Applications of Metal-Organic Framework Materials

Wenkui Chai1, †, Youhong Shen2, †, Jiahe Wang3, †, Geling Zhang4, *, †

1CATS College Cambridge 1 High Street, Chesterton, Cambridge CB4 1NQ, UK.
2Dulwich International High School, Suzhou, 215000, China.
3International Department of the High School Affiliated to Shaanxi Normal University, Xi’an, 710000, China.
4Guangdong Country Garden School, Guangdong, 528000, China.

*guanghua.ren@gecademy.cn
†These authors contributed equally.

Abstract-Metal-organic framework (MOFs) is a new group of porous crystal materials with ultra-high porosity. Its extraordinary surface area, fine and adjustable void surface characteristics and potential industrial-scale scalability make it an attractive target for further research. By searching for the data, we have integrated and summarized the important applications of MOF materials in many fields, such as catalysis, and its enclosed single metal or bimetallic ions provide efficient and synergistic catalytic ability; In adsorption, the special ionic liquid absorbent overcomes the shortcomings of other materials, greatly improves the chemical stability, reduces the corrosivity, and makes the process more environment-friendly and controllable. However, there are still many challenges, and the high cost and complicated preparation process are urgent problems to be solved at present. We need to have a deeper understanding of the growth mechanism of MOF films, improve their quality and thermoelectric stability, and combine them into low-cost polymer films through more reliable theoretical models to eliminate the defects of MOF materials as much as possible. We will continue to pay attention to the development of MOF materials, summarize the advantages of MOF materials, find out the shortcomings, and propose solutions to provide ideas and references for future research.

1. Introduction
Eighty years ago, few people in the world had heard of plastic, but in 1939, nylon, a kind of plastic, became a household name nearly one year after its debut at the New York World Expo. Nylon has been all the rage since the stockings industry started, and then it started to innovate the application of plastics in various fields. Clothing, household goods, electronic products, the pharmaceutical industry and other fields have been impacted by plastics unprecedentedly. After more than ten years' development, plastic has become a necessity and has been defined as the material of the 20th century. But now, in the 21st century, earth-shaking changes are taking place in the field of materials. New material is following the pace of plastics, and it is expected to become the decisive material in the 21st century in the future, that is, metal-organic framework materials (MOFs).

Plastic has become so popular because of its versatility, which consists of long and repeated monomers. Therefore, this polymer's physical and chemical characteristics, such as size, hardness, elasticity, and conductivity, can be determined by simply changing its monomers directly. Like plastic, MOF is a multifunctional application material, and it is also composed of repeating units with very small
structures. It is connected by organic molecules to form a micron-sized high-rise structure, which can free divergence in all directions and forms special crystals through the rigid, uniform and precise atomic arrangement. This unique uniform structure enables scientists to study, design and process MOF materials from a new perspective. By accurately locating the position of each atom in the polymer and using modern technology, they can quickly simulate different crystal structures by modeling before laboratory synthesis to meet the different requirements of MOF materials in different applications.

So far, the research and application of MOF materials are still relatively few. Therefore, this paper introduces in detail the characteristics, main application fields and working mechanism of MOFs materials in various fields and puts forward what it should be.

2. Application of MOF materials

2.1 Catalysis

In recent years, metal organic framework materials (MOFs) have shown potential application prospects in many fields, aroused widespread research interest and achieved rapid development. Our research group mainly focuses on the following two aspects to carry out research and has obtained some preliminary research results.

Design, synthesis and pore tuning/modification of high-porosity stable MOFs. By applying a simple hydrophobic PDMS coating to the classic water/moisture unstable various MOFs, the water/moisture stability of these MOFs is greatly enhanced; more importantly, this hydrophobicity The thin layer of PDMS will not affect the intrinsic pore characteristics of MOFs and the use of catalytic sites [1, 2].

The synthesis of nanocomposites based on MOF pore confinement and MOFs as hard templates and their application in catalysis. Based on the pore confinement effect of MOFs, through a rational synthesis method, metal precursors are introduced into highly pore stable MOFs and reduced to obtain monometallic or bimetallic nanoparticles confined in the pores/cages of MOFs and provide high-efficiency/cooperative catalytic performance. It is particularly important that our host-guest synergy is based on the catalytic behavior of MOF and the catalytic performance of confined metal nanoparticles and the synergy of catalytic activity and selectivity between bimetallic nanoparticles together achieve more in one pot. Based on the high order and porosity characteristics of MOFs, the doped porous carbon nanocomposite is obtained by decomposing it, which exhibits excellent catalytic reaction performance in heterogeneous catalysis and fuel cell oxygen reduction reactions.

CO oxidation has generated considerable interest because of its importance in terms of emission control and its relative simplicity as an ideal model reaction in heterogeneous catalysis.

Noble metal nanoparticles (NPs) dispersed on solid support could be active catalysts for CO oxidation. However, it is well known that these metal particles tend to agglomerate and grow, which decreases the overall active surface area and causes the loss of catalytic activity. Metal-organic frameworks (MOFs), as a new class of functional porous materials, have been shown to be suitable for embedding and supporting metal NPs similar to zeolites. It is expected that the ordered crystalline structures of MOFs with the large and tunable cavity, high surface area, and controllable porosity could confine the migration and aggregation of metal NPs. Gao et al. [3] found that Pd/MOF-5 was an active catalyst for the Sonogashira coupling reaction between aryl iodides and terminal acetylenes without the assistance of ligand and copper [4, 5, 6]. Ishida et al. reported Au clusters supported onto several kinds of porous coordination polymers (PCPs), including MOF-5 by solid grinding, and they investigated their catalytic properties for the liquid phase alcohol oxidation with molecular oxygen. Metal organic framework MIL-101(Cr) was employed to support preparing Au NPs catalysts by liquid-phase synthesis method, and Au/MIL-101(Cr) catalyst exhibited high catalytic activities in the liquid phase aerobic alcohol oxidation. However, most of the reported works with MOFs based catalysts are for catalytic applications in the liquid phase. There are few reports about gaseous reactions over MOFs supported catalysts. Jiang et al. pioneeringly reported the preparation of Au NPs supported on ZIF-8 (ZIF: zeolite imidazolate frameworks) catalysts by solid grinding method and used them as the catalysts for CO oxidation. The catalyst gave the medium activity for CO oxidation, and a full CO conversion was
obtained at 200 °C for 5.0% (w) Au/ZIF-8.

Herein, we report the uniformly deposited Pd NPs on a microporous aluminium terephthalate MIL-53 to obtain a series of heterogeneous catalytic composite materials. In addition, the catalytic activities and reused stability of the as-prepared Pd/MIL-53(Al) catalyst for CO oxidation were detailly investigated.

The silver-functionalized UiO-66 MOF [7] is prepared by a simple one-pot solvothermal reaction and characterized by X-ray diffraction, nitrogen adsorption-desorption, electron microscopy, X-ray spectroscopy, and thermogravimetric analysis. The functionalized MOF prepared by the test removes radioactive iodine from water. Furthermore, due to the excellent affinity of Ag particles and iodide, an excellent extraction capacity of 131I (~1 MBq/g) is obtained. In practical applications, the obtained porous UiO-66-SO\textsubscript{3}H@Ag material is combined into a 3D printing device using polyvinylidene fluoride as a binder by a simple method. The developed UiO-66-SO\textsubscript{3}H@Ag 3D device shows the high efficiency of 131I removal, excellent reusability and good performance of extracting 131I from sewage and hospital waste samples. In all cases, more than 90% recovery is obtained rate.

Nowadays, the actual application of organometallic frameworks is also used for coating other materials most of the time, such as drug transportation, coating metal elements or coating catalysts—because of the use of MOF materials. As a result, the surface area is increased. Larger, fewer catalysts can catalyze more reactants, and the reaction rate will also increase. Luo’s team [8] used ZIF-8/Pt/SiO\textsubscript{2} catalyst was prepared by combining atomic layer deposition technology and vapor phase conversion method. The Pt metal nanoparticles were deposited on SiO\textsubscript{2} nanowires, and the ZIF-8 film covers Pt and SiO\textsubscript{2} nanowires to form a sandwich structure. The structure of the catalysts was characterized by XRD, TEM, BET, IC-MS, XPS and CO-DRIFT, and the function of ZIF-8 film was studied by using the semi-hydrogenation of 1-heptyne as the probe reaction. The Pt particles are highly dispersed on the SiO\textsubscript{2} nanowires before and after the ZIF-8 overcoating, and the ZIF-8 film coats continuously on the entire catalyst with high conformity. The ZIF-8 film induces an electron density increase of Pt surface and increases the olefin selectivity from 14% to 70% in the 1-heptane hydrogenation reaction. A thinner ZIF-8 film increases the catalytic activity and cannot change the selectivity of olefin.

2.2. Adsorption

2.2.1. For Gas
The adsorption of CO\textsubscript{2} by traditional liquid alkanolamine adsorbent can not meet the requirements of green development in industrial applications. NH\textsubscript{2}-\beta-CD-MOF [9] was first constructed by an American company by amino-functionalizing \beta-CD, the cheapest, readily available and biocompatible form. The selective adsorption of NH2-\beta-CD-MOF on CO\textsubscript{2}/N\textsubscript{2}(947.52) is also better than that of existing materials. The adsorption mechanism of CO\textsubscript{2} was analyzed by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy.

The adsorption capacity of amino-functionalized \beta-cyclodextrin-MOF (NH\textsubscript{2}-\beta-CD-MOF) can reach 12.3 cm\textsuperscript{3}/g, which is 10 times that of \beta-CD. It is noteworthy that NH\textsubscript{2}-\beta-CD-MOF has a good adsorption selectivity for CO\textsubscript{2}/N\textsubscript{2} compared to reported materials (947.52). In addition, in practical application, the ideal MOF adsorption material should still have good adsorption capacity and selectivity in the presence of water. The introduction of the amino group as a polar functional group can improve the selective adsorption of MOF and show that the amino group can competitively bind foreign water molecules and improve the water stability of NH2-\beta-CD-MOF. NH\textsubscript{2}-\beta-CD-MOF is not only cheap, green and non-toxic but also can be recovered by secondary ultrasound. After repeated recycling tests, NH\textsubscript{2}-\beta-CD-MOF has a high carbon dioxide adsorption capacity.

2.2.2. For Liquid
Researchers at Lawrence Livermore National Laboratory have developed a cleaner, more stable and more efficient way to capture carbon dioxide using ionic liquids as carbon dioxide absorbents.

The current carbon capture technology mainly uses the chemical adsorption method. Carbon dioxide
reacts with amines, which combine at low temperatures and separate at high temperatures. It is generally possible to separate the carbon dioxide from the waste gas containing carbon dioxide by passing it through an amine solution and then releasing the carbon dioxide by heating it in an appropriate place [10]. Monoethanolamide is currently used as a CO₂ absorber in a few commercial carbon capture coal-fired power plants. But monoethanolamides are corrosive, require large equipment, and are only effective at mild to moderate CO₂ pressures. Therefore, its cost and efficiency are not very ideal.

Amities Medi of the lab has been working to find new carbon dioxide absorbers. He tested several ionic liquids that can effectively dissolve carbon dioxide and got a lot of useful data. Unlike typical organic solvents, ionic liquids generally do not become vapors, so they are not prone to harmful gases and are easy to use. Medi found that using ionic liquids as CO₂ absorbers could overcome many of the drawbacks of monoethanolamides, making them cleaner and easier to use than the methods currently used. Its chemical stability is good, low corrosion, vapor pressure is almost zero, can be made into a film. Ionic liquids are of a wide variety, and there are many ions to choose from with potentially high carbon dioxide solubility.

2.3. Gas Separation

The separation of gas molecules with similar physical and chemical properties is a very important process closely associated with the manufacture of fuels, polymers and plastics. In the gas separation market and in small-scale enterprises, membrane separations are the most popular due to their low cost and the facile large-scale production. Furthermore, the emergence of metal-organic frameworks is ideal adsorbents for gas separation due to their large surface area, ultra-high porosity and modularity, and acceptable thermal stability. In existing studies, MOF membranes for gas separation can be divided into two main categories, pure MOF membranes and mixed matrix membranes (MMMs) [11, 12].

2.3.1. Pure MOF Films

Compared to conventional polymer and molecular sieve membranes, MOF film materials have advantages such as structural diversity, ultra-high porosity, and high orientation [13]. Metal-organic framework films are synthesized on inorganic or polymer supports by seeded secondary growth or in-situ growth synthesis methods. The following MOFs are commonly used to construct MOF films: IRMOF-1, Cu-BTC and ZIFs. In 2008, Lai and co-workers [14] first reported the in situ solvothermal syntheses of continuous, well-intergrown MOF-5 membranes prepared on the porous α-alumina substrate. Then they used MOF-5 membranes for gas separation research. The discovery that the diffusion of simple gas molecules through this material follows the Knudsen diffusion behavior has opened up a whole new field of research into the use of MOF membranes for gas separation. Zeolitic imidazolate frameworks (ZIFs), a subfamily of microporous MOFs based on transition metals (Co, Fe, Zn, Cu) and imidazolates as ligands, became one of the most studied MOFs in the field of separation membranes due to the excellent stability and tunable pore size. The in-situ synthesis method is also applied to the ZIF-8. Caro and co-workers [15] prepared sodalite (SOD) topology ZIF-8 membranes with molecular sieving performance by microwave-assisted synthesis, which performs high thermal stability. They also succeed in the preparation of ZIF-22 membrane on the 3-aminopropytriethoxysilane (APTES) -modified TiO₂ by using in situ growth method, shown in Figure 1, which represents the selectivity of H₂/CO₂, H₂/O₂, H₂/N₂, and H₂/CH₄ are 7.2, 6.4, 6.4 and 5.2 respectively.
Fig. 1 Preparation of a ZIF-22 membrane by using 3-aminopropyl-triethoxysilane (APTES) as the covalent linker between the ZIF-22 membrane and the titania support [15].

2.3.2. Mixed Matrix Membranes

Compared to pure MOF membranes, mixed matrix membranes (MMMs) with a polymer matrix and MOF as filler have the advantages of lower cost, easy processing, good mechanical strength, better selectivity and permeability, which has a good prospect for commercial application.

HKUST-1 (Hong Kong University of Science and Technology Cu3(BTC)2) [16, 17] is a metal organic framework (MOF), which exhibits a cubic, paddle-wheel structure and is composed of copper metal sites and triangular 1,3,5-benzenetricarboxylate organic linkers. After an activation process, these water molecules can be removed, and the coordination site at the metal atoms is left unoccupied. Hence HKUST-1 shows high gas adsorption capacity. A variety of metal cations can be used to prepare the structure of HKUST-1 (M = Cr, Fe, Zn, Mo), and with the invention of M2(dobdc), this suggests that metals are an important variable to consider when tuning material properties. In the case of metal ions possessing exposed coordination sites, adsorption can vary depending on the charge density on the metal coordination site [18].

Another well-studied family of MOFs bearing exposed metal cation sites is MOF-74 (Mg(DOT)). Because of its high density of coordinatively unsaturated metal sites, it has high CO2 adsorption capacities at 1 bar and 296 K. In experiments, Mg-MOF-74 shows an efficient separation of CO2 (20%) from CH4 (80%), which reflects attractive performance from a kinetic and thermodynamic point of view. In fact, the value of Mg2 (dobdc) represents the highest low-pressure gravimetric and volumetric adsorption capacity of the metal-organic framework for CO2. This shows the great potential of metal-organic framework materials in the field of gas separation.

3. Outlook

Pure MOF films have good thermal and chemical stability and are suitable for the physically and chemically complex environments of industrial applications, but the high cost, the complexity of the preparation process and processing difficulties limit their further application. In addition, the film growth mechanism needs to be studied in more depth, and the quality and thermoelectric properties of the films need to be further improved.

By combining the advantages of lower cost polymeric membranes, mature processing technology and uniform pore size of inorganic porous materials, mixed matrix membranes effectively overcome the inherent disadvantages of poor mechanical strength and difficulties in large-scale preparation of inorganic membranes, ultimately effectively improving the mechanical strength of the resulting films. At the same time, mixed matrix membranes require the use of only a very small amount of inorganic materials.
porous material compared to inorganic crystalline membranes, thereby substantially reducing the cost of separation membranes. However, there is an inherent problem of poor filler-substrate interfacial compatibility, which leads to defects in the MMMs and a reduction in selectivity. Therefore, more effective interfacial design strategies and more reliable theoretical models are needed to eliminate defects in membrane materials as far as possible.

4. Conclusion
As a new type of material, metal-organic framework (MOF) materials have good prospects for development and application in various fields such as the energy industry and drug delivery because of the characteristics such as high specific surface area, ultra-high porosity, as well as and high structural tunability. The research on MOFs synthesis, design and application has been discussed in depth. This review discusses the practical applications of MOF materials in catalysis, adsorption and gas separation, including porous carbon nanocomposites, amino-functionalized β-cyclodextrin-MOF and mixed matrix membranes, all of which perform well in their respective fields. However, there are still many challenges to overcome, such as high costs, complex preparation processes and processing difficulties, limiting the practical applications of MOF materials in production, leaving much room for the development of MOFs. Therefore, in the future, there is a need to rationalize the preparation methods to obtain higher performance, more economical and easier to fabricate MOF materials, and to investigate the influence of preparation methods on the performance of MOF materials, so that MOFs can be put into quantitative production for industrial applications.

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