



## Review

## Metal–organic framework-derived porous materials for catalysis

Yu-Zhen Chen<sup>a,b,1</sup>, Rui Zhang<sup>a,1</sup>, Long Jiao<sup>a</sup>, Hai-Long Jiang<sup>a,\*</sup><sup>a</sup> Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China<sup>b</sup> College of Chemistry and Chemical Engineering, Qingdao University, Qingdao, Shandong 266071, PR China

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## ABSTRACT

Metal–organic frameworks (MOFs), constructed by metal ions/clusters and organic linkers, featuring crystalline porous structures, have been intensively employed as templates/precursors for the synthesis of diverse porous materials including porous carbons, metal-based compounds (such as metal oxides/carbides/phosphides) and their composites. The large surface area, high porosity and excellent tailorability of MOFs can be well inherited to their derivatives, making MOF-derived porous materials very promising for catalytic applications. Herein, we systematically summarize the versatile synthetic strategies to fabricate MOF-derived porous materials and give an overview on their recent progress on organic heterogeneous catalysis, photocatalysis and electrocatalysis. Finally, the challenges and prospects related to MOF-derived porous materials for catalysis are also discussed.

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**Abbreviations:** BDC, 1,4-benzenedicarboxylate; BTC, benzenetricarboxylate; NDC, 1,4-naphthalenedicarboxylate; TPT, 2,4,6-tris(4-pyridyl)-1,3,5-triazine; MeIm, 2-methylimidazole; DOBDC, 2,5-dihydroxyterephthalate; TCPP, tetrakis(4-carboxyphenyl)porphyrin; H<sub>2</sub>bpydc, 2,2'-bipyridine-5,5'-dicarboxylic acid; Ted, triethylenediamine; FA, fumaric acid; MOF-5, Zn<sub>4</sub>O(BDC)<sub>3</sub>; MOF-253, Al(OH)(bpydc); HKUST-1, Cu<sub>3</sub>(BTC)<sub>2</sub>; NENU-5, [Cu<sub>2</sub>(BTC)<sub>4/3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>6</sub>[H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>]; ZIF-8, Zn(MeIm)<sub>2</sub>; ZIF-67, Co(MeIm)<sub>2</sub>; Co<sup>II</sup>MOF, Co<sub>9</sub>(btc)<sub>6</sub>(tpt)<sub>2</sub>(H<sub>2</sub>O)<sub>15</sub>; UiO-66-NH<sub>2</sub>, Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC-NH<sub>2</sub>)<sub>6</sub>; PCN-224, Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(TCPP)<sub>2</sub>; PCN-224(Zn), Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(Zn-TCPP)<sub>2</sub>; M-MOF-74, M<sub>2</sub>(dobdc)(H<sub>2</sub>O)<sub>2</sub>·8H<sub>2</sub>O M = Ni or Co; MIL-53, [M(OH)(BDC)]<sub>n</sub>, M = Al or Fe; Fe-MIL-88A, Fe<sub>3</sub>O(FA)<sub>3</sub>·(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>); Fe-MIL-88B, Fe<sub>3</sub>O(BDC)<sub>3</sub>·(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>); MIL-88B-NH<sub>2</sub>, Fe<sub>3</sub>O(H<sub>2</sub>N-BDC)<sub>3</sub>; Fe-MIL-101, [Fe<sub>3</sub>F(H<sub>2</sub>O)<sub>2</sub>O(BDC)<sub>3</sub>]<sub>n</sub>H<sub>2</sub>O, n ~ 25; Ti-MIL-125, Ti<sub>8</sub>O<sub>8</sub>(OH)<sub>4</sub>(BDC)<sub>6</sub>; Ni-MOF, Ni<sub>3</sub>(BTC)<sub>2</sub>·12H<sub>2</sub>O; Co-PBA, Co<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>; MAF-6, RHO-[Zn(eim)<sub>2</sub>] (Heim = 2-ethylimidazole); Al-PCP, Al(OH)(1,4-NDC)·2H<sub>2</sub>O; F-T synthesis, Fischer–Tropsch synthesis; FTY, mol of CO converted to hydrocarbons per gram of Fe per second; QD, quantum dot; PBA, Prussian blue analog (PBA); NF, nickel foam; GO, graphene oxide; rGO/rgo, reduced graphene oxide; NPs, nano particles; NPC, N-doped porous carbon; M, metal; MO, metal oxide; MC, metal carbide; MS, metal sulfide; MP, metal phosphide; TOF, turnover frequency; ORR, oxygen reduction reaction; OER, oxygen evolution reaction; HER, hydrogen evolution reaction; CO<sub>2</sub>RR, CO<sub>2</sub> reduction reaction; MOR, methanol oxidation reaction; XRD, X-ray diffraction; XAFS, X-ray absorption fine structure spectroscopy; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; FTIR, Fourier transform infrared spectroscopy.

\* Corresponding author.

E-mail address: [jianglab@ustc.edu.cn](mailto:jianglab@ustc.edu.cn) (H.-L. Jiang).<sup>1</sup> These authors contributed equally to this work.

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## 1. Introduction

Nanoporous materials, such as the classical zeolites and mesoporous silica, have been intensively investigated as ideal platforms for various applications, including gas storage, chemical sensing, energy conversion, catalysis, etc [1–7]. Particularly, due to the high surface area and confined pore space that can be functionalized, nanoporous materials have demonstrated great superiority. For instance, zeolites, constructed by micropores in the range of 0.3–1.5 nm, have excellent gas adsorption capability. Moreover, zeolites are able to differentiate molecules with different sizes, which is of vital significance in selective catalysis. These merits, along with the stability, contribute to the important applications of zeolites in petrochemical industry and synthesis of fine chemicals [8,9]. As for mesoporous silica with larger pore sizes, the applications are mostly focused on drugs delivery, energy conversion and storage, as well as catalysis, thanks to their uniform mesopores, moderate surface area, good biocompatibility and ability to interact with guest species [10–13]. Given the pore size gap between microporous zeolites and mesoporous silica, it is important to find alternative materials possessing ordered pore structures to bridge the above gap.

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), featuring well defined pores with diameters ranging from 0 (nonporous) to 9.8 nm, have been proven to be outstanding candidates for bridging the gap between zeolites and mesoporous silica. They have achieved rapid development over the past two decades for diverse applications, such as gas sorption/separation [14–16], catalysis [17–28], chemical sensing [29–31], energy storage and conversion [32–34], etc. Featuring well-defined crystalline structures, adjustable pore topology, ultra-high surface areas and excellent tailorability, MOFs have shown huge potential especially in catalysis [35–38]. However, due to the fragile coordination bonding between metal nodes and organic ligands, the instability, especially moisture sensitivity [39], limits the practical applications of MOFs. Taking photocatalytic water splitting as an example, the reaction environment (aqueous solutions) and the existence of sacrificial agent may exert a negative influence on the stability of MOFs [40]. Moreover, in electrocatalytic reactions, the low electrical conductivity further impedes the application of pristine MOFs and very limited related studies were reported [41,42]. The good thing is that, when served as templates/precursors, MOFs can be converted to much more stable and conductive carbon/metal-based porous materials than pristine MOFs, with inherited characters of pristine MOFs to a large degree, such as large surface area, composition diversity and dispersion, tailored porosity [43–49]. In addition, considering that most MOFs

are constructed by transition metals (Mn, Fe, Co, Ni, Cu, etc.) and organic ligands containing C, H, O, N, S, etc., which are usually necessary elements in catalytic systems, the derivatives with the same elementary compositions as parent MOFs would possess great potentials in catalysis [50–59]. In addition, compared with traditional catalysts, the MOF-derived porous materials have more advantages, such as large surface area, high porosity, adjustable morphology and uniform heteroatom doping, which are considered to be crucial to their catalysis. Therefore, many MOF-derived porous materials even afford better performances than their parent MOFs.

As a matter of fact, the derivation of MOFs opens up an avenue to the preparation of diversified porous materials with unique advantages in comparison to traditional nanoporous materials, mainly on the following points: (i) simple and convenient synthetic procedures without additional templates (providing a simple method to fabricate porous materials); (ii) ordered porous structure and easy adjustment of pore size (guaranteeing high-flux mass transfer and easy accessibility of active sites); (iii) high surface area (exposure of high-density active sites); (iv) controllable size and inherited morphology of pristine MOFs (benefitting the optimization of catalytic performance); (v) facile doping of highly dispersed heteroatoms (modulating the local electronic structure of catalysts); (vi) accurate control of active sites through the predesign of MOF precursors (favoring the establishment of structure–performance relationship). Therefore, MOF-derived porous materials, with large surface area, high stability and tunable structures, are very promising candidates for catalysis [50–61].

In this review, we present a systematic introduction of derivation strategies of MOFs to porous materials at first. Then an overview on the recent progress of MOF-derived nanomaterials for various catalytic applications is summarized. For heterogeneous catalysis, MOF-derived porous materials have great potential in rational loading of active sites and functionalization with heteroatoms, which is critical for reactions such as oxidation, reduction and CO<sub>2</sub> fixation. Moreover, many metal-based compounds, such as metal oxides, metal sulfides and others derived from MOFs are semiconductors, which are favorable for photocatalysis. The porosity of MOF-based porous materials creates the opportunity for rapid consumption of photo-induced charge carriers, resulting in improved photocatalytic efficiency. In terms of electrocatalysis, the large surface area, appropriate pore sizes as well as conductivity in the porous materials derived from MOFs are closely related to the performance of electrocatalysts. Finally, particular challenges as well as research opportunities of porous materials derived from MOFs for further development toward catalysis are also critically discussed.

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