



Review

Heterogeneous catalysts based on mesoporous metal–organic frameworks

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ABSTRACT

Mesoporous metal–organic frameworks (meso-MOFs) are emerging as promising functional materials for heterogeneous catalysis due to their high surface area, porosity, readily adjustable structures and tunable functionalities. Their properties and functions are often dictated by the size and shape of pores in their frameworks. Mesopores in MOFs can decline mass transfer and exchange resistance in a confined space, leading to the improvement of their catalytic performances. However, it is challenging to synthesize and apply meso-MOFs for catalysis owing to the requirement of a combination of good chemical stability and large pore size. So far, there have been few efforts to comprehensively discuss these issues. Based on selected recent reports, this review will provide a concise overview in the field of meso-MOFs, associated with their synthetic strategies and intriguing tactics of generating active sites for heterogeneous catalysis.

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Abbreviations: Meso-MOFs, mesoporous metal–organic frameworks; PCNs, porous coordination networks; SBU, secondary building unit; CUSs, coordinatively unsaturated sites; H₂BDC, 1,4-benzene dicarboxylic acid (terephthalic acid); H₃BTC, 1,3,5-benzene tricarboxylic acid (trimesic acid); L1, 5-nitroisophthalic acid; L2, 5-cyanoisophthalic acid; L3, 5-hydroxyisophthalic acid; L4, pyridine-3,5-dicarboxylic acid; H₃BTB, 4,4',4''-benzene-1,3,5-triyl-tris(benzoic acid) or 1,3,5-tri(4-carboxyphenyl)benzene; H₃TATB, 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid; H₃hmt, methyl substituted truxene tricarboxylic acid; H₃BTATB, 4,4',4''-(benzene-1,3,5-triyltris(azanediyl))tribenzoic acid; H₃TATAB, 4,4',4''-s-triazine-1,3,5-triyltri-p-aminobenzoic acid; H₄TBAPy, 1,3,6,8-tetrakis(p-benzoic acid)pyrene; TCPP, tetrakis(4-carboxyphenyl)porphyrin; H₄L, 4,4',4''-((4,4',4''-(porphyrin-5,10,15,20-tetrayl)tetrakis(benzoyl))tetrakis(azanediyl))-tetrabenzoic acid.; MIL, Matériel Institut Lavoisier; IRMOF, isoreticular metal–organic framework; HKUST, HongKong University of Science and Technology; H₃BBC, 4,4',4''-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoic acid; H₃PTB, pyridine-1,3,5-tribenzoic acid; SUMOF, surface-mounted metal–organic framework; NU, Northwest University; hmt, hexamethylenetetramine; dabco, 1,4-diazabicyclo[2.2.2]-octane; PCN, porous coordination network; DFT, density functional theory; ZABUs, zinc-adeninate octahedral building units; NDC, 2,6-naphthalene-dicarboxylate; UCMCM, University of Michigan Crystalline Material; DUT, Dresden University of Technology; PSMO, post-synthetic metathesis and oxidation; MMOF, mesoporous metal organic framework; SC, supercritical; IL, ionized liquid; EG, ethylene glycol; IML, isostructural mixed linkers; HML, heterostructural mixed linker; LML, large mixed linker; TML, truncated mixed linker; DBA, 4-(dodecyloxy)benzoic acid; UiO, Universitetet i Oslo; TFA, trifluoroacetic acid; POST, Pohang University of Science and Technology; ZIF, zeolitic imidazolate framework; InPF, indium polymeric framework; DMNP, dimethyl 4-nitrophenyl phosphate; TEMPO, 2,2,6,6-tetramethyl-piperidine-1-oxyl; SALI, solvent assisted ligand-incorporation; AIM, atomic layer deposition in MOFs; SIM, solution-phase grafting in MOFs; ALD, atomic layer deposition; 4-AAP, 4-aminoantiprine; NUPF, Nanjing University Porphyrinic Framework; POMs, polyoxometalates; PTA, phosphotungstic acid; CPE, cyclopentene; GA, glutaraldehyde; MNPs, metallic nanosized particles; TMBQ, 2,3,5-trimethylbenzoquinone; TMHQ, 2,3,5-trimethylhydroquinone; GVL, γ -valerolactone; SMTs, single-molecule traps; HRP, horseradish peroxidase; Cyt c, cytochrome c; MP-11, microperoxidase-11; APBQ, N-antipyryl-p-benzoquinoneimine.

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1. Introduction

Metal-organic framework (MOFs), also named as porous coordination polymers (PCPs), are porous organic-inorganic hybrid materials [1]. The self-assembly of cationic systems with diverse organic ligands can guide the formation of a secondary building unit (SBU), allowing infinite possibilities to design targeted framework geometries analogized to zeolite [2,3] with particular pore structures [4]. By contrast with the pure organic or inorganic materials, the organic-inorganic hybrid MOFs materials have ordered crystalline, high BET surface areas, as well as tunable pore shapes and sizes, besides the sufficient structural diversity [5]. Moreover, the presence of coordinatively unsaturated metal sites (CUSs) and the encapsulation capacity of catalytically active species in their pores and/or channels, guarantee MOFs to be amazing functional materials for heterogeneous catalysis. Over past decades, they have been demonstrated as active heterogeneous catalysts for various organic reactions, such as acid-base and redox reactions [6–11], esterification [12,13], trans-esterification, epoxidation [14–16], hydrolysis [17], acetalization [18], methanolysis [19], Knoevenagel condensation [20] and hydrogenation [21].

Noticeably, the catalytic activity of MOFs is often dictated by the pore size and shape, as well as chemical environments of the cages and/or channels. For example, narrow pores inhibit loading large guest species and/or anchoring functional molecules, meanwhile they also suppress mass diffusion and transfer. According to IUPAC [22,23], pores with size in the range of 20–500 Å are considered as mesopores, herein, the MOFs with mesopores denoted as meso-MOFs. Importantly, mesopores in MOFs on one hand can decline mass transfer and exchange resistance in a confined space, leading to enhanced catalytic activity; on the other hand they allow large guest species to be wrapped in the framework owing to the enlarged pore windows, facilitating the catalysis applications of MOFs. However, the frameworks of yielded meso-MOFs are usually collapsed or interpenetrated to maximize packing efficiency after removal of the solvent molecules [24–26]. Obviously, it remains a great challenge to synthesize and apply meso-MOFs for catalysis due to the requirement of a combination of good

chemical stability and a large pore size. Therefore, elaborate strategies should be designed to overcome this puzzle [27].

Until 2012, most reported open MOFs are microporous (pore sizes <2 nm), and only a small fraction of MOFs possess ordered mesoscale domains (2–50 nm), which has been reviewed by Cui et al. [1] and Zhou et al. [28], respectively. Five years past, a few novel strategies for synthesis of meso-MOFs have been emerged, such as defect engineering strategy that not only can modulate the pore size and shape, but also can tune the catalytic activity sites: coordinatively unsaturated sites (CUSs). Their significant applications especially in heterogeneous catalysis give rise to a rapid expanding of the researches on meso-MOFs. Many reviews dealing with catalytic applications of MOFs are already available so far [4,27,29–54]. Nevertheless, a comprehensive work, focusing on recent advances in the heterogeneous catalysts based on meso-MOFs, is urgently required to provide an overview, concerned with their synthetic strategies and intriguing tactics for generating catalytically active sites. This review article will fill this blank, and provides concise and precise updates on the latest progress regarding on meso-MOFs. Furthermore, it covers meso-MOFs in the aspects of the design tactics, applications in heterogeneous catalysis, current challenges and future directions for this research field.

2. Tactics to design meso-MOFs

Generally, MOFs having either channels or cages with sizes larger than 2 nm are attributed to meso-MOFs. Most of channel-type meso-MOFs always demonstrate two types of representative adsorption isotherms (Types IV and V) [22,55], both of which show a characteristic hysteresis loop due to capillary condensation occurring in mesopores. The type IV isotherms are more common for most of the channel-type meso-MOFs owing to their hierarchically micro- and meso-channels. However, the cage-type MOFs do not exhibit any aforementioned types of isotherms. MOFs are constructed by metal nodes/clusters as connectors and organic ligands as linkers. The design and functionalization of organic ligands, as well as the coordination guidance and the diversity in physical

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