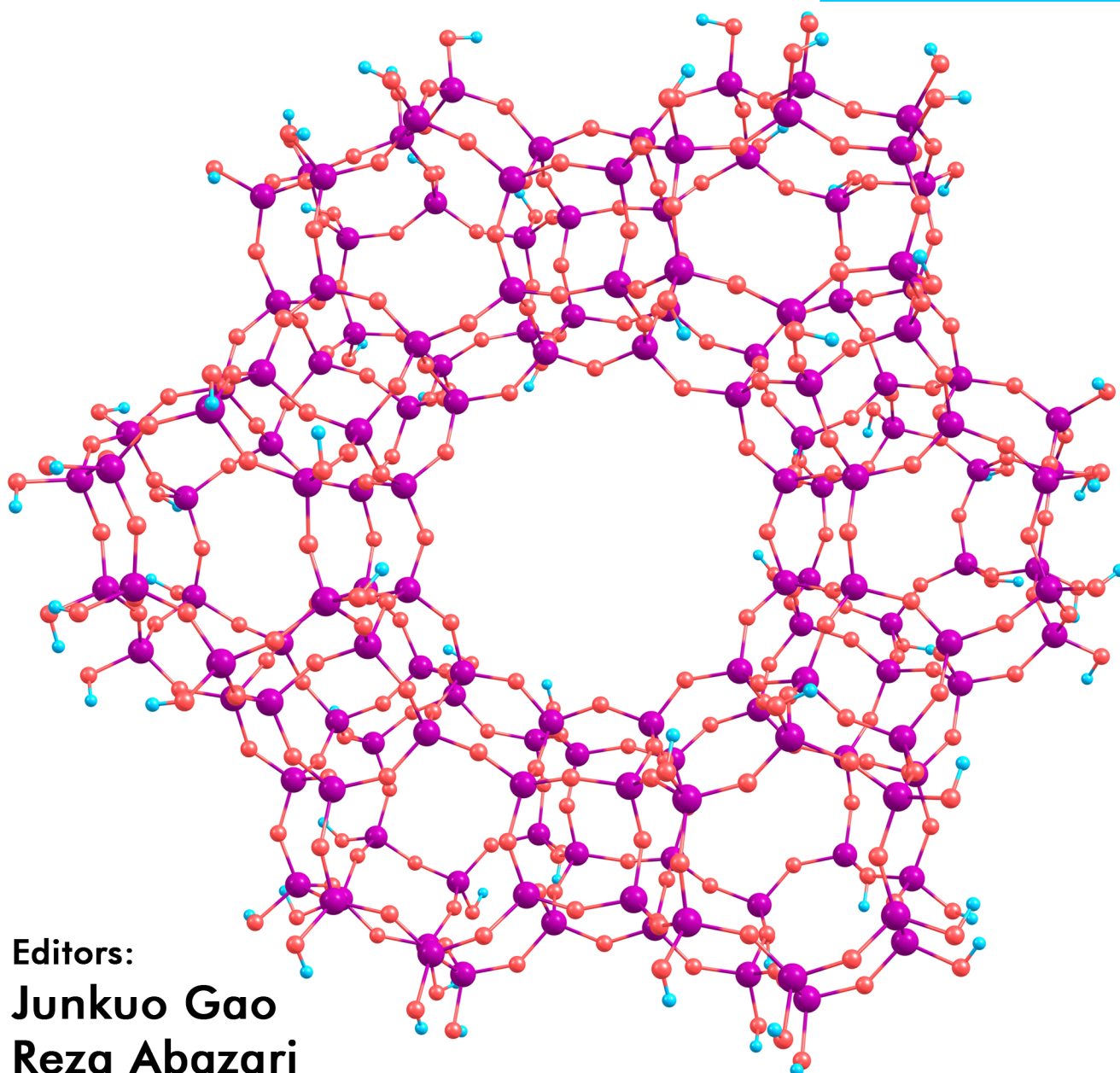


ADVANCED CATALYSTS BASED ON METAL-ORGANIC FRAMEWORKS

PART 1



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Bentham Books

Advanced Catalysts Based on Metal-organic Frameworks (Part 1)

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ISBN (Online): 978-981-5079-48-7

ISBN (Print): 978-981-5079-49-4

ISBN (Paperback): 978-981-5079-50-0

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First published in 2023.

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PREFACE

The energy crisis combined with environmental pollution has been recognized as one of the most serious global concerns. Therefore, huge attempts have been devoted in recent decades to resolving these challenges by introducing more advanced materials with higher efficiency. Specially-designed catalysts are among the first candidates proposed to combat environmental contaminations. Metal-organic frameworks (MOFs) are a novel class of crystalline porous substances possessing high surface area, excellent structural properties, chemical adjustability, and stability which can be used in different applications including catalysis. The significant benefits of MOFs in the field of catalysis can be found in their tunable porosity, uniformly-distributed active sites, and excellent porosity offering accessible active sites through their open channels facilitating the mass transport and diffusion, and finally, their robust structure ensuring recyclability. Thus, MOFs can efficiently offer the positive features of both homogeneous and heterogeneous catalysts, at high reaction efficiency and recyclability. Catalytic properties of MOFs can be further enhanced when used as precursors and/or templates. Their combination with other compounds as a hybrid can further improve their catalytic activities due to synergic effects. The huge attempts to reinforce and modify this class of materials raise our hopes in the bright future of MOFs in the field of catalysis.

Due to unique features of inorganic-organic hybrid compositions, MOFs, compared with traditional porous materials, have a variety of advantages: (1) Good crystallinity. MOFs with highly ordered structures, could be precisely and intuitively analyzed by X-ray diffraction technology, which is helpful to determine structure-property relationships; (2) Good designability and facile functionalization. Applying to crystal engineering, MOFs can not only be pre-designed with expected structures (topologies) and functions, even the coordination diversity of metal ions and organic ligands, but also easily operated by post synthetic methods; (3) High porosity. MOFs are highly porous materials with a large specific surface area (exceeding to 7000 m² g⁻¹), and more importantly, the size, shape and composition of pores can be well tuned by a lot of methods, which is beneficial for host-guest studies; (4) Flexibility. Due to the flexibility of coordination bond and organic linkers, most of the MOFs are somewhat flexible, which endows MOFs with peculiar properties like dynamic irritating response to external conditions (temperature, pressure, humidity, *etc.*), and these features make MOFs more intelligent in applications.

The MOF-based materials offer favorable catalytic performance owing to their unique structural attributes and subsequent modulation. Their range of chemical functionalities and porosities facilitate to adsorb/activate other substrates/CO₂, leading to facile CO₂ conversion. The rise in the number of MOF based catalytic materials with improved performance has opened a new avenue for CO₂ capture and conversion. One of the most important attributes an MOF has is its chemical tunability along with its interactions with other substrates. MOFs as photocatalysts are benefited from a large surface area, suitable band-gap, the ideal structure for charge transfer, and high photo-corrosion resistance.

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CHAPTER 1

Strategies, Synthesis, and Applications of Metal-Organic Framework Materials**Zuo-Xi Li^{1,*} and Chunxian Guo^{1,2,3,*}**¹ *Institute of Materials Science and Devices, School of Material Science and Engineering, Suzhou University of Science and Technology, Suzhou, Jiangsu, 215009, PR China*² *Jiangsu Laboratory for Biochemical Sensing and Biochip, Suzhou, Jiangsu, 215009, PR China*³ *Collaborative Innovation Center of Water Treatment Technology & Material, Suzhou, Jiangsu, 215009, PR China*

Abstract: Metal-Organic Frameworks (MOFs), as one type of famous porous material with many advantages (good crystallinity, design ability, facile modification and flexibility), show a wide range of applications in gas adsorption and separation, ion exchange, fluorescent recognition, nonlinear optics, molecular magnets and ferroelectrics, heterogeneous catalysis, semiconductors, and so on. The research of MOFs span many disciplines, such as inorganic chemistry, organic chemistry, coordination chemistry, supramolecular chemistry, crystal engineering and materials science. The design, synthesis, and applications of MOFs have attracted tremendous attention in broad scientific areas. Therefore, it is worth releasing a professional publication to elucidate so many related issues. In this chapter, we start with the introduction of MOFs, including the definition, classification, concepts, terminologies, and some well-known research. Then we carefully summarize the design and synthesis of MOFs from three aspects of raw materials, synthetic methods, and design strategy, aiming to get the goal of controllable syntheses of MOFs. Following this, we report the developments and applications of MOF materials in adsorption and separation, organic catalysis, luminescence, and drug delivery. Finally, we briefly outline challenges and perspectives of MOF materials, and provide some promising research subjects in this area.

Keywords: Controllable Syntheses, Crystal Engineering, Long-range Ordered Pores, Properties.

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1. INTRODUCTION OF METAL-ORGANIC FRAMEWORKS

Metal-Organic Frameworks (MOFs), also known as porous coordination polymers (PCPs), are crystalline porous materials with periodic networks formed by the self-assembly of metal ions (or metal clusters) and organic ligands through coordination bonds. The concept of MOFs was proposed and firstly reported by the group of Yaghi in 1995 [1]. In their work, it is proved that MOFs are microporous framework materials, which are adjusted through selecting proper organic ligands and metal ions. Furthermore, MOFs can adsorb guest molecules and remain stable after the guest molecules are removed. With the quick development of MOF materials, other some similar terms were proposed from different perspectives as well, such as MILs (Materials of Institute Lavoisier Frameworks) by Férey's group [2], ZIFs (Zeolitic Imidazolate Frameworks) by Yaghi's group [3], MAF (Metal Azolate Frameworks) by Chen's group [4], PCPs (Porous Coordination Polymers) by Kitagawa's group [5] and PCN (Porous Coordination Networks) by Zhou's group [6]. In recent years, the bonding interactions in MOFs have not only referred to coordination bonds, but also included other interactions, such as hydrogen bonds, van der Waals force, π - π interactions between aromatic rings, *etc.* Due to the abundant interactions, the structures and functionalities of MOFs are becoming more and more diversified. In 2013, to classify coordination polymers (CPs), coordination networks (CNs) and MOFs, International Union of Pure and Applied Chemistry (IUPAC) published a set of terms and definitions [7]. According to the recommendations, MOFs are CNs with potential voids, where CPs refer to coordination compounds that extend through repeating coordination entities in one dimension (1D, including cross-links between two or more individual chains, loops or spiro-links), or coordination compounds that extend through repeating coordination entities in two or three dimensions (2D or 3D). That is to say, MOFs are a subset of CNs, also a branch of CPs.

Due to unique features of inorganic-organic hybrid compositions, MOFs, compared with traditional porous materials, have a variety of advantages: (1) Good crystallinity. MOFs with highly ordered structures, could be precisely and intuitively analyzed by X-ray diffraction technology, which is helpful to determine structure-property relationships; (2) Good designability and facile functionalization. Applying to crystal engineering, MOFs can not only be pre-designed with expected structures (topologies) and functions, even the coordination diversity of metal ions and organic ligands, but also easily operated by post synthetic methods; (3) High porosity. MOFs are highly porous materials with a large specific surface area (exceeding to $7000 \text{ m}^2 \text{ g}^{-1}$), and more importantly, the size, shape and composition of pores can be well tuned by a lot of methods, which is beneficial for host-guest studies; (4) Flexibility. Due to the

flexibility of coordination bond and organic linkers, most of the MOFs are somewhat flexible, which endows MOFs with peculiar properties like dynamic irritating response to external conditions (temperature, pressure, humidity, *etc.*), and these features make MOFs more intelligent in applications.

Nowadays, as a new type of functional molecular material, the design and synthesis of MOFs with the desired structure and properties have become one of the frontier fields of coordination chemistry, supramolecular chemistry, crystal engineering and materials science. The research of MOFs span many disciplines and categories, such as inorganic chemistry, organic chemistry, coordination chemistry, material chemistry, and synthetic chemistry, which have shown broad applications in heterogeneous catalysis, molecular recognition, gas adsorption, ion exchange, molecular magnets, ferroelectric materials, fluorescent materials, nonlinear optical materials, and so on. In this chapter, we aim to introduce the synthesis methods, construction strategies and potential applications of MOFs, as well as some recent developments in this area.

2. SYNTHESIS OF MOFS

As a kind of coordination compounds, MOFs are composed of inorganic metal ions, organic ligands and guest molecules inside the frameworks. The synthesis process of MOFs is very similar with that of other coordination compounds, and the key for the synthesis of MOFs is the formation of coordination bonds between metal centers and coordination atoms from organic ligands. Compared with covalent bonds, the bond energy of coordination bonds is much smaller, and so most of the MOFs have a simple and mild synthesis condition. Due to great potential applications of MOFs, some of them have begun to be commercialized. Therefore, to meet requirements of rapid, controllable and large-scale production, new methods including microwave synthesis, ultrasonic synthesis, electrochemical method, mechanochemical method, spray drying and mobile chemical synthesis have been gradually developed, besides traditional methods.

2.1. Raw Materials

2.1.1. Metal Nodes

In the synthesis of MOFs, various central metal nodes provide empty orbitals for the formation of coordination bonds, which can be regarded as binders to anchor organic ligands. Most of the metal nodes have relatively definite coordination numbers and configurations, which are one key factor to determine the structures of final products. It is worth mentioning that metal nodes in MOFs are not only

CHAPTER 2

Post-synthetic Modification and Engineering of Metal Nodes and Organic Ligands of MOFs for Catalytic Applications

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Abstract: Metal-organic frameworks (MOFs) emerged as adjustable and multipurpose materials, which are now intensively investigated worldwide. They are composed of a wide range of organic and inorganic building units which are a susceptible base for various post-synthetic modifications (PSMs). In the last years, altering MOFs composition has significantly contributed to their broad application in many fields, especially in heterogeneous catalysis. PSMs are employed to improve the physicochemical properties of MOFs such as stability or selectivity, but mostly to generate catalytically active sites. Here, we report diverse methods of metal- (exchange, doping, redox transformations) and ligand-based (functionalization, exchange, installation, removal) PSMs of MOFs, which can be effectively used for catalytic purposes. PSMs can either extend the MOF framework with catalytically active functionalities or contribute to defect engineering for open metal site formation. Moreover, combining different modifying procedures has been introduced as a tandem approach when various reactions prompt several changes in the framework. Epitaxial growth was also presented as PSM, which can govern catalytically beneficial features mostly for thin films, unattainable to achieve by conventional methods. Recent MOFs' PSM findings were reviewed to show new pathways and a continuously developing field of reticular chemistry which come across with the expectations for novel and more efficient catalysts.

Keywords: Coordination sites, Epitaxial growth, Ligand exchange, Ligand functionalization, Ligand installation, Ligand removal, Linkers, Metal exchange, Metal incorporation, Metal-organic frameworks, Metal nodes, MOF, MOF stability, Post-synthetic modification, PSM, Redox transformations, Transmetalation.

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1. INTRODUCTION

The search for new materials applied in the catalysis is grounded in the constant necessity for alternative and more efficient catalytic reaction pathways [1]. By any means, a proper catalyst does not influence the thermodynamic equilibrium, yet it provides opportune conditions for the substrate molecules to change the reaction kinetics [2]. In consequence, it lowers the energy barrier of the reaction, leading to its faster occurrence [3]. In heterogeneous catalysis, where the catalyst is usually in the form of a solid, catalytic reactions take place on the catalyst surface, thus it has to stand out with specific features [4, 5]. Firstly, the catalyst has to be stable enough during the proceeding reaction to only assist it, without creating interfering compounds, and in the end, it should remain unchanged. Moreover, it should be characterized by a well-developed surface area to provide a place for reagents, but above all, it must indicate abundance in catalytically active centers to allow substrates to interact [6, 7].

In the last few decades, intensive research devoted to MOFs showed that they meet the requirements of good catalysts [8 - 10]. Their extremely high porosity, the multiplicity of topologies, and improved stability created a wide spectrum of their applications in catalysis [11, 12]. On top of that, the possibility of post-synthetic modifications (PSMs) pushes MOFs utility even further [13 - 16]. It can translate into increasing their performance and selectivity or even giving them novel catalytic abilities [17, 18]. Usually, PSM is performed when the desired framework is particularly difficult to obtain in the direct synthesis. Despite it constitutes as an additional processing step, extended synthesis may be ultimately cost-effective [16].

Active sites in MOFs which provide catalytic abilities may occur in various forms [19]. Metal nodes exhibit catalytic activity if only they are accessible for substrates. When reagents are not able to approach nodes directly due to the steric hindrance, defect generation is required. For instance, linker displacement creates coordinatively unsaturated metal sites, known as open metal sites (OMSs), which mainly contribute to supporting catalytic reactions. The other types of active sites are outer surface terminating groups, which are exclusively located on the external side of the MOF particles. Therefore, decreasing particles size increases the number of active sites and catalytic activity. Moreover, terminating groups can constitute a base to attach different functional groups which are catalytically active. For instance, sulfonic or amino moieties may result in the formation of Brønsted acidic or basic centers, respectively [11]. They can also be generated by defect engineering, which does not always involve lattice constructions dislocation or modification. Besides organic linkers, inorganic nodes often are coordinated with solvent molecules or ligands which do not form the cage. Their

removal at a specific temperature or by vacuum generates active sites which act as Lewis acids [20]. It all indicates that MOFs as materials constructed from inorganic and organic components, can be post-synthetically modified in many ways, due to the possibility of active sites generation on several levels (Fig. 1). The first one is the metal-based PSM, where cations in metallic nodes can be substituted by different metals (transmetalation) [21], changed through redox transformations [22], incorporated with new species [23], or become more available through vacancies creation [24]. The second way is to interplay with organic struts *via* any reaction that will not damage the pristine framework unless intentionally for vacancies generation [25]. In order to increase catalytic activity and selectivity of MOFs, organic building units can be modified through ligand exchange, installation, and removal. Furthermore, MOFs owing to their large channels are capable of encapsulating catalytically active entities *i.e.* nanoparticles, molecules, or clusters *via* host-guest interactions [26]. Up to now, the most successful guest assemblage within framework cavities is conducted locally by impregnating MOFs with precursors, followed by thermal treatment, photochemical decomposition of precursor, or its redox reactions. This ‘ship-in-a-bottle’ approach enables confining and immobilizing guests without the risk of precursors aggregation if only the process is conducted in mild conditions and MOF maintains its structure [27].

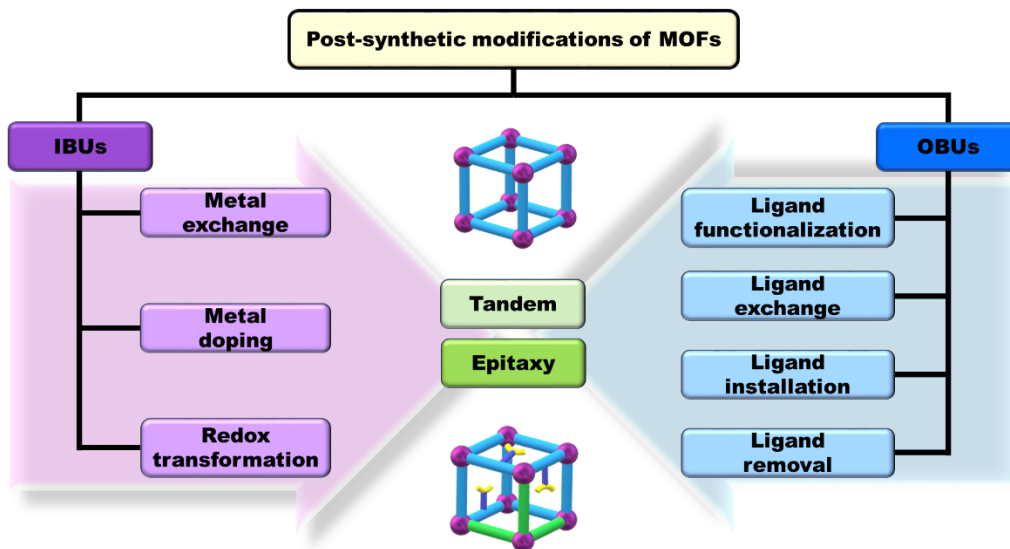


Fig. (1). Post-synthetic modifications of metal–organic frameworks (IBUs - Inorganic Building Units; OBUs - Organic Building Units).

MOFs and Their Composites as Catalysts for Organic Reactions

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Abstract: In recent years, metal-organic frameworks (MOFs) have significantly contributed to broadening the frontiers of science. Due to their distinctive properties including well-developed surface area, high porosity, multifarious composition, tunable and uniform pore structures, and comprehensive functionality, they were applied in different fields such as separation, drug delivery, fuel storage, chemical sensing, and catalysis. The application of pristine MOFs as materials that speed up the reaction rate could be restricted mainly because of the limited number of active sites and their low mechanical and thermal stability. In order to enhance their catalytic properties, metal-organic frameworks can be functionalized or integrated with a variety of materials to obtain composites or hybrids. The review outlines the state of art concerning the application of MOFs and their composites as catalysts in various organic transformation processes. A particular focus was given to the oxidation of alkanes, cycloalkanes, alkylbenzenes, alcohols, thiols, sulfides. Furthermore, the role of metal-organic frameworks in hydrogenation and C–C coupling reactions were also presented.

Keywords: Alkanes, Alkenes, Brønsted acid sites, Catalysis, C–C coupling reactions, Composites, Hybrids, Hydrogenation, Lewis acid sites, Linkers, Metal nodes, Metal–organic frameworks, MOF, MOF active sites, MOF stability, Oxidation, Reduction, Sulfides, Thiols.

1. INTRODUCTION

In recent times, metal-organic frameworks (MOFs) have attracted great attention of scientists from different fields. These materials are classified as hybrids being

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composed of inorganic parts (metal nodes) connected by coordination bonds to organic linkers. The most common representatives of MOFs are MOF-5, UiO-66, MIL-101, HKUST-1, PCN-14 and ZIF-8 [1 - 4]. They exhibit distinctive properties including well-developed surface area, high porosity, multifarious composition, tunable and uniform pore structures, and comprehensive functionality [5, 6]. As porous materials, MOFs fill the gap between zeolites (possessing small pore size) and silicate (having larger pore size). So far metal-organic frameworks with micropores to mesopores have been described in the literature [7, 8]. Due to the presented above unique features, MOFs have the potential to be applied in different fields such as separation [9], fuel storage [10], drug delivery [11, 12], chemical sensing [13, 14], and environmental remediation [15]. These porous polymers have also been recommended as catalysts in different processes [16 - 18]. The catalytic activity of MOF originates either from metal ions or functional groups attached to the organic linkers of the framework. Additionally, high density and spatially separated active sites of metal-organic frameworks are crucial features that support their function as catalysts [19]. Furthermore, the post-synthetic modification or *in situ* processes enable to adjust the metal-organic framework structure and introduce additional functional acid-base groups ($-\text{SO}_3\text{H}$, $-\text{NH}_2$, *etc.*) or embed active metal nanoparticles (Pt, Ru, Cu, *etc.*) and metal complexes inside the MOF cages (or anchored on their surface) that are beneficial to design an appropriate catalyst for the target application. The high porosity and permeable channels facilitate the delivery of reactants to catalytic sites. Therefore, MOFs and their composites represent a new class of recyclable heterogeneous catalysts owing remarkable properties. Although their application as catalysts is still at the developing phase, a series of studies have been performed in this area so far, showing that MOFs exhibit considerable catalytic properties including high activity, appropriate stability, and reusability [20 - 22].

Despite the fact that the application of MOFs and MOF-derived materials for various catalytic reactions has been documented in recent reviews [23 - 25], in this fast-growing research field, we would like to provide an overview of the catalytic behavior and advantages of the MOFs and their composites in different valuable organic processes such as oxidation, hydrogenation, and C–C coupling reactions.

2. MOFs AND THEIR STABILITY

Stability is the fundamental factor in the development of materials. In this context, it should be highlighted that although MOFs have unique properties, their full potential application is limited, mainly due to their low chemical, mechanical,

thermal, and hydrothermal stabilities [16]. Chemical stability refers to the resistance to different solvents, acids, bases, and solutions with strongly coordinating anions (for example, phosphate anion), while the mechanical and thermal stability is related to the capability of materials to preserve their structure under exposure to pressure, heat, and vacuum. The chemical stability of metal-organic frameworks is related to the strength of the metal-ligand bond [26]. It should be noted that mostly the thermodynamic factors have an influence on the metal-ligand coordination bond strength [27]. Therefore, the stronger the coordination bonds, the more stable MOFs can be created [28]. It was proved that the chemical stability of UiO-66 and SUMOF-7 series declined with the lengthening of the linker and an increase of pore sizes [1, 29]. This is due to the kinetic factors, that are associated with the coordination number, the rigidity of the linker, and surface hydrophobicity.

The structural framework of MOFs can be decomposed both in acidic solutions, which can accelerate the formation of a protonated linker, and in basic solutions facilitating the formation of a hydroxide ligated node [5, 30]. However, the chemical stability can be enhanced by using high valence metal ions including Zr^{4+} , Fe^{3+} or Cr^{3+} and by the interactions with different ligands (imidazolates and triazolates). Outstanding stability in water is therefore achieved for azolate MOFs thanks to the strong metal–nitrogen bonds [31]. Nevertheless, despite recent progress in understanding and improving the chemical stability of MOFs, it was proved that MOFs fabricated by the traditional methods are less competitive compared to commercial catalysts when applied in a harsh reactive environment [32].

It should be added that the nature of reagents can also have an influence on the stability of MOFs. Timofeeva *et al.* observed the destruction of MAF-6(S) structure due to the leaching of Zn^{2+} caused by the polar reagents [33]. In turn, Linder-Patton *et al.* detected that the surface of ZIF-8 was unstable in the catalytic processes in the presence of hydrophobic reagents with polar functional groups [34].

The mechanical stability of MOFs decreased with the increase in porosity. However, it was shown that when metal–organic frameworks are filled with solvent, they were more mechanically stable than the same materials with empty pores [35 - 38].

It should be underlined that the thermal, chemical, and hydrothermal stabilities are crucial in terms of MOF's characterization and application as catalysts in various reactions. When metal-organic frameworks undergo decomposition, it is hard to determine their structure by using X-ray diffraction. The thermal stability of

Metal-Organic Frameworks and Their Derived Structures for Biomass Upgrading

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Abstract: Biomass valorization is receiving increasing attention over the past years with the consumption of traditional fossil fuels as well as the deterioration of the global environment. The transformation of biomass into highly value-added chemicals and important feedstocks will be of keen interest and great impact. The conversion process of biomass requires efficient and durable catalysts with high selectivity and stable structures. This chapter focuses on the employment of metal-organic frameworks (MOFs), MOF composites (metal, metal oxide, or polyoxometalates combined with MOFs), and MOF-derived materials (carbon, carbon-supported metal or metal oxide by using MOF as precursors) as solid catalysts for the upgrading of biomass into important fine chemicals. First, we will give a short introduction of biomass and MOFs, and then the brief biomass valorization reactions by MOFs and MOF-based catalysts based on the types of substrates. The last segment is summary of the state of the art, challenges, as well as prospects of MOFs and MOFs-derived structures for biomass transformation.

Keywords: Biomass, Heterogeneous catalysts, Metal-organic frameworks, Platform chemicals, Porous materials, Transformation.

1. INTRODUCTION

1.1. Biomass

Conventional fossil resources, crude oil, coal, and natural gas are used to satisfy our energy consumption, improve the national economy and people's livelihood. However, severe environmental issues occurred due to the high consumption of

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traditional fossil energy, such as the greenhouse effect, acid rain, atmosphere and marine pollution [1, 2]. At the same time, these conventional fossil sources are not renewable and will be depleted one day. Hence, it is necessary and urgent to develop alternative renewable energy resources such as biomass, solar energy, wind energy, as well as hydrogen energy owing to their features of being rich in sources, wide distribution, renewable and environmental-friendly. Amongst, biomass is regarded as the only potential reliable candidate for the replacement of conventional fossil energy sources to produce fuels and fine chemicals [3 - 7].

Biomass can be obtained from an inexpensive and wide range of substances, such as forest products (green plants, forestry, woods, logging residues), crops (agricultural and husbandry wastes as well as breeding), domestic and industrial wastes (kitchen waste, biodiesel or bioethanol production, and paper industry and so on), so as to avoid the competition with human food.

Lignocellulose, in general, is the most abundant form of biomass. The main construction of lignocellulosic biomass is lignin (20%-30%), cellulose (40%-50%), and hemicellulose (18%-28%) (Fig. 1) [8, 9]. Lignin is composed of an aromatic polymer with methoxylated phenylpropane units, cellulose is a crystalline homopolysaccharide polymer and made up of glucose units, while hemicellulose is a complex polymer in amorphous state (xylose monomer unit is the main component) [10 - 13].

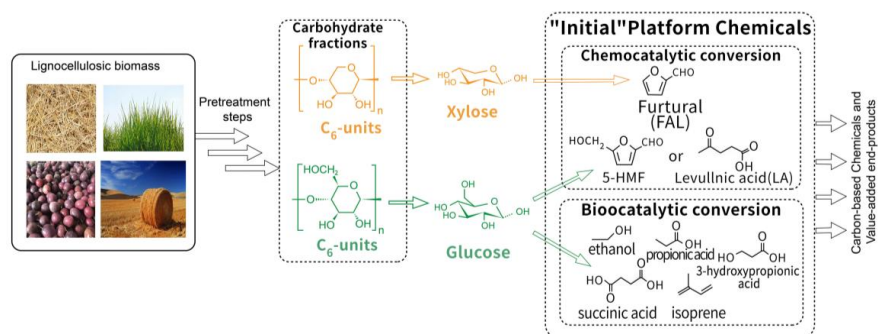


Fig. (1). Lignocellulosic-derived initial platform chemicals. Reprinted from ref. 14 with permission from American Chemical Society, Copyright 2018 [14].

Cellulose is a homopolymer consisting of glucose units with a high degree of polymerization (10000 to 15000 in wood and cotton) [15]. It is hard to be hydrolyzed ascribed to the existence of intramolecular and intermolecular hydrogen bonding between the units of anhydro glucan [16]. The bottom and top part of the cellulose chains are entirely hydrophobic, and both ends of the chains

are usually hydrophilic. This long range ordered hydrogen bonding feature makes cellulose a highly crystalline and robust material toward chemical reactivity. Through strong acid hydrolysis process, cellulose can be degraded into glucose tetramer, glucose trimer, glucose dimer, and even glucose (Fig. 2) [17]. Further dehydration of glucose obtains a very important chemical intermediate of 5-hydroxymethylfurfural (HMF) [18], which can be widely used for the production of various indispensable industrial feedstocks such as 5-formyl-2-furancarboxylic acid and 5-hydroxymethyl-2-furancarboxylic acid intermediates, 2,5-furandicarboxylic acid *via* furan-2,5-diformylfuran (DFF) [19], 2,5-dihydroxymethyl-tetrahydrofuran (DHMTHF) through di(hydroxymethyl) furfural (DHMF) intermediate [20]. Besides, other important products like levulinic acid (LA), and γ -valerolactone (GVL) can be also obtained from HMF [21, 22].

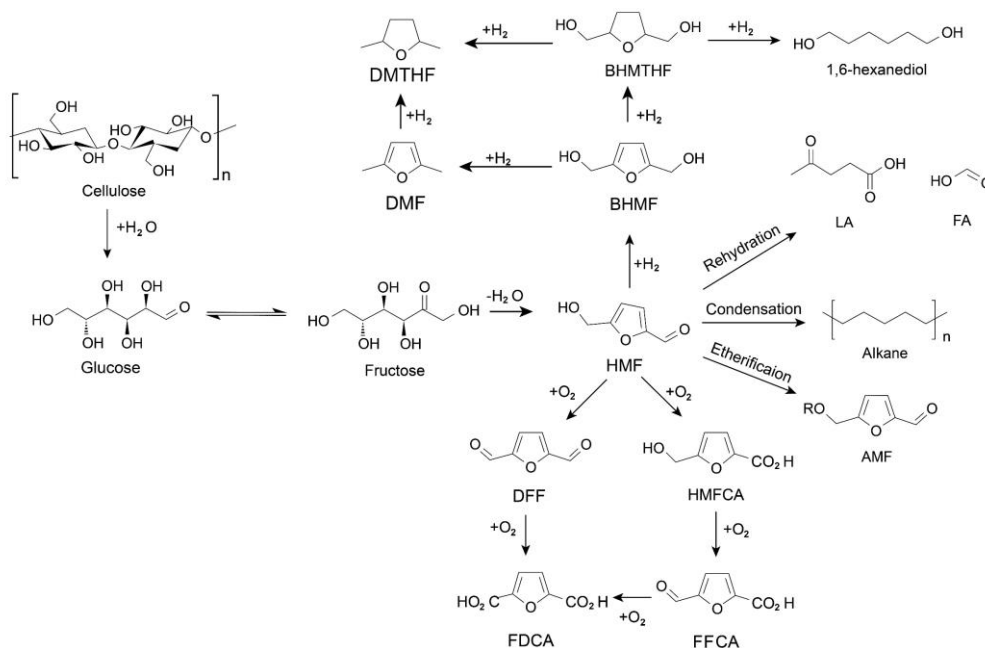


Fig. (2). Conversion of cellulose into diverse chemicals. Reprinted from ref. 23 with permission from American Chemical Society, Copyright 2018 [22].

Hemicellulose is sugar polymer which is made up of five and six-carbon sugars: this raw material can be transformed to C5 sugar monomers (Fig. 3) [24]. The most abundant constitute of hemicellulose is xylan, which is usually composed of xylose polymer. Hemicellulose is amorphous due to its branched feature, at the same time, it is facile to be hydrolyzed into its basic monomer in comparison to

MOF-Based Materials for CO₂ Conversion

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Abstract: Due to the rapid and continuous increase in CO₂ concentrations in the atmosphere by the massive combustion of fossil fuels, the global ecosystem is being affected severely. Therefore, balancing the CO₂ content in the atmosphere should be our main agenda nowadays. For minimization of CO₂ concentration, carbon capture and its conversion to valuable chemicals are being perused worldwide. Metal-organic framework (MOF)-based materials having a porous structure and tuneable structural features, are best candidates for the purpose. Herein, we provide a detailed discussion on the design, synthesis and catalytic applications of MOF-based materials for various CO₂ conversion reactions.

Keywords: Carbon dioxide, Catalysis, Cyclic carbonate, Metal-organic frameworks (MOFs), Methanol, MOF composites, Photocatalyst.

1. INTRODUCTION

Considering the global climate issue, the conversion of atmospheric carbon dioxide (CO₂) into energy and other useful chemicals becomes a burgeoning field of scientific research. It will not be early to say that the next quest for the human race is for sustainable growth. Increased CO₂ emissions from the burning of fossil fuel is a key factor for environmental concern as the increase in the transport of people and goods is set to continue over the coming years. According to a study carried out in 2019, the CO₂ emissions from human activity have reached 34 Gt [1]. Hence, the need to develop a safe, economic and clean methodology for CO₂ capture and its conversion into a valuable chemical could be a great milestone for

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the survival of the human race. Therefore, it is inevitable to examine and address the development of new and efficient catalysts for catalytic conversion of CO₂ into fuels and valuable chemicals. Significant efforts are given to develop a highly efficient catalyst bearing high surface area, high CO₂ uptake property, and stable catalytic activity to facilitate energy efficient capture and subsequent conversion [2]. However, the biggest obstacle in the process of its conversion is high thermodynamic stability and kinetic inertness as the carbon of CO₂ is in the most oxidized state keeping its energy level low. Hence a catalyst is needed to activate it and this will be going to possess long-term goals [3].

MOFs are an exciting class of new materials possessing very high surface areas, high porosity and myriads of chemical functionalities which are tunable [4]. They've been used with great success in many applications, including adsorption/separation [5], water splitting [6], gas separation [7], drug delivery [8], conversion of CO₂ to economically valuable products [9], photovoltaics [10], catalysis [11], batteries [12] and so on. In the forthcoming discussion of this chapter, the current state of research focused on the application of MOF-based materials as catalysts for CO₂ conversion into fuels and chemicals has been discussed. There are mainly three different routes available for CO₂ conversion, 1) thermal catalysis of the majority of reactions involves hydrogenation reaction at a relatively low temperature and produces carbon monoxide, methanol and methane, 2) photocatalytic conversion where the catalyst is exposed to solar light and generated photoelectrons induce a redox reaction involving CO₂, and 3) electrocatalytic conversion involves the reduction of CO₂ by the transfer of two, four, six, or eight number of electrons and controlling the formation of single and desired products is the grand challenge behind this pathways. This route of CO₂ conversion is gaining significant momentum as it offers higher cost-effectiveness because of milder operating conditions, high efficiency, controllable reaction conditions, and recyclability of the electrolyte and the catalyst. There are other methods too but fundamentally, all are just the same or a combination of the aforementioned three routes.

Finally, we end up this discussion pertaining to the challenges associated with MOF-based catalysts, their pertinent solutions, and some highlights on their future scenarios for the conversion of CO₂ to fuels and valuable chemicals.

2. SYNTHESIS OF VALUE-ADDED ORGANIC COMPOUNDS USING CO₂ AS PRECURSOR

MOFs have porous structures and high CO₂ uptake properties. Therefore, plenty of MOFs or MOF-based materials have been exploited for the conversion of CO₂

to several valuable organic compounds. Some of the representative CO₂ conversion reactions catalyzed by-MOF-materials are recorded in Table 1.

Table 1. List of representative CO₂ conversion reactions catalyzed by MOF-based materials.

Type of Reaction	Equation	Active site(s)
Cycloaddition	$\text{R-Oxirane} + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{R-Cyclic Carbonate}$	Lewis acid, Lewis base, Brønsted acid, organic salt, organic base, etc.
	$\text{N-oxirane} + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{N-Cyclic Carbonate} + \text{N-Cyclic Carbonate}$	
Olefin oxidative carboxylation	$\text{R-olefin} + [\text{O}] + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{R-Cyclic Carbonate}$	Oxidant, Lewis acid, Lewis base, halide
Terminal alkyne carboxylation	$\text{R}^1\text{-C}\equiv\text{C-H} + \text{R}^2\text{X} + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{R}^1\text{-C}\equiv\text{C-CO-O-R}^2$	Cu(I)
	$\text{R-C}\equiv\text{C-H} + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{R-C}\equiv\text{C-COOH}$	Ag, Pd-Cu NPs
Propargylic alcohol carboxylic cyclization	$\text{R}^3\text{-C}\equiv\text{C-C(OH)(R}^1\text{)(R}^2\text{)} + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{R}^3\text{-C}\equiv\text{C-Cyclic Carbonate}$	Ag(I), Cu(I)
Three-component carboxylic cyclization of propargyl alcohols, CO ₂ , and primary amines	$\text{R}^3\text{-C}\equiv\text{C-C(OH)(R}^1\text{)(R}^2\text{)} + \text{R}^3\text{-NH}_2 + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{R}^3\text{-C}\equiv\text{C-Cyclic Urea}$	Ag(I)
Propargyl amine carboxylic cyclization	$\text{R}^3\text{-C}\equiv\text{C-C(OH)(R}^2\text{)(HN-R}^1\text{)} + \text{CO}_2 \xrightarrow{\text{Catalyst}} \text{R}^3\text{-C}\equiv\text{C-Cyclic Urea}$	Ag(I)

The transformation of CO₂ to the value-added compounds will be “killing two birds with one stone” *i.e.* the atmospheric CO₂ level can be reduced while producing essential chemicals. To do so, several MOFs-materials have proven to be excellent heterogeneous catalysts. Conversion of CO₂ mainly happens through the following processes:

- cycloaddition of CO₂ to epoxides to form cyclic carbonates,
- fixation of CO₂ through carboxylation of terminal alkynes

Metal-Organic Framework Composites for Photocatalytic Water Purification

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Abstract: The rapid rise in photocatalytic technology with efficient removal capabilities has attracted wide attention. Recently, metal-organic frameworks (MOFs), a kind of coordination polymers, have also been applied in the field of photocatalytic water purification due to their characteristics such as high specific surface area and adjustable pore structure. However, the weak water stability, low reutilization rate, and poor photocatalytic ability of the constructed MOFs restrict their application in environmental remediation. To tackle these problems, many researchers have devoted themselves to designing highly efficient MOF-based composites by adding other substances. This chapter mainly focuses on the research status of MOF-based composites in the photocatalytic elimination of various pollutants from water. Additionally, the synthetic strategies for MOFs and their composite materials as well as for photodegradation of pollutants in water are reviewed and exemplified. The possible removal mechanisms of some MOF-based composites have also been briefly analyzed. Finally, the achievements and prospects on future research of MOFs and their composite materials have been described in detail.

Keywords: Adsorption, Metal-organic framework composites, Photocatalysis, Water purification, Water treatment.

1. INTRODUCTION

To meet the needs of the alarming growth of the world population, the rapid development of the industrial sector has produced the required products and a lot of polluted organic wastes [1]. The generated organic pollutants can cause serious environmental pollution, which will threaten the existence and development of human beings [2]. Industrial wastewater discharged into lakes, rivers, and drinking water environment often contains heavy metal ions or common organic contaminants. They are highly likely to menace the lives of aquatic creatures and

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the health of human beings [3]. Some common organic pollutants in rivers are dyestuffs, phenols, pharmaceuticals and personal care products (PPCPs), herbicides, pesticides, as well as other organics [4]. In addition, some inorganic pollutants are also included and mixed pollutants may coexist in real water [5]. These pollutants are highly stable, remain very long-term bioactive, cause a big effect on the type of microbial species, and they may also produce certain viruses [6]. Due to their high solubility, the decontamination process of inorganic pollutants is more durable and extremely resistant. The predominant concentrations of these pollutants in the water are virulent or deadly, even at ppm or ppb levels. These pollutants are of high risk because they can easily be amplified by organisms and cause harm to organisms higher up the tropical food chain [7]. As a consequence, it is urgent to search for a valuable water treatment technology to remove the pollutants. So far, numerous approaches for the elimination of these pollutants have been utilized, for example, membrane separation, ion exchange, photocatalysis, adsorption, and so on. Among these water treatment techniques, photocatalysis is a burgeoning method and is identified as the most valuable technique on account of its affordable cost, easy operation, and good practicability [8]. As a consequence, photocatalysis is deemed to be the most effective method for removing these pollutants [9]. Hence, fabricating an efficient photocatalyst with enhanced photocatalytic performance is of great practical importance.

MOFs can be self-assembled from organic ligands and metal salts or metal clusters. Up to now, these MOF materials have been considered as a new kind of crystalline porous material [10]. Their applications in the field of photocatalysis have gradually emerged and been systematically studied based on the large surface area and adjustable pore sizes [11 - 13]. Initially, they are mainly used for photocatalytic H_2 generation [14], photocatalytic degradation, and metal ion reduction. However, due to the high e^- - h^+ recombination efficiency, low solar energy conversion efficiency, and poor electrical conductivity, photocatalytic efficiency is not ideal. Hence, many research groups have established MOF-based composites to boost the photodegradation capacity of MOFs. The constructed composites have been reported to be used in photocatalytic water purification. At the same time, they are expected to achieve better photocatalytic performance.

In this chapter, the applications of MOF-based composites in photocatalytic water purification in recent years are reviewed (Fig. 1). Firstly, the present chapter provides a brief review of their preparation strategy and photocatalytic substrates of MOF-based composites. Then, we study MOF-based composite materials from the aspect of photocatalytic degradation of organic pollutants, inorganic pollutants, and mixed system pollutants in water in the following context. Subsequently, we introduce the application of adsorption-photocatalysis

synergism in water purification. Finally, we summarize the photocatalytic water purification of MOF-based composites and give a prospect of the development of the composites in the future. We hope that this chapter will provide a better guide to the future challenges of MOF-based composites in photocatalytic water purification.

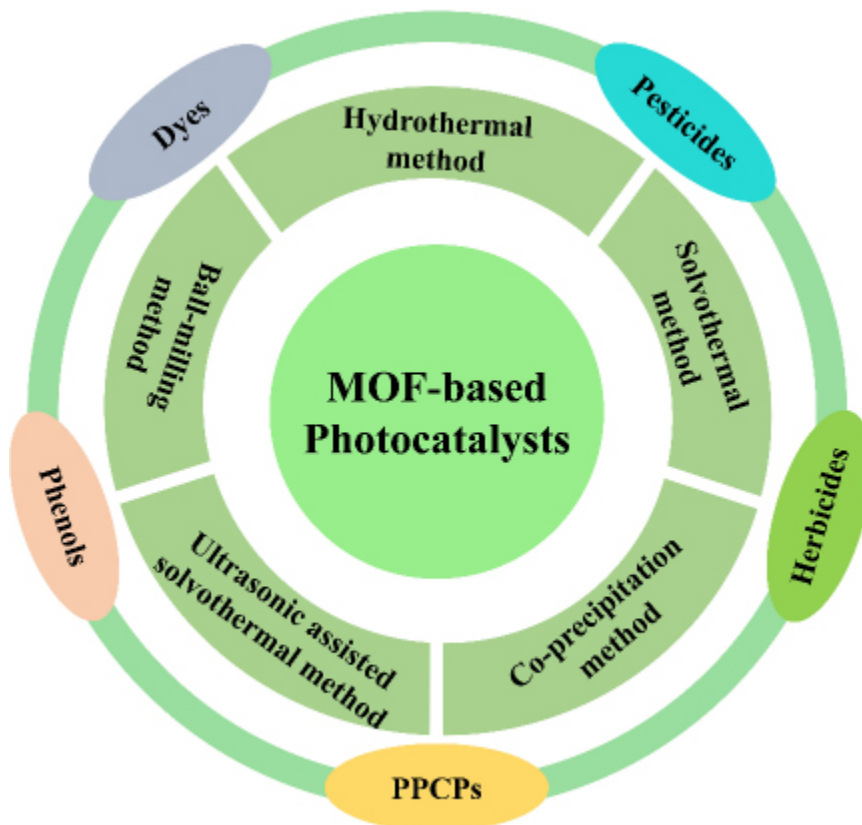


Fig. (1). Schematic diagram of the preparation method and photocatalytic water purification onto MOF-based composites.

2. SYNTHESIS OF MOF-BASED COMPOSITES

Recently, more and more researchers set about constructing MOF-based composites. The MOF-based composites with diverse synthetic methods can be generated by regulating and controlling the reaction conditions. Various synthesis strategies to prepare MOF-based composites have been exploited, leading to diverse morphologies and properties, so they can be applied to the photodegradation of contaminants in wastewater. In the current section, we delineate the preparation strategy of different MOF-based composites. Their use to treat the different organic pollutants in wastewater is also summarized in the

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