Microporous metal–organic frameworks: Synthesis and applications

Mahnaz Ahmadi a, Maryam Ebrahimnia a, Mohammad-Ali Shahbazi b,c, Rüstem Keçili d,⇑, Fatemeh Ghorbani-Bidkorbeh a,⇑

a Department of Pharmaceutics, School of Pharmacy, Shahid Beheshti University of Medical Sciences, Tehran, Iran
b Department of Biomedical Engineering, University Medical Center Groningen, University of Groningen, Antonius Deusinglaan 1, 9713 AV Groningen, Netherlands
c W.J. Kolff Institute for Biomedical Engineering and Materials Science, University of Groningen/ University Medical Center Groningen, Antonius Deusinglaan 1, 9713 AV Groningen, The Netherlands
d Anadolu University Yunus Emre Vocational School of Health Services, Department of Medical Services and Techniques, 26470 Eskisehir, Turkey

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ABSTRACT
Metal-organic frameworks (MOFs) have emerged as porous hybrid materials composed of metal ions and organic ligands. MOFs have attracted the attention of many researchers due to their promising characteristics, including high porosity, surface area, and drug loading capacity, tunable pore size and structure, good biodegradability and biocompatibility, and ease of functionalization. MOFs are categorized into three groups based on their pore widths, including microporous, mesoporous, and macroporous MOFs. MOFs with micropores have shown special features. The internal pore widths of microporous MOFs are less than 2 nm, which leads to their high porosity and surface area. Microporous MOFs could be synthesized through different strategies, including modulator-induced defect-formation, structure-directing agents, pillared-layer assembly, bridging helical chain secondary building units, coordination capabilities of P=O moieties in the structure of a ligand, and using octahedral cage-like building units. Because of their unique properties, microporous MOFs have shown great potential for many applications such as separation, storage, catalysis, and sensing. A description of synthesis approaches and applications of microporous MOFs in recent years is provided in this review.

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⇑ Corresponding authors at: Department of Pharmaceutics, School of Pharmacy, Shahid Beheshti University of Medical Sciences, Niayesh Highway, Valiasr Ave, Tehran 1996835113, Iran (F. Ghorbani-Bidkorbeh).
E-mail addresses: rkecili@anadolu.edu.tr (R. Keçili), f.ghorbani@sbmu.ac.ir (F. Ghorbani-Bidkorbeh).

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Moreover, expanding the organic linker structure could make such as benzene-1,3,5-tricarboxylic acid (H\textsubscript{3}BTC) and 1,3,5-structures and geometries to coordinate with metal nodes [12–14]. In this regard, pore sizes of MOFs could have a vital role in forming porous MOFs and tailoring the pore post-synthetic modifications [21,22]. Usually, the organic linker building block molecules, adding different functional groups to microporous MOFs are less than 2 nm, mesoporous MOFs have porous MOFs are larger than 50 nm [20]. Microporous MOFs have some advantages compared with other porous MOFs due to their high porosity, large surface area, and tunable properties such as metal ions and organic ligands. MOFs can be synthesized under mild conditions by forming coordination bonds. Therefore, these systems are also called coordination polymers [1].

MOFs have numerous advantages, such as high porosity, surface area, drug loading capacity, tunable pore size, and structure. They also possess high biodegradability, biocompatibility, and easy functionalization [2–5]. Due to these characteristics, MOF-based systems have many applications in various fields, including gas adsorption [6], catalysis [7], sensing and detection [8–10], separation [11,12], and biomedical applications [13,14].

One of the most critical characteristics of MOFs is their high porosity, which is the ratio of void volume to the total volume of MOFs. MOFs’ high porosity and specific surface area have led to numerous applications [15,16]. According to the International Union of Pure and Applied Chemistry (IUPAC) report, porous materials such as MOFs are divided into micropores, mesopores, and macropores, based on pore size [17]. The internal pore widths of microporous MOFs are less than 2 nm, mesoporous MOFs have pore sizes between 2 and 50 nm [18,19], and pore sizes in macroporous MOFs are larger than 50 nm [20].

The pore size in MOFs can be tuned by selecting appropriate building block molecules, adding different functional groups to the organic ligands or metal ions, or through pre-synthetic and post-synthetic modifications [21,22]. Usually, the organic linker has a vital role in forming porous MOFs and tailoring the pore shapes and sizes [23]. In this regard, pore sizes of MOFs could be adjusted by utilizing various organic linkers with different structures and geometries to coordinate with metal nodes [12–14]. Moreover, expanding the organic linker structure could make ultrahigh porosity in MOFs [16]. For instance, the elongated ligands such as benzene-1,3,5-tricarboxylic acid (H\textsubscript{3}BTC) and 1,3,5-benzenetricarboxylic acid (H\textsubscript{2}BTC) can be applied to produce highly porous MOFs [24,25].

Microporous MOFs are usually synthesized via solvothermal [26,27], hydrothermal, microwave [28,29], and ultrasonic-assisted methods [30].

Furthermore, different strategies have been developed for controllable synthesis of microporous MOFs and their frameworks, including the modulator-induced defect-formation approach [31], using structure-directing agents, pillared-layer assembly [29], acoustic cavitation within collapsing bubbles [30], bridging helical chain secondary building units [32], coordination capabilities of P=O moieties in the structure of a ligand [23], and octahedral cage-like building units strategy [33]. Microporous MOFs have some advantages compared with other porous materials, such as high porosity with over 6000 m\textsuperscript{2} g\textsuperscript{-1} surface area, tunable porosity, and immobilization of functional sites in pore surfaces [34]. Large micropore volumes and high surface areas are desirable characteristics of MOFs for many applications [35], including gas separation [36], storage [37], catalysis, luminescence sensing [38], and fluorescent sensing [39]. Microporous MOFs with adsorption or molecular sieving effects could be used as membranes to separate different gases. Chemical tunability has made MOFs suitable for the specific detection of the ingredients in a gas mixture. Moreover, modification of unsaturated metal sites or incorporation of proper functional groups to the backbones of the organic linkers imparts a catalytic activity to the microporous MOFs. Also, the sensing ability of microporous MOFs originates from incorporating appropriate functional groups, such as a fluorophore, into their structure. The storage of gases such as methane, hydrogen, and acetylene is another application of microporous MOFs due to their high porosity, large surface area, and tunable properties [36–39].

Many studies have reviewed MOFs’ applications and experimental synthesis techniques [40–43]. Some studies have considered specific MOF types or applications [44,45]. Additionally, a review article has provided different strategies to make mesoporosity (such as topological design, defect-doping, templating, and modular building) and presented applications of mesoporous MOFs [46]. However, no similar articles have thoroughly reviewed design strategies and applications of MOFs, emphasizing microporosity. Notably, most of the reported MOFs are microporous materials regarding their pore widths, which increases the necessity of this investigation. Hence, a study of structure design, synthetic strategies, and applications of microporous MOF seem to be requisite. Herein, the valuable properties of microporous MOFs and their various applications will be summarized. Also, several structure design strategies will be introduced for achieving microporosity in MOFs. Thus, this review aims to provide an overview of microporous MOFs and can pave the way for scientists in microporous MOF design, considering the challenges in commercialization and applications.

**Chemistry of microporous MOFs**

**Physical and chemical properties**

The physical properties of MOFs, such as mechanical, magnetic, and optical properties, can affect their performance in different fields. There are several studies investigating the behavior of MOFs under mechanical stress. Among all types of MOFs, zeolitic imidazolate frameworks (ZIFs) are a class mainly studied on their mechanical properties [47]. For example, Moggach et al. demonstrated that ZIF-8 crystals swelled when the pressure was increased to 0.18 GPa instead of compressing. This phenomenon was caused by hydrostatic fluids hyper-filling the pores in the MOF structures, which led to the enlargement of the frameworks. However, the imidazolate ligands screwed under higher pressure (1.47 GPa) which increased the available pore volumes [48]. Besides experimental studies, computational simulations could also help to understand the mechanisms of compression and deformation under mechanical stress. Coudert et al. investigated the mechanism of amorphization in ZIF-8 and ZIF-4 via a dynamic molecular study. They reported that ZIF-8 and ZIF-4 might be sensitive to shear forces under high hydrostatic pressure [49]. Overall,
the mechanical properties of MOFs can be regulated by various techniques, including using flexible linkers, tuning the strength of host–guest interactions, and changing the particle sizes [50].

Another attribute of MOFs is magnetism, which depends on the intrinsic nature of metal ions and the interactions of organic ligands and metal ions. Magnetism in MOFs can be achieved by incorporating paramagnetic metals or open-shell organic ligands in their structure. The most magnetic MOFs contain paramagnetic metals, especially the first-row transition metals, such as V, Cr, Mn, Fe, Co, Ni, and Cu. The magnetic properties of MOFs can be derived from the cooperative interactions of the paramagnetic metal ions and organic radicals [51].

As another feature of MOFs, optical properties were observed primarily on lanthanide MOFs (Ln-MOFs) due to lanthanides’ electronic configuration and opto-physical properties [52]. The optical properties of MOFs could be changed when a guest molecule is incorporated into the pores of the MOFs. Investigation of the optical properties of MOFs can pave the way for their optical applications [53].

Various chemical interactions within MOFs, such as strong coordination bonds and weaker hydrogen bonds, can enable different chemical properties. The chemical properties of MOFs, such as chemical composition and the chemistry of the molecular building units, can affect the structural rigidity and flexibility of the frameworks [54]. High thermal and chemical stability are other chemical characteristics of MOFs caused by strong structural bonds. For example, ZIF-8 has shown exceptional chemical stability among different MOFs [55]. Post-synthetic modification (PSM) of MOFs can provide a tool for changing and regulating their chemical properties, such as pore reactivity [56].

**Porosity, surface area, and structural properties**

High porosity is a crucial feature of MOFs, making them appropriate for different applications, such as gas storage, separation, catalysis, sensing, and encapsulation of biomolecules. The porosity of MOFs can be evaluated according to the adsorption isotherms of nitrogen (N2) or argon (Ar) at their boiling points, at 77 K and 87 K, respectively [57]. These isotherms also provide information about surface area, pore-volume, and pore size distribution [58]. Generally, structural variety, crystallinity, permanent porosities, ultra-low densities, and well-defined pores and channels have made MOFs attractive for researchers [59]. High surface area is also desirable for many applications of MOFs, such as catalytic processes, electrochemical applications [60], adsorption [61], and drug delivery [62].

**Processability and large-scale production**

Several companies have been developed for the large-scale production of MOFs, such as BASF, MOF WORX, MOF Technologies, and NuMat. Development of MOFs from laboratory scale to commercial applications and their scalability and processability requires creative methods [63–65]. Flow chemistry, electrochemistry, and mechanochemistry have benefited the companies mentioned earlier. For example, mechanochemical synthesis provides physical mixing of components without requiring any solvents or long heating times, which reduces the costs and chemical wastes [66]. As another method for improving the scalability of MOFs, microwave irradiation can accelerate the production of MOFs due to requiring less energy than conventional methods [67].

Industrial production of MOFs requires many key factors to consider, including a flexible method for producing large quantities of MOFs using the same equipment, avoiding harsh reaction conditions such as high temperature and pressure to reduce costs and increase safety, and switching the process from batch to continuous mode for higher output per unit [65].

**Synthesis of microporous MOFs**

**Synthesis methods**

Various synthesis techniques for microporous MOFs preparation have different advantages and disadvantages, as depicted in Fig. 1. A popular method for preparing microporous MOFs is the solvothermal/hydrothermal method, in which the reactions proceed at high temperatures and pressures. The advantages of this method are the high crystallinity in the structures and the ability to tune the particle sizes and shapes. However, the solvothermal/hydrothermal method needs a long reaction time, organic solvents, and high temperatures and pressures [68–71]. Microwave-assisted synthesis has been known as a facile and rapid technique for pro-
producing small and uniform particles. However, a secondary-phase formation in the process is one of the drawbacks of this method [72,73]. As another synthesis route, sonochemical synthesis can form small nanocrystals with good crystallinity, but external parameters can affect this procedure [74,75]. Besides, electrochemical synthesis can produce a thin MOF film with unknown mechanisms [76]. Another approach to MOFs synthesis is the mechanochemical method that can produce pure crystals and hybrids of MOFs with minimum solvents. However, this method may need solvents for the purification step. Also, the scale-up process has some challenges [77]. As the last technique, microemulsion synthesis can prepare various MOFs with controlled compositions and morphologies. However, this method leads to low product yields, and the presence of solvents and surfactants is considered a challenge to this method [78]. Different methods for synthesizing MOFs with their advantages and disadvantages can be selected and applied depending on the conditions and type of MOF.

Synthesis strategies of microporous MOFs

There are different strategies for the controllable design and synthesis of microporous MOFs and their frameworks, namely, the modulator-induced defect formation [31], using structure-directing agents [35], pillared-layer assembly [29], acoustic cavitation within collapsing bubbles [30], bridging helical chain secondary building units [23], and octahedral cage-like building units strategy [33].

Modulator-induced defect formation

In the modulator-induced defect formation strategy, a modulator is used for the controlled synthesis of microporous MOFs. This approach is applicable for preparing various porous MOFs in which the sizes and volumes of pores can be easily regulated [31].

Bumstead et al. investigated the role of a modulator in the framework interpenetration in a zirconium amino-terephthalate MOF Uio-66(NH2). In this MOF, the 4,4,4'- (2,4,6-trimethylbenzene-1,3,5-triyl) tribenzoate (TMTB) tritopic was used as a linker, and formic acid and benzoic acid were applied as modulating agents. Using formic acid as a modulator resulted in a more interpenetrated structure because benzoic acid groups of benzoic acid could bind to the clusters sterically and inhibit the growth of interpenetrating lattice. Finally, it was proved that the structure of the MOF is microporous through single-crystal X-ray diffraction (XRD) and N2 adsorption isotherm at 77 K [79]. Also, Cavka et al. synthesized microporous UiO-66 with Zr6O4-(OH)4(BDC)6 (BDC = 1,4-benzenedicarboxylate) formula using monocarboxylic acid as a modulator. Removal of the modulator led to the release of large pore spaces and hierarchically porous UiO-66 (HP-Uio-66). Fig. 2 demonstrates the Zr-MOF structures prepared with different linear ligands through the modulator-induced strategy [80].

Structure-directing agents

Using structure-directing agents such as surfactants is favorable for preparing microporous MOFs [35]. Qui et al. [81] utilized cetyltrimethylammonium bromide (CTAB) as a cationic surfactant to synthesize microporous HKUST-1 MOFs. Seoane et al. [35] synthesized MIL-100 MOFs in the presence of CTAB, which obtained hierarchical porosity and topology of microporous MOFs along with possessing mesopores. This study investigated the effects of different synthesis conditions, such as surfactant concentration and pH, on the structural properties of the final MOFs.

Also, Hu and coworkers [82] demonstrated that surfactants could be used in the template-directed synthesis of microporous structures through a solvothermal method. They synthesized NH2-MIL-125(Ti) as a microporous MOF for catalysis and adsorption applications. In this investigation, CTAB was employed as a surfactant. Moreover, Ar adsorption and desorption isotherms at 87 K illustrated the microporous structures of four samples with different molar ratios of CTAB/NH2-BDC. In addition, the pore size distribution demonstrated the alteration of micropores to mesopores and macropores. Furthermore, this study exhibited various morphologies of MOFs obtained by morphology-controlled and CTAB-assisted synthesis methods to synthesize NH2-MIL-125.

Pillared-layer assembly

Some of the complex structures of MOFs are made up of separate units, including the monomeric cations and two-dimensional anionic units. In these structures, cationic units act as pillars, and anionic layers can be linked to each other by cations through hydrogen bonding [29]. Pillared-layer assembly is a controllable route to prepare porous MOFs with favorable pores and structures via modification of the pillar module in the interlamellar zone. The pillared-layer networks can be built through coordination bonds, and most literature has introduced organic ligands as pillars. Coordinative unsaturated ligands could be used to control the structure of the transition metal complex and construct porous frameworks with attractive features through coordination bonding. In this regard, Ding et al. [29] used 2,2’-bimidazole (H2biim) as a ligand because of its favorable properties. H2biim can be coordinated with the metal ion through the imino group, and the amino group acts as a donor in hydrogen bonding. Also, H2biim could be a bidentate, tridentate, or tetradeinate ligand based on its protonation state, and in this study, H2biim was applied as a tridentate ligand (Hbiim−). The complex was fabricated by combining [M(H2biim)]6+ cation and [M(Hbiim)(BTC)]2− anion as two separate units in which [M (H2biim)]6+ acted as the pillar for connecting to the anionic layer through hydrogen bonding, which resulted in pillared-layer micro-

Fig. 2. The structure of Zr-MOF with 1,4-benzene-dicarboxylate (BDC), 4,4’-biphenyl-dicarboxylate (BPDC), and terphenyl dicarboxylate (TPDC) as organic linkers (UiO-66, UiO-67, and UiO-68 from left to right) [Adapted with permission from [80]].
Microporous MOFs. “M” in these structures referred to Co or Ni that could produce two isostuctural complexes. These microporous MOFs were synthesized under hydrothermal conditions.

**Acoustic cavitation within collapsing bubbles**

Qiu et al. [30] synthesized microporous MOFs via zinc acetate dihydrate and benzene-1,3,5-tricarboxylic acid (H$_2$BTC) under ultrasonic irradiation. Investigations have shown that the chemical effects of the ultrasound rise from acoustic cavitation within collapsing bubbles, which creates local hot spots and high temperatures and pressures. The interfacial region near the bubbles has demonstrated a high temperature and pressure gradient. The creation of high-velocity molecules led to the formation of free radicals, mechanical shocks, and high shear gradients. Therefore, the chemical reactions were performed under ultrasonic irradiation. In the study of Qin et al., the coordination bonds between the metal ions and the organic ligands were formed through high transient temperature and pressure. Moreover, other ultrasound effects could influence the crystallization process [30].

**Bridging helical chain secondary building units**

The organic ligands guide the construction of secondary building units and can control the pore shapes and surroundings in the final product. Microporous MOFs can also be synthesized by bridging helical chain secondary building units from suitable ligands. Hong et al. [23] reported the synthesis procedure of microporous lanthanide MOFs by linking the helical chain secondary building units built up from the H$_2$BTC ligand. The formula of this MOF is (Yb(BTB)(H$_2$O)(DEF)$_2$), in which DEF is N,N-diethylformamide. Linking one-dimensional helical chain building units and the BTB$_3$ ligands built three-dimensional coordination networks. Yb ion was coordinated with the six O atoms of carboxylic acids in six various BTB$_3$ and one water molecule. The obtained result was a structure with pentagonal bipyramid geometry, and Yb-O bond distances were measured to be approximately 2 Å.

Moreover, the solvothermal reaction was the synthesis procedure of these lanthanide MOFs [23]. Lanthanide metals have attracted the attention of researchers as metal centers due to their diverse structures and unique characteristics. Hexavalent uranyl (VI) cations among actinide elements could be used as building units with diverse structures and coordination geometries. Wang et al. [33] selected H$_2$TPO (tris-(4-carboxyphenyl)phosphineoxide) and U(VI) as the ligand and the metal, respectively. H$_2$TPO contains a P=O group that can precisely extract actinides from the solution. Also, U(VI) has an affinity to the carboxylate groups in different conditions. Thus, ligating U(VI) and the carboxylate groups of the ligands, which include P=O moieties, could assemble microporous MOFs. The experimental process of this synthesis was performed through the solvothermal reaction between UO$_2$(NO$_3$)$_2$·6H$_2$O and H$_2$TPO ligands in the DMF solvent.

**Octahedral cage-like building units strategy**

One strategy for designing and synthesizing microporous MOFs is using polyhedral cage-like building blocks. He et al. [83] built microporous MOFs through mixed ligands and cage-like building blocks. One carboxylate group from H$_2$BDC and six from biphenyl-3,4,5-tricarboxylate (H$_2$BPTC) were encapsulated in the tetrahedral Zn$_4$(μ$_4$-O) cluster of the asymmetric unit and formed a secondary building unit, [Zn$_4$O(CO$_2$)$_7$]. In the MOF structure, the BPTC$_3$ and the [Zn$_4$O(CO$_2$)$_7$] were involved as three and seven-connected nodes, respectively. Indeed, the MOF was regarded as octahedral packing prepared from six [Zn$_4$O(CO$_2$)$_7$] and four BPTC$_3$ ligands. [Zn$_4$O(CO$_2$)$_7$] units occupied the vertices of the structure, BPTC$_3$ occupied eight faces, and two BDC$_2$-ligands bridged two equatorial edges in the octahedral cage. In this study, the microporous MOFs were prepared by the reaction of H$_3$BPTC and terephthalic acid (H$_2$BDC) with Zn(NO$_3$)$_2$ through solvothermal synthesis [83].

**Applications of microporous MOFs**

**Separation**

In recent years, some MOFs have demonstrated promising molecular sieving effects on separating materials such as gases...
and hydrocarbons due to the precise tuning of their pore structures. Likewise, one of the most significant applications of microporous MOFs is separation, owing to their desirable features [36,84]. Microporous MOFs have some advantages compared with other porous materials, such as high porosity with over 6000 m^2g^{-1} surface area, tunable porosity, and immobilization of functional sites in porous surfaces [34]. Moreover, the adsorptive properties of solid MOFs have enabled their potential for gas adsorption and separation. This ability is due to the chemical tunability of MOFs, which capacitates them for specific detection of the ingredients in gas mixtures [85]. Generally, MOFs are promising candidates for separating CO_2 and hydrocarbons such as olefine based on surface functionalization, pore sizes, shapes, and membrane effects [34]. For example, microporous MOFs showed high adsorption selectivity for CO_2 and CH_4 [38]. MOFs containing functional groups with high affinity to CO_2 possess a heightened ability to separate CO_2 over N_2 and CH_4 [86]. For instance, nitrogen-containing functional groups on the surface of MOFs could demonstrate the properties of Lewis bases and create polarizing sites on the pores. The Lewis acid-base interactions between these sites with the quadrupole moments of CO_2 lead to CO_2 adsorption [87]. An et al. [88] synthesized BioMOF-11, which contained high quantities of amino groups and hydrocarbons due to the precise tuning of their pore structures [34]. Moreover, the adsorptive properties of solid MOFs could demonstrate the properties of Lewis acids and bases and create polarizing sites on the pores. The Lewis acid-base interactions between these sites with the quadrupole moments of CO_2 lead to CO_2 adsorption [87].

Also, based on the size exclusion mechanisms, regulating pores’ sizes and shapes makes MOFs suitable for selective adsorption of CO_2. The interaction of CO_2 molecules and pore surfaces can be controlled by optimizing the sizes and shapes of pores [86].

Yaghi et al. [89] prepared ZIFs and evaluated their efficiency in separating CO_2 over N_2 and CH_4. The results showed that the ZIF-78 with the smallest pore size, equal to the pore sizes of microporous MOFs, exhibited the highest uptake and selectivity for the separation of CO_2. Moreover, the ZIF-78 with polar functionalities could enhance the selectivity of CO_2 adsorption.

Besides, hydrocarbon compounds are essential chemical energy resources utilized in different industries. For example, acetylene and methane can produce energy via combustion oxidation. Also, olefins such as ethylene and propylene are used in preparing polymers. Overall, the separation of hydrocarbon mixtures such as light hydrocarbons (C_1 to C_3 hydrocarbons) [34] is critical for petrochemical industries [36].

Das et al. [90] synthesized a microporous Zn_{2}([PBA]_2[BDC]) MOF (UTSA-36, PBA = 4-(4-pyridyl) benzoic, BDC = benzenedicarboxylic acid). The pore size of this MOF was obtained between 3.1 and 4.8 Å for the adsorption and separation of C_2H_2, C_2H_4, and C_2H_6 from CH_4. Fig. 4 demonstrates the adsorption capacity of UTSA-36 for C_2H_2, C_2H_4, C_2H_6, and CH_4 at various temperatures. UTSA-36 could take up C_2 hydrocarbons (C_2H_2, C_2H_4, and C_2H_6) significantly more than C_1 methane, which exhibits the potential of this MOF for separating C_2H_2/C_2H_4, C_2H_4/CH_4, and C_2H_6/CH_4 mixtures.

After this work, two other microporous MOFs were studied for C_2-C_1 separation [91,92]. Natural gases containing methane (CH_4) can be considered energy sources because of their clean and economic characteristics. For example, the separation of the CH_4/N_2 mixture has shown challenges because CH_4 and N_2 exert very similar physical properties. Microporous MOFs could be used to separate CH_4/N_2 due to their structural and chemical properties. Chang et al. [93] studied the separation process of CH_4/N_2 mixture through three-dimensional microporous Cu-MOFs with hydrophilic and hydrophobic pores. The interactions of H atoms in the CH_4 molecules with three C–H atoms of the ligands in the hydrophobic pores and three O atoms in the hydrophilic pores produced robust van der Waals bonds. However, the interactions of N_2 molecules with hydrophilic and hydrophobic pores were weak because of the weak polarity of C–H and the coordination environment of Cu, respectively. Therefore, highly efficient Cu-MOFs were used to separate CH4 and N2 [93].

Furthermore, the separation of acetylene (C_2H_2) from C_2H_4 is challenging. Acetylene is a necessary initial material for producing industrial products. Several approaches for separating acetylene from C_2H_4 include its partial hydrogenation to ethylene and using an organic solvent to extract olefines. However, the adsorption process has demonstrated a higher efficacy in performing this separation. Microporous MOFs could adsorb these two gases with high selectivity due to their various pore sizes [34].

Moreover, C_5–C_6 alkanes are vital ingredients of gasoline. Separating these isomers could help obtain high-quality gasoline and enhance its octane rating. Microporous MOFs could perform this separation process via adsorptive separation. Microporous MOFs possess a higher adsorption capacity than zeolites. Wang et al. [94] synthesized a microporous MOF using tetratopic carboxylate linkers with high performance for separating C_5–C_6 isomers. Linear alkanes must be separated from branched isomers. In this study, Zr-bptc (bptc$^{4-}$ = 3,3,5,5-biphenyltetracarboxylate) could adsorb linear isomers and exclude branched isomers based on the size exclusion mechanism.

In addition, the adsorption-based separation of the olefin/parafin mixture by porous materials can decrease energy consumption. Propylene is an essential olefine in the petrochemical field. Wang...
et al. [95] reported the separation of propane and propylene by microporous MOFs with the formula of Y₆(OH)₈(abtc)₃(H₂O)₆(-DMA)₂, in which abtc is 3,3,5,5'-azobenzene-tetracarboxylates and DMA is dimethylammonium. These MOF systems could adsorb propylene and exclude propane through the size exclusion process. This mechanism can provide a platform for separation with high selectivity.

In addition to adsorption, membrane-based separation is also a valuable mechanism for gas separation. This approach has many advantages, including low cost, high efficiency, facility, and recycling ability. Membrane-based separation is usually performed using the molecular sieving effect for gas molecules. MOFs are the ideal candidates for this mechanism because of their varied structures, easy pore functionalizing, and the ability to regulate pore sizes and shapes [34]. Lai et al. [104] designed the MOF membranes for the first time in 2009. They prepared continuous films containing MOF-5 crystals and demonstrated that small gas molecules such as N₂ could permeate the MOF-5. Also, ZIFs, as subsets of MOFs, showed high potential as separating membranes due to their narrow sizes [96]. Li et al. [97] synthesized a rigid ZIF-7 membrane with a pore size of 3 Å. The ZIF-7 demonstrated a suitable cutoff between H₂ and CO₂ gases, and this sieving effect enhanced the selectivity in H₂/CO₂ separation.

Due to their characteristics, microporous MOFs exhibit high capacity and selectivity for gas separation. In the future, microporous MOFs are expected to obtain higher industrial applications in gas separation [34].

**Catalysis**

The tunability of the MOF structure has been beneficial for many applications, especially in catalysis. The catalytic activity of MOFs depends on modifying unsaturated metal sites or attaching proper functional groups to the backbones of the organic linkers [98,99].

Organic transformation of CO₂ could be used for synthesizing suitable chemical materials. The epoxide is a high-energy substrate, and cycloaddition of CO₂ to epoxide could fabricate cyclic...
carbonates or carbamate. Many endeavors have been made to improve heterogeneous catalysis for synthesizing these cyclic compounds from CO₂ and epoxides. However, these approaches have shown many disadvantages, such as low catalytic activity and complex reaction conditions. Microporous MOFs with high surface area and CO₂ selectivity are desirable heterogeneous catalysts for the chemical fixation of CO₂. Gupta et al. [100] synthesized a Zn-based microporous MOF ([Zn₂(3-trpom)(L)₃]·2H₂O)₆ (3-trpom = tetraakis(3-pyridyloxymethylene) methane and H₂L = 4,4’-(dimethylisocyanatedibenzene) for CO₂ adsorption to form cyclic carbonate due to their Lewis basic and unsaturated open metal sites and oxygen functionalities. Fig. 5 shows a single-crystal structure of this MOF with available channels illustrated in the center of the picture, with a large scale of Lewis-basic and coordinatively unsaturated metal sites.

He et al. [38] synthesized microporous MOFs ([Zn₉(4BDPO)₁₂(-DMF)₁₂]·6DMF·52H₂O) in which H₄BDPO (2,4-bis(3,5-dicarboxyphenylamino)-6-ol triazine) was used as an organic ligand and DMF is N,N-dimethylformamide. N-rich functional groups of triazine that were incorporated into the MOF could act as Lewis’s basic sites. Therefore, this MOF demonstrated a high catalytic potential for selective adsorption of CO₂ and CH₄. Fig. 6 exhibits N₂ sorption isotherms at 77 K, in which the pore width distribution was obtained at about 7.3, 10.9, and 12.7 Å, confirming the MOFs’ microporous structure.

Moreover, Horike and coworkers [101] investigated the catalytic activity of [Mn₄Cl₃(BTT)₃(CH₃OH)₁₀]₂. The organic ligand was obtained from 1,3,5-benzene-tristetrazol-5-yl (H₃BTT), and the Mn²⁺ ions on the surface of the MOF acted as Lewis acids. The pore sizes of 10 Å of the MOF provided enough surface for the Mn sites. These coordinatively unsaturated metal centers made desirable conditions for the interactions with external molecules, which could form in the pores of the MOF. The results confirmed that this MOF could be served as a heterogeneous catalyst.

Also, Lu et al. [100] prepared a microporous MOF ([CH₃₂-NH₃]₃Cd₄L(H₂O)₂]·12H₂O) in which free molecules of water and [(CH₃₂NH₃)⁺ cations were present. In addition, the presence of the Lewis acid Cd(II) sites in the MOF made it an appropriate catalyst for the cycloaddition of CO₂ with epoxides [102]. This process was explained more above [100].

Microporous MOFs could be utilized as heterogeneous catalysts because of their advantages, such as tunable pore size, high surface area, and functionality [100,102].

**Sensing**

Many advantages of MOFs, such as simple synthesis and tunable structures, porosity, and functionalization, have made them suitable systems for receiving foreign molecules. A MOF system with these benefits was presented for loading organic fluorophores to form luminescent materials with sensing applications [103,104]. For example, embedding functional groups such as carboxyl, hydroxyl, amide, and other N-containing groups into the ligands of microporous MOFs could control the pore structures and improve their features, especially sensing properties [105].

The interactions between the backbones of MOFs and the analyte molecules lead to the fluorescence sensing ability of MOFs. In this process, initially, the analyte molecule can be adsorbed by the MOF. After that, the energy transfer between the analyte molecule and the MOFs backbone results in emission quenching. The energy transfer can be defined as the transfer of excited-state energy from the donor to a neighboring ground-state acceptor, which results in simultaneous deactivation and excitation of the energy donor and acceptor, respectively [106].

As an example of biosensor MOFs, Tian et al. [39] fabricated microporous MOFs with the formula of [Cd(L)·solvent]ₙ, which encapsulated fluorescein isothiocyanate (FITC) dye molecules for sensing 3-nitropropionic acid (3-NPA). 3-NPA is a mycotoxin in sugarcane that could be considered a toxin for food contamination. Fig. 7 illustrates three strategies for designing MOF luminescent sensors [39].

The imperative roles of ions in biological systems have led researchers to use ion detection and sensing methods. Microporous magnesium-based MOFs (Mg-MOFs) incorporated with suitable functional sites on the walls could easily bind to lanthanide ions for luminescence sensing. Gao and coworkers [107] reported a microporous Mg-MOF as a sensor for Eu³⁺ ions with high selectivity. The existence of non-coordinating nitrogen atoms in the nano-holes of the MOF made it an appropriate host for guest metal ions.

Nitroalkanes and nitroaromatics materials are nitro compounds known as explosives and contaminants in various fields, such as military, agriculture, and industry [38,108]. Microporous zinc (II) MOF could be highly efficient for selective luminescence sensing and detecting nitroaromatic compounds, such as TNP (2,4,6-trinitrophenol). For instance, He et al. [38] developed a microporous Zn-MOF with the formula of [Zn₉(4BDPO)₁₂(-DMF)₁₂]·6DMF·52H₂O for sensing TNP. H₄BDPO or 2,4-bis(3,5-dicarboxyphenylamino)-6-ol triazine is an organic ligand in the MOF structure with many N-rich functional groups. Also, this MOF has shown luminescent properties due to the closed-shell d₁₀ configurations of electrons in Zn(II) that do not have a luminescence quenching effect.

Moreover, Zhou and coworkers [109] synthesized a microporous MOF [Eu₃(MFDA)₆(NO₃)(DMF)₃] with H₂MFDA ligand (9,9-dimethylfluorene-2,7-dicarboxylic acid) and red light-emitting properties. They investigated the sensing ability of the solvent-
free MOF through luminescence quenching experiments. The fluorescence quenching technique's high sensitivity and fast response made it suitable for sensing and detecting nitro compounds. Electron transfer by donor–acceptor (nitro compounds–fluorophores) led to the luminescence response of the MOF.

Furthermore, utilizing MOFs as luminescent materials in biosensing applications could provide a sensing platform for single- and double-strand DNA (ssDNA and dsDNA), which can be attributed to the different affinities of MOFs to ssDNA and dsDNA. Wang et al. [110] reported two MOFs, including 1) Cd(L)\((\text{HDMAC})_2(\text{DMF})(\text{H}_2\text{O})_3\) and 2) Zn(L)(\text{HDMAC})_2(\text{DMF})(\text{H}_2\text{O})_6, in which H2L, bis-(3,5-dicarboxy-phenyl)terephthalalamid, was used as the ligand due to its aromatic structure and amide group linker. This ligand's presence could improve the MOF framework's flexibility and form an additional hydrogen bond with the analytes.

Compounds 1 and 2 demonstrated strong ligand-based photoluminescence properties in the suspension, and nitroaromatic compounds could quench their fluorescence. Thus, these MOFs could be served as promising luminescent probes for nitroaromatic explosives. In addition, compounds 1 and 2 could quench the emission of a fluorophore-labeled ssDNA. Different affinities of these compounds to ssDNA and dsDNA allowed the selective recovery of fluorescence signals by the complementary target DNA. The potential of these MOFs in sensing nitroaromatic explosives and DNA strands is related to the π-electron-rich ligands (H4L), which help form π–π stacking interactions and excited state electron transfer with analyte molecules.

Storage

MOFs possess many advantages compared with other solid absorbents, such as high porosity and surface area, the functionality of pore surface, and tunable characteristics [111]. Beneficial features of microporous MOFs could make them favorable for storing gases, such as hydrogen, methane, acetylene, and propylene [111–115].

Maintaining a balance between the porosity and density of MOFs, incorporating them with a functional site for regulating the interactions between the methane and MOFs, and optimizing the pore spaces have led to the high capacity of methane storage by MOFs [116,117].

Ye et al. [111] synthesized a microporous MOF using Cu(NO3)2 and naphthalene diimide-based tetracarboxylic acid (fJU-101a MOF). The tetratopic linker in the MOF structure could join the paddlewheel units and create a nanosized pore cavity that eases gas storage, particularly methane storage. High-pressure methane adsorption isotherms in 0–100 bars at 270 K and 296 K revealed the potential of fJU-101a MOF in methane storage. According to the results, increasing the storage pressure could increase the total volumetric methane uptake [111].

Microporous MOFs are favorable storage tools compared with hydrogen tanks and carbon-based absorbents and have demonstrated notable H2 storage abilities due to their high porosity and surface area. There are two approaches to improving H2 adsorption using MOFs. The presence of very narrow pores in the frameworks and coordinatively unsaturated metal sites increase the affinity of frameworks and metals to H2 molecules. Dinca and coworkers [113] studied a stable microporous MOF with a high surface area and significant H2 uptake. This investigation used polytetrazolate bridging ligands containing N-donor atoms that could form rigid frameworks and subject metal coordination centers [113].

Wen et al. [114] synthesized a microporous MOF with the formula of [CuL(H2O)2]7DMF·4H2O with Lewis basic nitrogen sites in which H2L is 5,5′-(pyrazine-2,5-diyl)bisphthalamic acid. The MOF displayed high acetylene (C2H2) uptake due to its high porosity and nitrogen sites, making it an effective adsorbent. The Lewis basic nitrogen site in the structure enhanced acetylene uptake and distinguished it from other gases in the separation process. Thus, the functionalization of a ligand with a pyrazine group, which includes two Lewis basic nitrogen sites, could create a MOF with high selectivity and storage capacity for acetylene in a single system. The synthesis and functionalization of the tetracarboxylic acid ligands are shown in Fig. 8.

Propylene (C3H6) is a fundamental energy source in industries, and its correct storage is essential for its applications. MOFs suit this process because of their tunable structure and pore properties. Fan et al. [112] reported a Cu-based microporous isostructural MOF (iso-MOF) in which the ligand functionalization could improve its propylene storage capacity. The presence of multiple channels in the iso-MOF structures enhanced their affinity to hydrocarbons, which are crucial for their storage and separation. Also, pore spaces, pyrazine rings, and high porosity with open metal sites adapted the system to separating hydrocarbons.

Many studies have investigated MOFs’ applications and experimental synthesis techniques [40–43]. In this context, Safaei et al. presented the synthesis and applications of MOFs with more emphasis on the details of experimental synthesis methods [118]. Besides, in some studies, a specific type of MOFs or a particular application is investigated. For example, Kinik and coworkers assessed the synthesis and applications of pyrene-based MOFs [44], and Liu et al. highlighted the synthesis methods and applications from an environmental perspective [45]. Also, several groups have provided review articles about microporous MOFs. For example, Wang et al. reviewed microporous MOFs for adsorptive separations of C5–C8 alkane isomers [94], and Zhang et al. showed a perspective of microporous MOFs for CO2 capture and separation [119]. Additionally, several groups have studied the hydrogen storage ability of microporous MOFs [113,120,121].

In addition, Liu and coworkers [46] introduced fabrication strategies for mesoporous MOFs, such as topological design,
defect-doping, templating, and modular building. They also described various applications of mesoporous MOFs. Since no similar article has comprehensively reviewed microporous MOFs’ design and synthesis strategies, this study aims to review structure design strategies to form microporosity and applications of microporous MOFs. In this study, first, the chemistry and methods of experimental synthesis of MOFs were briefly presented as a remembrance. Afterward, synthesis strategies for controllable structure design of microporous MOFs were defined in detail. Several successful synthetic strategies achieve microporosity in MOFs, allowing microporous structures with controlled topologies, large pore volumes, and high integrity in the frameworks. Finally, various applications of microporous MOFs were also investigated.

Challenges and future perspectives

The main driving force for broad research in MOFs is these materials’ potential applications. Despite many advantages of microporous MOFs, there are still many challenges remaining. One of the challenges is the commercialization and approval of MOFs, which requires a collaboration between the industry and academic institutes. Despite the few commercialized MOFs, it is expected that in the future, these materials will play a crucial role in different fields. Furthermore, other challenges in MOFs utilization, especially in industrial applications, involve their production and characteristics, such as porosity and thermal and chemical stability. In this regard, the accurate design of microporous MOFs and further studies can improve their features. To this end, several issues require to be considered, including availability and the cost of raw materials, synthesis conditions and procedures, the need for high yield, low impurities, and minimum solvent use. Increasing the ability to tune the structures and compositions and advancing synthesis and characterization methods require an emphasis on MOF engineering in the future. Hence, future endeavors may emphasize the fabrication of multifunctional MOF-based platforms through different mechanisms to achieve high efficacy. Due to the recent research advancements on MOFs, it is predicted that promising developments in MOFs will be made to promote their characteristics and applications.

Conclusion

MOFs have attracted the attention of many researchers in recent years because of their exceptional properties, such as high porosity and surface area, tunable structure, and feasibility of functionalization. Specifically, microporous MOFs are suitable for various applications due to their fascinating characteristics, including ultrahigh porosity and large surface areas. There are several strategies to synthesize microporous MOFs. Usually, these approaches are based on using modulators and structure-directing agents or forming cavities and secondary building units. Depending on the intended products and synthesis conditions, a strategy could be utilized for the controlled synthesis of microporous MOFs. Microporous MOFs can be used in numerous applications due to their properties. According to the literature, separation is the most common application of microporous MOFs. Microporous MOFs possess the ability to separate gases through adsorption or molecular sieving mechanisms.

Moreover, incorporating the appropriate functional groups or modifying unsaturated metal sites leads to the catalytic activity of microporous MOFs. The ability of microporous MOFs to sense materials has been obtained from incorporating appropriate functional groups, such as a fluorophore, into the microporous MOFs. Also, the storage capability of gases is obtained due to the high porosity and surface area and the tunability of microporous MOFs properties. Though microporous MOFs have represented many advantages and applications, there is a need for more research regarding some applications, such as biomedical applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References
