Synthesis and Application of Doped Metal-Organic Framework (MOF) Nanomaterials

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Abstract. In recent years, MOF has been widely studied as new material. Due to its structure's diversity, flexibility, and tunability, it is favoured by many scholars and has been used in many fields. However, due to the diversity of MOF types and the wide range of applications, there is a lack of systematic description of the application of MOF materials at present. This paper concluded several aspects of the application of MOF to close this loophole. In this paper, the preparation method including the gas-phase method, hydrothermal method, and liquid-phase epitaxy method of the MOF is introduced, then followed by the method of bringing metal nanoparticles into the prepared frame to make the doped MOF including the impregnation method and double solvent method, and then by adsorption, catalysis, and gas sensor, three aspects are briefly introduced MOF in these fields of application are introduced in these areas in different refining branch such as carbon monoxide adsorption, catalytic hydrogenation, and alkanes as nitric oxide gas sensor. Meanwhile, the challenges for this kind of material are long-term stability, heat resistance, and high cost. This paper is expected to summarize the application of MOF and hope it can bring more economic benefits and scientific value.

Keywords: Metal-organic framework, Nanomaterial, Gas sensor, Metal nanoparticle

1. Introduction

New materials are prerequisites that determine various fields from daily life to technological development and greatly impact chemistry and the chemical industry [1, 2]. MOFs are a new class of hybrid crystalline materials with porous crystalline structures composed of metal cations or metal cation aggregates linked by organic ligand molecules [1, 3]. And the inherent porosity is obtained by highly ordered 3-dimensional (3D) structures in which metal ions coordinated with the bridging organic nodes. The types of structural frameworks of MOFs are abundant and the most studied structures include the octahedral IRMOF series, the zeolite ZIF series, the octahedral nanopore cage-like PCN series, and the regular octahedral UIO series, etc. These structures contribute to crystals with ultra-high porosity and high thermal and chemical stability, endow the material with high absorption rates and provide active sites that allow for changes in the internal chemical environment [3]. Therefore, MOFs can be used for gas adsorption, storage, and release, and also for heterogeneous catalysis and gas sensitivity detection so MOFs have remarkable application prospects in many fields such as medical treatment, environmental protection, and drug synthesis [1].

Since the types of MOF framework structures are various but the preparation methods are not particularly complicated, there is a need to summarize the current preparation method with a high success rate, a simple procedure, and a wide range of usage as a reference. Most of the existing reviews lack a summary of the preparation method even though the experimental methods for the preparation and modification of MOF frameworks are well researched. In addition, because the fields of application of MOF are extremely broad and can be interconnected with a variety of disciplines, the review to summarize various applications in different fields enables to present the broad prospects of MOF materials and provide a remarkably comprehensive introduction. However, the existing reviews are limited to one application of the MOF materials and focus on the existing data of one property but do not explore the application potential. Therefore, this review aims to combine the preparation and modification method with the application to complement missing parts of existing reviews.

The review includes the formation and application of MOFs and summarizes the existing defects of MOF materials, and prospects for the future development of the system are presented. This review summarizes the current preparation methods which have a high success rate and wide usage, as well as the modification methods to improve the properties of MOF materials. Meanwhile, the review summarizes widely concerned applications of MOF materials which include the preparation of metal frameworks, the introduction of nanoparticles, and the application of gas adsorption, catalysis, and gas sensing. In addition to these general discussions, the limitations of the current approaches in MOF applications are also mentioned to identify possible solutions.

2. Preparation of MOF materials

2.1. Synthetic of MOF

2.1.1. Gas-phase method.

The gas-phase method is a method in which the gas phase is introduced into a reaction system that contains easily vaporized metal precursors as a substrate and then the gas phase is absorbed. MOF is obtained after heating and reduction of reducing gas [4]. The experimental conditions of this method are relatively simple, and it has little influence on the overall frame structure of MOF materials. However, the disadvantage is that the selection range of active metals is limited, as the organic precursors of active metals should be volatile. For MOF materials composed of some inert metals or rare earth elements, it cannot be prepared by this method. Maike Müller et al. [5] use [CpCuL] and $ZnEt_2$ as volatile precursors and precursor@MOF-5 are synthesized after gas-phase absorption. Under the condition of 200-220 °C, precursor@MOF-5 is converted to Cu@MOF-5 and ZnO@MOF-5 by hydrogen decomposition or photoassisted thermal decomposition. Leo D. Salmi et al. [6] use zinc acetate ($ZnAc_2$) and 1,4-benzene dicarboxylic acid (1,4-BDC) as the precursors, and MOF-5 thin film was prepared at 225-350 °C.

2.1.2. Hydrothermal method.

The hydrothermal method depends on the reaction in the critical condition of the solvent in the gas phase and liquid phase, with the reactants sealed in the reaction kettle where most of the reactants are dissolved in water under high temperature and high pressure. The hydrothermal method is characterized by simple operation, low cost, and the synthesis of nanocrystals with special morphology and excellent properties. Feng Chao et al. [7] used the hydrothermal method to synthesize a new Mn-based MOF $[Mn(Hpzca)_2]_n$ which has high specific capacitance and good cycle stability, with the ligand (H_2pzca = 1H-pyrazole-4-carboxylic acid). Sun Shuyang et al. [8] dissolved $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ in water, respectively, and at the hydrothermal condition of 120 °C Ni/Co mixed MOF with high electrochemical performance is synthesized.

2.1.3. Liquid-phase epitaxy method.

Liquid-phase epitaxy is a suitable method for the growth of surface-coordinated MOF films (SURMOFs) which is the layer-by-layer (LBL) growth method of MOF films by liquid phase epitaxy (LPE) on the substrate surface coordinates. This method can precisely control the thickness of the film and optimize the growth direction of the metal frame with the formation of a uniform surface [9]. The formation of surface ligands and layer-by-layer assembly growth of MOF films with the liquid-phase epitaxy generally depends on the alternate immersion of the two-dimensional or three-dimensional substrate in the target-introduced metal ions (or metal clusters) and organic ligand solutions. The substrate needs to be modified with easily coordinated functional groups (carboxyl groups, hydroxyl groups, etc.) in advance and needs to be immersed in the solvent (usually water, ethanol, methanol, etc.) after the formation of the films to remove the reactants that are not involved in the coordination on the surface.

Compared with other MOF framework formation methods, liquid phase epitaxy has the advantages of precise control of film thickness, extremely low surface roughness, controllability of MOF growth direction, and the ability to obtain new physicochemical properties with the uniform embedding of various functional guests in the layer-by-layer growth process [9, 10]. In 2015, Gu et al. [11] unprecedentedly developed the automatic liquid phase epitaxy method and studied the bandgap and energy band structure of HKUST-1 MOFs in detail. Since the program can precisely control the relevant parameters such as the wetting time which ensures consistency, the obtained SURMOF surface topography has high flatness and can be mass-produced. In 2019, Esther [12] et al. used the layer-by-layer liquid phase epitaxy method to form and characterize SURMOF on Au substrate which proves that the method is universal.

2.2. Doping of nanoparticles to the metal framework

2.2.1. Impregnation method.

Impregnation is a traditional method for loading catalytic species into porous materials [13] and is now widely used for the modification of MOF frameworks. The introduction of the target particles by the method depends on the capillary action and diffusion phenomena. The particles sucked into the pores due to capillary action will diffuse in the pores through the warming of the evaporating solvent, which is the mixture of the loading solution and the mesoporous material, and eventually stay inside the pores. The MOF modification is usually accomplished by sonicating the MOF framework with the solution and heating it to evaporate the solvent after the introduced species is configured into a solution.

The main advantages of the traditional impregnation method include easy control of the content of metal ions in the carrier by concentration and simple experimental operations. However, there exist the problems of low particle introduction efficiency and requirements of high concentration or repeated impregnation to achieve high loading [13]. In 2021, Quentin Touloumet et al. [14] prepared aluminum fumarate MOF composites by impregnation method. The composites showed high thermal water absorption and hydration kinetics of trifluorocyanate up to 2.7. In 2015, Hu Zhou et al. [15] first used the impregnation method to produce Pt-doped MOF/graphene oxide composites to increase the hydrogen storage performance and the composite exhibited a significant enhancement of hydrogen uptake attributed to the spillover mechanism.

2.2.2. Double solvent method.

The double solvent method is a new method based on the impregnation method to introduce metal ions into porous MOF frameworks. It is based on the different solubility of metal salts in two solvents to complete the introduction of metal ions without leaving ions on the surface. The usual operations include the dissolution of the metal salt with an aqueous phase and preparation of the hydrophobic solvent mixed with a suspension of the organic solvent and the MOF precursor. The aqueous phase metal salt solution will be added dropwise to the MOF carrier mixture when stirring. Due to the hydrophilicity of MOF, the metal salt solution can be absorbed into the voids completely according to the capillary force, thus completing the introduction of metal ions [16].

Compared with the impregnation method, the double solvent method can introduce metal ions into MOF nanopores without aggregation on the surface, which increases the introduction rate of metal ions and reduces the influence of surface pollutants on the catalytic reaction [16-18]. In 2013, Mahendra Yadav and Qiang Xu [19] used the double solvent method to immobilize highly dispersed metal nanoparticles (including H_2PtCl_6, H_2PdCl_4, $HAuCl_4$, or $RhCl_3$) in the pores of metal-organic framework (MOF) MIL-101 to avoid metal NPs (formed by the metal precursor nucleation) aggregated on the outer surface of the MIL-101 framework, and X-ray diffraction (PXRD) was used to demonstrate that the integrity of the MIL-101 framework was maintained and the metal ions were successfully introduced. In 2015, Yong Liu et al. [16] prepared ultrafine MNP/MIL-101(Cr) catalysts by the double solvent method and incorporated ultrafine Au, Ag, Pd, and AuPd bimetallic nanoparticles into the mesopores of MIL-101(Cr) without MNPs deposited on the outer surface of the host framework. Meanwhile, the catalyst exhibited excellent catalytic performance.

3. Application

3.1. Adsorption of gas

3.1.1. Adsorption of CO_2.

Global warming is a serious issue for environmental protection, and the main influencing factor is the emission of CO_2. MOF, as a porous material with high heat resistance, is suitable for adsorbing the waste gas from the factory, shown in figure 1 [20]. Andrew et al. tested and measured the CO_2 adsorption capacity of several structures of MOF, the capacity ranges from 345 m^2/g (MOF-2) to 4508 m^2/g (MOF-177) [20].

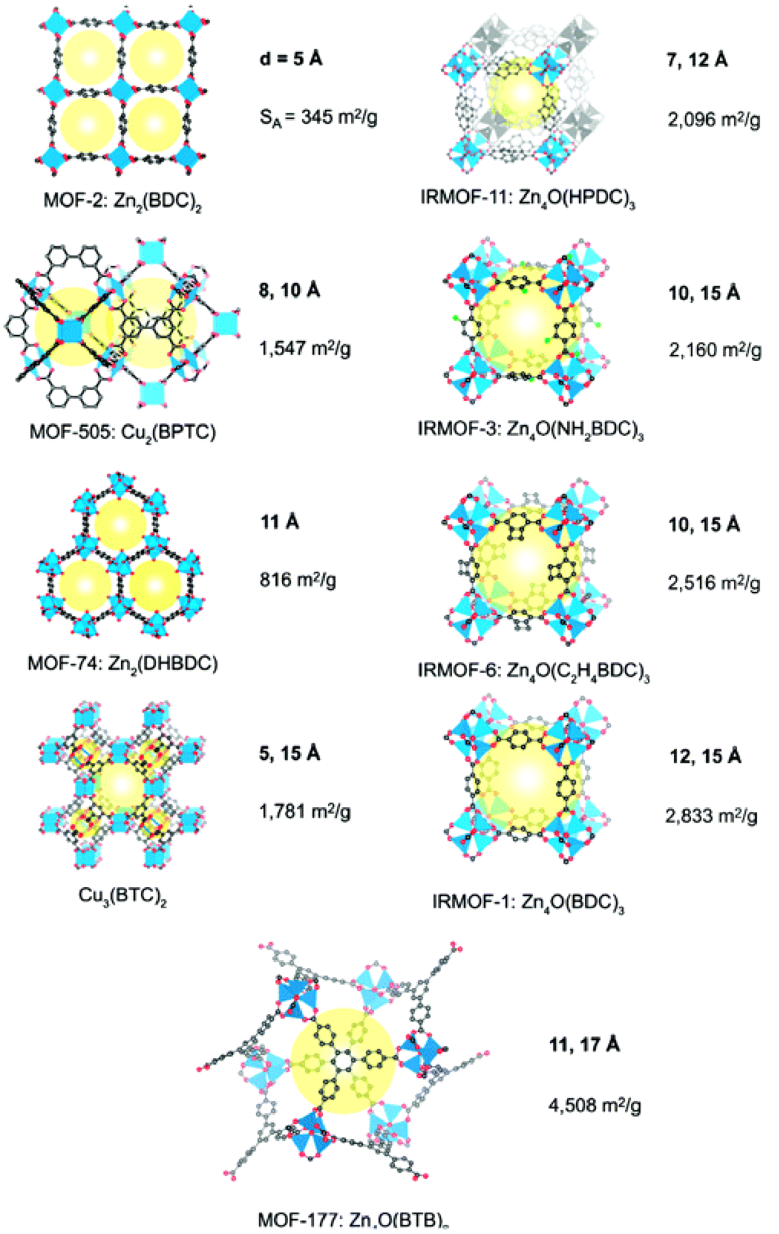

Figure 1. CO_2 capacity of different structures of crystallization [20].

Despite the ordinary MOF, the benchmark technology was used to solve the problems of difficult installation, high cost, and difficult maintenance. Hu and colleagues developed a new method (RS) to grow the MOF framework on the alumina layer without defects [21]. Recently, the study of reusing the CO_2 in the MOF also got attention. Hu et al. [22] had synthesized ZIF-8 to convert the CO_2 into cyclic carbonate, it can be recycled up to 5 times and has various morphology. That is to capture the carbon dioxide and convert it to the desired substance, which will have a promising future.

3.1.2. Adsorption of H_2.

Hydrogen is considered the fuel of the future. It has high energy, low cost, and clean product [23]. MOF can be the material that stores hydrogen stably and effectively to its adjustable structure. It has been researched a lot to improve its hydrogen capacity. Butova et al. [24] put forward a method that can synthesize MOF-801 quickly and tested the efficiency of hydrogen storage. The capacity can be reached up to 1.3 wt% (70 mmHg). To improve the capacity, developments through different aspects must be done. Researchers adjusted the morphology and improved the capacity to 30.5 g/L [25]. However, it is still not enough for the capacity to apply to the business market, and hydrogen storage at room temperature is also of vital importance for further application.

3.1.3. Adsorption of O_2.

Oxygen storage is also a subject that needs to be studied. Convenient, fast, and safe oxygen storage can facilitate the transportation of oxygen. Oxygen storage can also be used in aerospace, medical and other industries. Compared with other porous materials, the uniform pore structure and the adjustability of MOF are favored by researchers. Wilmer et al. firstly set up a database to select MOF used for different applications, and examine their capacity and potential [26]. HKUST-1 and NU-125 were established as the structure with the most potential. Dr. Jared and his colleague tested these kinds of MOF and presents the excess oxygen isotherm to research the capacity of oxygen. It can be reached at more than 10 mol/kg, which is promising.

3.2. Catalyst

The transition metal can be embedded in the MOF due to its special structure. For organic reactions, some reaction conditions are harsh, and the speed can be slow. To solve this problem, researchers have used the introduction of guiding groups or the preparation of specific substrates to solve this problem. However, there are still problems such as the orientation group is not easy to leave, so heterogeneous catalysts such as MOF containing transition metals can solve this problem well. And few reactions with MOF catalyzed will be illustrated.

3.2.1. Reduction.

Firstly, the hydrogenation of olefin can be catalyzed by transition metals and is one of the widely used reactions, so the use of MOF to catalyze such reactions has attracted attention. Yuan et al. introduced Zn-MOF-74@(Pd@Fe_2O_3) [27] to catalyze hydrogenation for alkene and phenylacetylene. It shows excellent pore structure and catalytic performance. Compared to normal transition metal catalysts, MOF can realize higher selectivity and with a transform efficiency of up to 96 %. Kazuki [28] and his colleague synthesized the catalyst Ni-MOF-74-300 with high activity and selectivity were obtained by pyrolysis at 300 °C which shows a significant effect on hydrogenation of 1-octane. From figure 2, after heat treatment, the MOF showed considerable activity. But up to now, such catalysts still have the problem of low recovery times and low activity after recovery

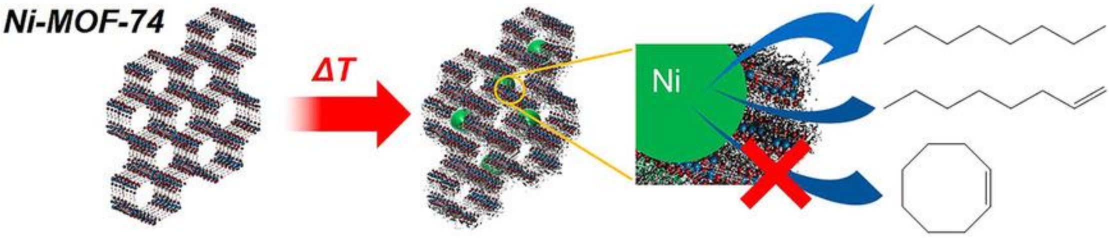

Figure 2. Heat treatment of Ni-MOF-74 [28].

3.2.2. Oxidation.

Oxidation of olefin plays an important role in molecular modification. One of the things worth mentioning is the oxidation of carbon monoxide. Carbon monoxide causes great harm to the human body in automobile exhaust and daily life. If it can be oxidized into carbon dioxide for secondary treatment, it will be of great significance. Yazdi et al. [29] used the spray-drying continuous-flow method to disperse Hybrid core-shell Au/CeO_2 in UiO-66. It presents 100 % CO conversion at 180 °C. Metals other than gold can also be used to catalyze such reactions, which are cheaper and more readily available than the previous catalyst. Lin [30] reported Pd/Ce-MOF which allows converting CO to CO_2 100 % at 180 °C for 8 hours.

3.3. Gas Sensor

3.3.1. Nitrogen oxides detection.

Due to the over-reliance of technology on chemical energy sources such as oil and natural gas, the content of nitrogen oxides (mainly including nitrogen monoxide and nitrogen dioxide) in cities is relatively high which causes acid rain and photochemical pollution. To monitor the concentration of NO and NO_2, the fabrication of a highly sensitive and specific gas sensor for nitrogen oxides is popular research. Compared with traditional metal oxides, the organic gas sensors construct the π-conjugated system, and the molecular interaction at the interface between the analytes and the active layer can improve the gas selectivity and sensitivity [31, 32]. In 2022, Eun Hye Kwon et al. [33] have combined CNFs and Z67 nanoparticles to form the Z67@CNF hybrid nanofibers which depend on a simple growth of Z67 particles on CNFs with cobalt-[tetrakis(4-carboxyphenyl)porphyrin] (Co-TCPP), and the relative process is shown in figure 3. The research shows that the hole mobility of the Z67@CNFs is 70 % larger than that of the Z67-only mixed in the P3HT device, which can provide a stable charge transfer with a high probability [33]. Additionally, the improvement in NO_2-sensing performance of the composite device made of Z67@CNF/P3HT is 70 % compared with the pristine P3HT device and 21 % compared with the Z67/P3HT device because of the better dispersion and the smaller grain size with a high ratio of surface and volume [33].

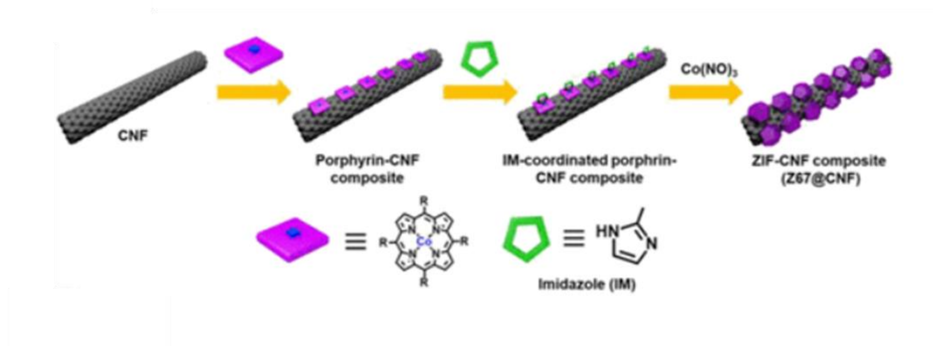

Figure 3. ZIF–CNF hybrid material synthesis procedure [33]

In 2022, Yueying Zhang et al. [34] have first developed the mixed-potential type MPSE NO sensor working at room temperature and enhanced its sensitivity to NO since the porous structure of Ni-MOF used in the sensor contributes to gas adsorption and rapid gas transport with the Ni unsaturated sites which offers a catalytic activity to the electrochemical reaction of NO. The research shows that the detection of the sensor based on Ni-MOF at 25 °C and 60 % RH is as low as 20 ppb NO which represents the high gas sensitivity at room temperature. Moreover, with the doping of MWCNT, the MPSE sensor's response to 500 ppb NO at 25 °C with 60 % RH has a three time increase from -8 mV to -34 mV.

3.3.2. Carbon monoxide detection.

As a colourless and highly flammable gas, carbon monoxide (CO) is mainly produced by petroleum refining, fossil fuel combustion, and automobile exhaust. Since excessive inhalation of carbon monoxide can cause poisoning, gas sensors need to monitor it at room temperature. MOF is a system doped with metal oxides and organics, in which the metal oxide structure can react with reducing gases (such as H_2, CO, etc.). Meanwhile, the formation of heterojunctions between organics and metal oxides can increase the concentration of charge carriers thus increasing the gas sensitivity of the complex [35]. In 2018, Yanqing Lv et al. [36] have used Ni-MOF-74 with a resonant microcantilever sensor to realize ultra-sensitive detection of CO. The sensor response is always 22.6 ± 0.3 Hz, and the detection repeatability is satisfactory. Additionally, the sensor shows a Langmuir-type response to CO within the concentration range of 10 ppb-2.6 ppm with good selectivity, repeatability, and long-term stability.

In 2020, Zhimin Yang et al. [37] synthesized MOFs-derived SnO_2 nanoparticles-decorated $MoSe_2$ nanoflowers with thermal decomposition for the development of highly sensitive gas sensors, and the preparation process is shown in figure 4. The research shows that the synthesized complex has a higher response value to CO and the recovery time is 80 % compared with the gas sensor made of pure SnO_2 which means that the MOF system has a faster detection rate for CO. Meanwhile, for each run, the resistance can fully recover its initial state showing a good reproducibility and exhibit excellent CO selectivity under other gas interferences.

Figure 4. Schematic of the preparation process for $SnO_2/MoSe_2$ composite [37].

3.3.3. Ethanol detection.

Ethanol is an organic volatile gas, and the monitoring of its content is very important in the fields of food processing and wastewater treatment. MOF as a gas sensor has a high sensitivity to alcohol volatiles with a mechanism similar to reducing gas. Moreover, the high porosity of MOFs contributes to the strong interaction with VOCs gases, resulting in easily measurable responses to different physicochemical parameters [38]. In 2014, Yinyun Lü et al. [39] synthesized porous Co_3O_4 concave nanocubes with a high specific surface area by MOF-template. They formed a co-based metal-organic framework (ZIF-67) as a template and synthesised production at different calcination temperatures which are 300 °C, 350 °C and 400 °C to figure out the effect of calcination temperature on the morphology and the sensing characteristics of ethanol gas. The research shows remarkable performances such as good selectivity to ethanol with high sensitivity, low detection limit (lower than 10 ppm) and rapid response and recovery (within 10 s). In 2022, A. JaganMohan Reddy et al. [40] have synthesized bimetallic MOFs with Zinc and Nickel by the solvothermal method and the synthesized MOFs are accentuated as good chemical gas sensors agents at room temperature towards ammonia, formaldehyde, and ethanol. At 50 ppm concentration of alcohol, response times are 28 s and 45 s for ZnNi(NA)-1:1 and ZnNi(NA)-1:3, respectively.

4. Outlook and Challenges

In recent years, the research on MOF materials is quite popular. MOF materials are widely used in gas adsorption, catalysis, biomedicine, and sensors, due to their unique pore structure and high specific surface area. However, there are still challenges in the production and application of MOF materials. Stability is the main factor affecting the application of MOF in the production of commercial chemicals, but MOF catalyst decomposes above 400 °C while traditional nanoparticles can operate at higher temperatures. Low stability limits the scope of use of MOF materials for example the anaerobic dehydrogenation of ethane or propane usually reacts at a high temperature which is thus unsuitable with MOF catalyst. Furthermore, the long-term stability of MOF may bring out a problem in the application of gas adsorption and sensor. MOF materials are required to work persistently for months to years but even the most stable MOF cannot endure long-term chemical corrosion and mechanical wear. In the area of biomedicine, studies on the stability and long-term toxicity of MOF materials in the biological environment are not mature. In addition, the high preparation costs of MOFs are also a barrier to industrial production since a small amount of MOF can only be synthesized in the laboratory at a time.

5. Conclusion

Over the past decade, MOF materials have attracted much attention for their excellent properties and wide range of applications, and the expanded research on MOF materials opens the door for new opportunities. In this overview, part of the preparation technology and application of MOF materials are summarized. In the aspect of preparation, there are many methods to synthesize MOF materials such as the gas-phase method, hydrothermal method, and liquid-phase epitaxy method which are three methods introduced in this overview. Different properties of MOF materials are obtained by different preparation methods to improve the applicability of materials. In addition, when introducing nanoparticles, there are generally two approaches that are the impregnation method and the double solvent method. Gas adsorption, catalysis, and gas sensors are applications introduced in this paper. The performance requirements of different applications are satisfied by changing the porosity and nanoparticles of MOF materials. Especially in selective adsorption or separation, MOF materials show outstanding performance. Furthermore, to meet specific requirements, MOF materials can be combined with the appropriate materials to improve their functionality, porosity, ease of bonding, and thermal/magnetic/electrical properties. Therefore, MOF materials will still have high economic benefits and scientific research value in the future.

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