

Recent advances in Fe-based metal-organic frameworks: Structural features, synthetic strategies and applications

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ABSTRACT

Metal organic frameworks (MOFs) are very exciting porous materials owing to their unique properties such as high surface areas, high pore volume, tunable functionalities and great thermal stabilities. The properties of MOFs can be diversely constructed by precise control of synthesis conditions. Amongst the thousands of MOFs that have been discovered to date, Fe-MOFs make up a percentage of these MOFs. Fe-MOFs are increasingly gaining great interest due to their unique properties and chemical versatility. However, comprehensive reviews on their emerging architectural features and designs as well as strategies for tailoring their applications. Therefore, in this review, we present a panoptic summary of the recent developments of Fe-MOFs, which includes synthetic strategies, activation methods, functionalization, overview of selected applications, current challenges impeding their commercialization, and suggested remedial actions. A holistic view of the interconnectedness of Fe-MOFs structural features, synthetic strategies and applications provides greater insights that highlight challenges hindering their wide-scale industrial applications. Moreover, newer approaches such as utilization of machine learning technique that are providing an opportunity for out-of-sight insights for material design and prediction of material properties are briefly highlighted. Remedial actions for challenges of transitioning Fe-based MOFs towards commercialization and industrial applications are also explored, and suggestions for these aspects are presented.

1. Introduction

Since their discovery in the 1990s, metal organic frameworks (MOFs) have gained huge interest amongst researchers, leading to over 100,000 MOF structures reported in the Cambridge Structural Database to date [1]. MOFs are a type of crystalline materials formed by a coordination of organic linkers and inorganic metal ions/clusters [2]. They have been explored for application in a variety of fields such as catalysis, biomedicine, gas separation and storage, and more especially hydrogen storage [3–5]. MOF applications are majorly driven by their high surface area (experimentally, some reach as high as 7000 m²/g) [6], great porosity, ease of functionalization and tuneability as well as their diversity in topology [7,8]. Due to the ease of tuneability of these

materials, various pore size distributions can be obtained, varying from micropores to mesopores. This is easily achieved by altering the length and structural properties of the organic linker [9]. The functionalization of organic linkers can greatly improve gas adsorption [10]. Permanent porosity and rigidity or flexibility properties (influenced by structural conformation and response to external stimuli) have further fueled the interest in these materials. Additionally, structural characterization of MOFs can easily be performed by x-ray diffraction (XRD), reducing the complexity of using computational methods for property prediction [11].

Amongst thousands of the already discovered MOFs, iron-based (Fe-MOFs) make up a small number of these MOFs (see Fig. 1.a). Fe-MOFs are of great interest due to their unique properties and their chemical

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versatility [12]. Fe-MOFs are typically made of Fe unsaturated metal centers (UMCs)/metal nodes [13]. The open metal sites of Fe-MOF proves to be beneficial on various catalyzed reactions [14,15]. See Fig. 1b for general structure of MOFs. High energy density of Fe UMC facilitates the strong coordination bond between Fe(III) and O atoms in the organic ligands (Fe—O) [16]. Most traditional porous materials such as zeolites exhibit less stability towards organic solvents and water, however, that is not the case with Fe-MOFs [16,17]. The high solvent and water stability of Fe-MOFs is because of Fe(III) ions being Lewis acids, while the organic linker is regarded as Lewis base. In general, Fe-MOFs have shown better performance in various applications due to higher flexibility which in turn controls the pore size distribution and pore internal environment. The control on pore size distribution allows these materials to be applied in various applications such as gas adsorption and storage [18,19]. Additionally, Fe-MOFs are either made of Fe^{3+} or Fe^{2+} which are conducive for biosensing, bioimaging and magnetic therapy [20–22]. Since iron is the fourth most abundant in the Earth's crust and has low toxicity, it thus affords easy scalable synthesis of these materials [23].

The need for development of affordable, clean, safe and sustainable energy has gained high interest amongst researchers to circumvent the depletion of fossil fuels and severe environmental pollution. Fe-MOFs have gained traction as effective adsorbents of hydrogen gas which is a great energy source. Despite a high number of publications on gas storage by Fe-MOFs, several challenges such as uncontrollable flexibility ("breathing effect") of these materials, low gravimetric and volumetric gas uptakes and the high cost of synthesis have still hindered the industrial application of these materials. Xia et al. [16], highlighted some of the challenges associated with Fe-MOFs, however, no remedial actions were provided. Shet et al. [25] expressed challenges associated with hydrogen storage such as the need of lightweight and pressure withstanding storage tanks and functionalization of organic linkers. To our best knowledge very limited review has been done to outline these challenges and provide corresponding solutions. This review strives to provide alternative precursors to circumvent high cost of synthesis and ways to ensure structural stability and open cavities of these materials. Open pores and structural stability have potential to increase gravimetric and volumetric uptake of gases. Several activation methods are outlined which can enhance structural rigidity of some of the Fe-MOFs. Various unconventional synthesis routes have been reviewed; however, machine learning (ML) assisted synthesis is yet to find use in Fe-MOFs synthesis. The potential of this method is presented in this review. Functionalization (either on the metal sites or organic linker) as a tool to

enhance gas uptake of these materials is discussed. Furthermore, remedial actions such as the use of waste feedstock as precursors are presented to tackle the high cost of synthesis.

2. Structural features of Fe-MOFs

MOFs with various network morphologies have been achieved by meticulously controlling synthetic conditions and chemical compositions. These materials have been built from low-valance (divalent) or high-valance (trivalent and polyvalent) metals coordinated to ditopic, tritopic and tetratopic organic linkers. These linkers are usually used depending on the intended application of the MOF. Different Fe-MOFs have been reported with different organic linkers, different connectivity, and core cluster building units. Most Fe-MOFs are made with Fe^{2+} / Fe^{3+} oxidation states and the most used organic linkers are the carboxylate-based linkers (see Fig. 1b).

The most popularly used ditopic linker is the benzene-1,4-dicarboxylic acid (1,4-BDC) linker; it has been employed in the synthesis of MIL-53, MIL-68, MIL-85, MIL-88B and MIL-101 (Table 1). In MIL-53, the 1,4-BDC is connected to FeO_6 octahedral core clusters which results in 3D channels of rhombohedral shape [26]. MIL-68 which has the same morphology as MIL-53 but differ in open cavities, has the linker coordinated to the corner-sharing $\text{Fe}(\text{OH})_2(\text{O}_{\text{car}})_4$ octahedral chains to form orthorhombic framework with trigonal and hexagonal one-dimensional channels [27]. MIL-85 is made of trimeric SBUs coordinated through $\mu_3\text{-O}$ [28]. Other ditopic linkers include: 2,6-naphthalenedicarboxylate, 4,4'-biphenyl-dicarboxylate, (*E*)-butenedioic acid (fumarate), and Trans, transmuconic acid (see Table 2 for MOFs made from these linkers).

Of the tritopic linkers, 1,3,5-benzene tricarboxylate is the commonly used linker. MIL-100 with MTN topology is constructed from trimetric acid coordinated to $[\text{Fe}_3(\mu_3\text{-O})(\text{COO})_6]$ SBUs. The framework displays two mesopores with opening sizes of 25 and 29 Å, which are penetrable through pentagonal and hexagonal micropore apertures [29]. 1,3,5-tris (4-carboxyphenyl) benzene has also been used on the synthesis of MIL-100 and resulted in large pore size of 68 Å penetrable through 20 and 26 Å apertures [30]. PCN-332 and PCN-333 (where PCN = Porous coordination network) are constructed with benzo-tris-thiophene carboxylate (BTTC) and 4,4',4''-s-triazine-2,4,6-triyl-tribenzoate (TATB) linkers respectively. The linkers are connected to $\text{Fe}_3(\mu_3\text{-O})(\text{OH})(\text{H}_2\text{O})$ to form very large pores [31,32].

MIL-127(Fe) with SOC topology is made of tetratopic 3,3',5,5'-azo-benzene-tetracarboxylate (TazBz) coordinated to Fe^{3+} octahedral

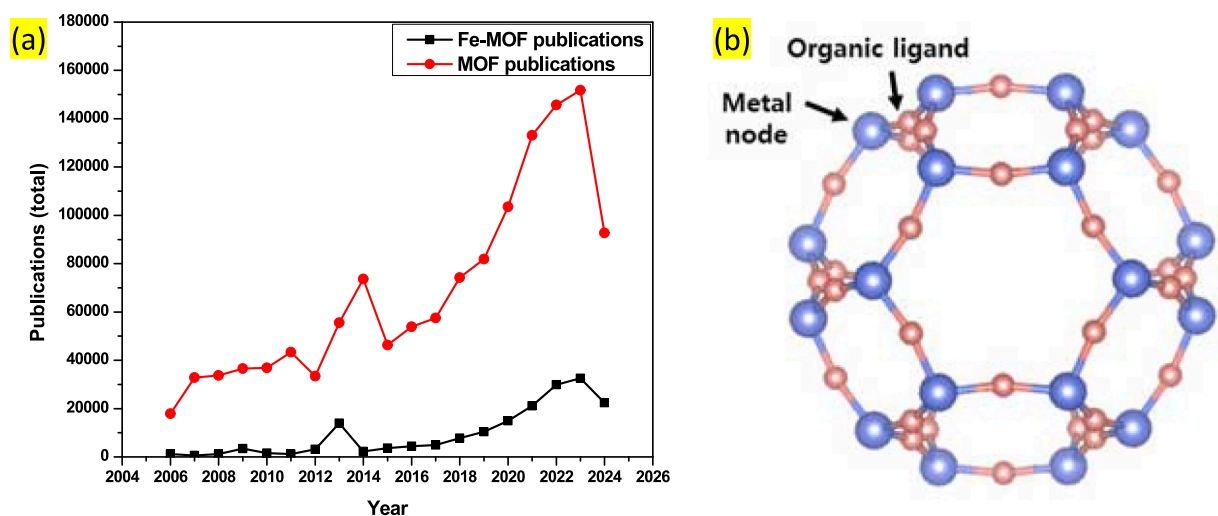


Fig. 1. (a) Number of published papers on metal-organic frameworks and iron-based metal-organic frameworks over the years (date retrieved from Dimensions database (25/07/2024)) and (b) general structure of metal-organic frameworks (Reprinted (adapted) with permissions from Ref[[24]]).

Table 1
Structural properties of a few selected MOFs.

MOF	Topology	Linker type	Pore type	Pore size (nm)	Pore apertures size (nm)
MIL-53	Tetrahedral	Ditopic	Flexible micropores	open pores (0.7–1) closed pores (0.34–0.36)	
MIL-88B	ACS	Ditopic	Micropores	0.6–1.2	0.5–0.6
MIL-100	MTN	Tritopic	Mesopores	2.5–2.9	1.2–1.4
MIL-101	MTN	Ditopic	Micro- and mesopores	1.2–1.6 and 2.9–3.4	0.8–1 and 1.6–1.7
MIL-127	SOC	Tetratopic	Micropores	1.2–1.6	0.7–0.8

trimers sharing one central $\mu_3\text{O}$ to form a 3D framework with two types of micropores [33]. 1,2,4,5-benzene tetracarboxylates (pyromellitic acid) connected to iron based edge-sharing octahedral chains constructs MIL-62 while coordination of the organic linker to trans corner-sharing iron-based chains constructs MIL-82 [34,35]. Other organic linkers such as nickel(II) tetracarboxylate porphyrin (Ni-TCPP), carboxylic acid 2,4,6-tris(4-pyridyl)-1,3,5-triazine (TPT) and dicarboxylic acid pyrazine (pyz) have also been employed to construct Fe-MOFs [36–38]. Table 1 summarizes structural properties of a few selected MOFs.

Generally, MOFs built from divalent cations are known to have low chemical stability compared to trivalent and polyvalent materials [39]. MILs are known for their chemical stabilities, large pore volumes and permanent porosities [40]. The Fe-MOFs (Fe-MIL-88B and MIL-101) are of interest in this report due to their unique properties.

MIL-88B (with general formula: $\text{Fe}_3(\mu_3\text{-O})(\text{BDC})_3(\text{H}_2\text{O})_2 \times$ (where BDC = 1,4-benzenedicarboxylic acid (terephthalic acid); X = compensating anion) is built by μ_3 -oxo-centered trimers of corner-sharing iron octahedra ($\mu_3\text{-OFe}_3$) connected by BDC ligands (adopting the ACS topology), wherein two archetypal forms of micropores, i.e. narrow hexagonal channels and triangular bipyramidal cages are distinguished [41]. The hexagonal channels stretched along the c axis (see Fig. 2.b) are defined by six Fe_3 -trimers connected by six BDC linkers, while the bipyramidal cages are fixed by five Fe_3 -trimers at the vertices coupled by six BDC ligands. Particularly, the narrow hexagonal channels along the c axis of Fe-MIL-88B are with an open window, which provides selective adsorption of molecules by molecular sizes and the mass transport restriction can be fixed. Additionally, Fe-MIL-88B has the potential to be an effective catalyst due to the abundance of accessible unsaturated metals centers (UMCs) throughout the hexagonal channels [42].

Another type of Fe-MIL MOFs is MIL-101 which adopts the zeotype crystal structure of MTN topology made of two hypersphere-hyperplane cages. The quasi-spheres possess internal diameters of 2.9 nm and 3.4 nm with apertures of 1.2 nm and 1.6 nm respectively.

(see Fig. 2.a) [43,44]. The framework of MIL-101 is made of terephthalate organic ligands and octahedrally connected metal clusters. The terminal water molecules are bounded to the octahedral metal ions and can easily be removed by heat treatment under vacuum [44]. Table 2 shows iron containing MOFs from the MIL family with their respective organic linkers.

3. Fe-MOF synthesis

MOFs are normally synthesized through self-assembly of metal clusters and organic linkers through careful control of synthetic parameters such as time and temperature to obtain crystalline materials. Synthesis conditions must favor nucleation and growth of the targeted morphology [55,56]. Variation of metal centers and organic linkers will lead to various morphologies, pore structure and pore dimensions. Several synthetic routes such as the conventional hydrothermal and solvothermal methods have been employed. Although these methods have been applied extensively, they have a fair share amount of challenges, such as long synthesis times, high costs of solvent and challenges with scale-up. Hence, additional unconventional methods (see Fig. 3) such as microwave assisted, sonochemical, mechanochemical, electrochemical, and supercritical carbon dioxide (ScCO_2) synthesis are

needed.

3.1. Conventional methods

In conventional solvothermal synthesis, a metal salt and organic linker dissolved in polar solvents such as *N,N*-dimethylformamide (DMF), *N,N*-diethylformamide (DEF), acetonitrile, ethanol and, methanol and then heated in autoclaves under autogenous pressure for prolonged periods [58,59]. Another conventional method with great potential, is the hydrothermal route. Aqueous and/or mineralizers are used as reaction medium for self-assembly of organic-inorganic precursors. Tan et al. [60], used hydrogen fluoride (HF) as mineralizing agent to fine tune crystallinity and crystal rate of Fe-based MOFs. Although the use of HF brings about fine crystals, the corrosive nature of the substance limits its wide use. Seo et al. [61], applied HF free synthesis route for MIL-100 by simply increasing concentration of the metal salts and organic linker, and improved crystallinity of the ensuing MOF material. Fang et al. [62], compared different mineralizing agents, i.e. HF, tetramethyl ammonium hydroxide (TMAOH) and sodium carbonate (Na_2CO_3) for the synthesis of MIL-100 and concluded that Na_2CO_3 improved structural properties and resulted in better adsorption of chromium (VI) ions.

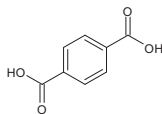
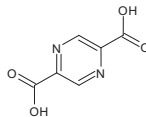
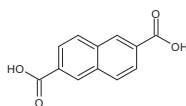
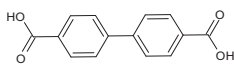
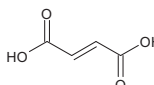
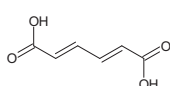
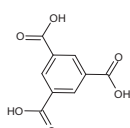
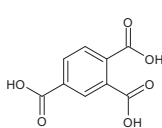
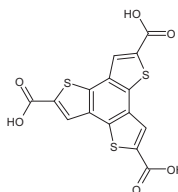
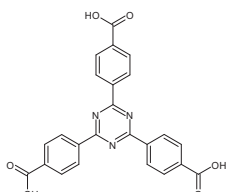
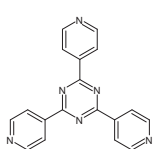
3.2. Unconventional methods

3.2.1. Microwave (MW)-assisted synthesis

This method relies on the interaction between charges of polar solvent molecules and metals with electromagnetic (EM) waves. The interaction in solids produces an electric current which in turn generate heat due to electric resistance of the solid [63]. In solution, polar molecules align with EM fields such that the interaction provides correct orientation and enough energy for collision [56]. This method affords fast crystallization, phase selectivity, narrow particle size distribution, and morphology control [64,65]. Taylor-Pashow et al. [66] synthesized Fe-MIL-101 via MW assisted synthesis by heating a solution of BDC and FeCl_3 in DMF at 150 °C and obtained crystals with diameter of 200 nm and Langmuir surface area ranging from 3700 to 4535 m^2/g , which were used for loading of imaging contrast agents (1,3,5,7-tetramethyl-4,4-difluoro-8-bromomethyl-4-bora-3a,4a-diaza-s-indacene (Br-BODIPY)) and anticancer drugs (ethoxysuccinato-cisplatin (ESCP)). Horcjada et al. [67] obtained octahedral crystals employing MW assisted method in water at 60 °C in 5 min. The prepared materials functioned as efficient antitumoural and retroviral drug carriers. An optimization study done on Fe-MIL-88 A synthesis proved that MW assisted synthesis (MW irradiation of 600 W) in water had faster reaction rates and yielded much smaller crystals (<100 nm) than conventional methods. The study was done at different temperatures (50, 65, 80, 100 or 120 °C) and times (1, 2, 3, 5 or 10 min) [68]. Metzler-Nolte's group investigated the 'breathing' effect of MIL-88B and NH_2 -MIL-88B via microwave synthesis by heating a solution of organic linker and FeCl_3 in DMF at 150 °C and power setting of 200 W for 10 min under stirring [69]. Facile and inexpensive approach for the synthesis of porous MOFs was probed by Aguiar et al. [70] employing modified domestic microwave, output power set at 80 % of the maximum power and temperature at 90 °C. Microwave-assisted self-assembly of Fe-MIL-101 was prepared by

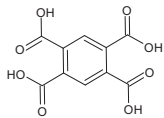
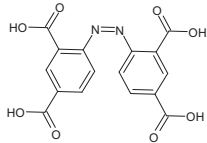
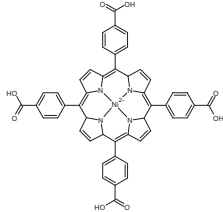
Table 2

Iron-based MOFs with their respective organic linkers.

Fe-MOF					Organic linker	Structure	Reference
MIL-53	MIL-68	MIL-85	MIL-88B	MIL-101	1,4-Benzene dicarboxylic acid		[47] [27] [28]
MIL-101					Pyrazine dicarboxylic acid		[38]
MIL-88C					2,6-naphthalene-dicarboxylate		[48]
MIL-88D					4,4'-biphenyl-dicarboxylate		
MIL-88A					(E)-Butenedioic acid		[48]
MIL-89					Trans, transmuconic acid		[49]
MIL-65		MIL-100			1,3,5-Benzene tricarboxylic acid		[50], [51]
MIL-67					1,2,4-benzenetricarboxylic acid		[52]
PCN-332					benzo-tris-thiophene carboxylate		[23]
PCN-333					4,4',4''-s-triazine-2,4,6-triyl-tribenzoate		[24]
					carboxylic acid 2,4,6-tris(4-pyridyl)-1,3,5-triazine		

(continued on next page)

Table 2 (continued)

Fe-MOF	Organic linker	Structure	Reference
MIL-62	1,2,4,5-benzenetetracarboxylates		[53]
MIL-127	3,3',5,5'-azobenzene tetracarboxylic acid		[54]
MIL-141	nickel(ii) tetracarboxylate porphyrin		[28]

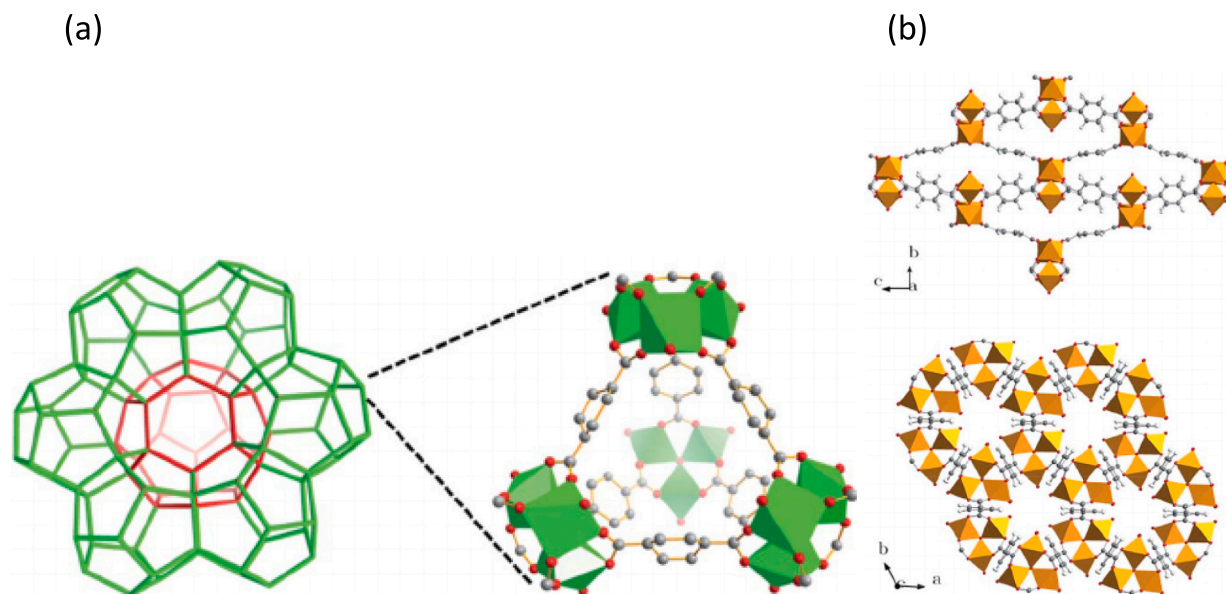


Fig. 2. (a) Depicted pentagonal and hexagonal opening of MIL-101 (Red lines represent the large cavity with hexagonal windows while green shows pores with pentagonal windows, the green octahedral shows metal clusters, red dots are oxygen atoms and grey dots depicts carbon atoms)(Reproduced from Ref. [45] with permission from the Royal Society of Chemistry) and (b) MIL-88B framework (Yellow polyhedral shows the metal clusters, red for oxygen atoms and grey for carbon atoms (Reproduced from Ref. [46] with permission from the Royal Society of Chemistry). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

heating the solution of BDC and FeCl_3 in DMF at 130°C for 2 h and used to make composites with platinum nanoparticles. The catalytic material showed great activity to produce hydrogen and benzimidazoles under visible light. A conversion of 83.4 % of *o*-phenylenediamine resulted in a yield of 79.8 % for 2-methylbenzimidazole, along with almost a complete generation of H_2 (72 %) [71]. This method provides an opportunity for up scaling since it has faster reaction times and uses less amount of solvent.

3.2.2. Sonochemical synthesis

Sonochemical synthesis deals with application of high energy ultrasound (20 kHz to 10 MHz) to initiate and sustain chemical reactions [72]. Contrary to MW assisted synthesis, there is no interaction between molecules and ultrasound waves due to wavelength being larger than

the dimensions of molecules. When ultrasound radiation is applied to liquids, there are bubbles (i.e. cavities) that form, soon as they reach their maximum size, they burst releasing energy with heating and cooling rates of $>10^{10}\text{ K/s}$, resulting in a very rapid synthesis reaction at these cavitation sites where homogeneity takes place [73]. Although acoustic frequency and intensity are the major parameters of this method, choice of solvent is paramount due to varying vapor pressures and chemical reactivity. Additionally, temperature and gas environment are vital [56,74]. Lee et al. [75] prepared Fe-MIL-53 via sonochemical method at 33 % of maximum power which drastically reduced reaction time to 2 h, which is far less than the reaction time of conventional methods. Fe-MIL88 A with high crystallinity and small particle size was prepared under shorter reaction time (2 h) using three different sonochemical methods, namely; ultrasound bath (150 W), ultrasonic pulsed

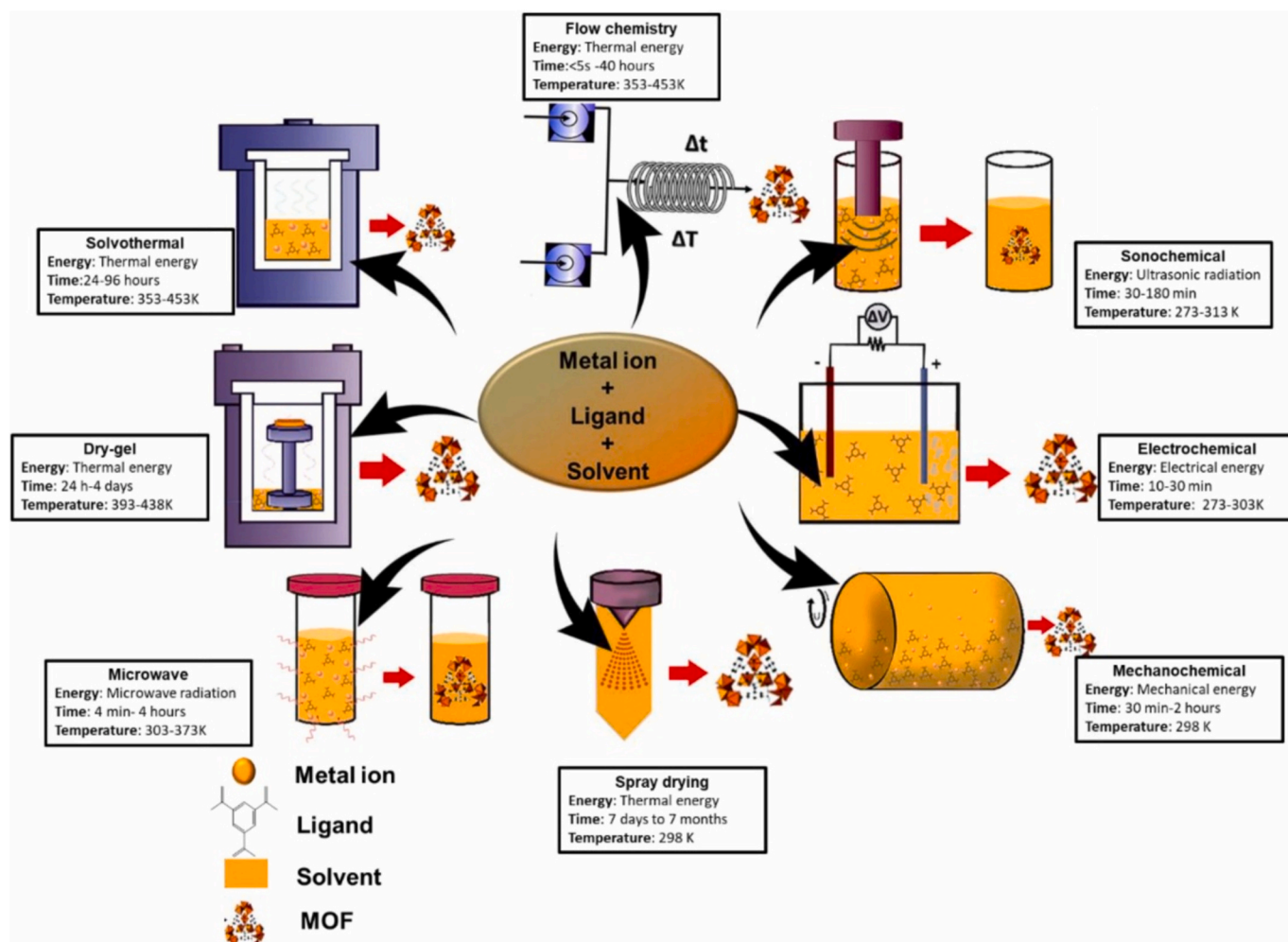


Fig. 3. Synthesis methods and conditions for Fe-MOFs (reproduced with permission from Elsevier) [57].

probe (750 W, 20 kHz and pulse duration of 10s) and continuous probe (20 W and 10 kHz) [76]. Ghanbarian et al. [74] also reported small and homogeneous particles of Cr-Fe-MIL-53 where the particle size was attributed to accelerated nucleation process. The material was prepared by treating a solution of FeCl_3 , CrCl_3 and BDC in water with 80 % maximum power for 15 min.

3.2.3. Mechanochemical synthesis

In this method, the reaction is initiated and sustained by direct absorption of mechanical energy (ME) which breaks intramolecular forces of precursors under solvent free environment. ME is usually supplied by grinding, milling, and mortar and pestle processes. Since solvent use is avoided, insoluble metal precursors which are normally difficult to dissolve in solvents can be used. This method is advantageous because it is environmentally friendly, synthesis times are shorter, and high yields and small particle sizes are obtained. It has been noted that the use of hydrated salts with basic anions and organic reactants proves to be efficient. The addition of a solvent promotes formation of coordination bonds between metal ions and organic linkers. In this regard liquid-assisted grinding (LAG), whereby, the addition of minimal amounts of solvents are added to enhance mechanochemical process [56,77–80]. Kaur et al. [81] prepared pillared-layer intercalated Fe-MOF via mechanochemical grinding by placing FeSO_4 and 4, 4'-bipyridine in a stainless steel container equipped with stainless steel balls with diameter of 10 mm for 15 min at 300 rpm speed. An auxiliary ligand, p-amino-benzoic acid (PABA) was then added in DMF/methanol solution then incorporated into the FeSO_4 and 4, 4'-bipyridine mixture and ground for

10 min. The container was left at ambient conditions for two days. Ball milling method was applied for the synthesis of highly crystalline Fe-MIL-88B with surface area of $261 \text{ m}^2/\text{g}$. A mixture of BDC and $\text{Fe}(\text{NO}_3)_3$ was ground with an agate ball at rotation speed of 500 rpm for 1 or 2 h [82]. Mortar and pestle method was used to prepare Fe-MIL-88 A where FeCl_3 and disodium fumarate were ground for 10 min and the MOF obtained possessed surface area much higher than the solution-based methods [83]. Piloni et al. [84] applied LAG method for the synthesis of high surface area ($1033 \text{ m}^2/\text{g}$) Fe-MIL-100 by grinding H_3BTC (where $\text{BTC} = 1,3,5$ benzene tricarboxylic acid) and $\text{Fe}(\text{NO}_3)_3$ for 1 h in tetramethylammonium hydroxide (TMAOH) solvent. The mixture was ground using 3 mm diameter balls using a vibratory ball-mill.

3.2.4. Electrochemical synthesis

Electrochemical synthesis applies principles of electrolysis, where metal ions are supplied into the process via anodic dissolution and organic precursor is employed as an electrolyte with conducting salt (e.g., Tetrabutylammonium hexafluorophosphate (TBAPF_6) and methyltributylammonium methyl sulphate (MTBS)) [85]. The use of protic solvents prevents the deposition of metal ions on the cathode with evolution of H_2 . The negatively charged organic linkers are driven by the electric field to the anode where they will coordinate with positively charged metal ions [86]. This method can be applied industrially as it affords the possibility of continuous process and high yields. The operating conditions of these methods vary depending on the metal source and organic ligand, the concentration of electrolyte varies between 0.1 M to 1 M, while the typical current density ranges from $1 \text{ mA}/\text{cm}^2$ to 50

mA/cm^2 . pH levels play an important role in the formation of MOFs; typical pH values are between 4 and 8 depending on the system being used. Energy consumption of this method varies depending on the voltage applied which ranges between 1 V to 20 V. Carefully optimized conditions can ensure current efficiency of 80 % [85,87]. Another attractive feature of this method is the possibility of exclusion of corrosive nitrates, perchlorates, and chlorides which can hinder large-scale production. Morphology and crystal size can be controlled by controlling the rate of metal ion dissolution. Faster reaction times and low operational temperatures are additional advantages of this method. Although the method was initially developed for synthesis of copper and zinc-based MOFs by BASF researchers, it has moderately been applied in the synthesis of iron-based MOFs [88]. The attractive properties of this method evoked great interest amongst researchers where some driven the focus to iron-based MOFs. See Table 3 summarizing the process conditions of these materials. Wu et al. [89] reported the direct room-temperature electrochemical synthesis of Fe-MIL-101 and obtained a surface area of $2368 \text{ m}^2/\text{g}$ for the MOF which was comparable to solvothermally obtained materials. Campagnol et al. [90] successfully prepared Fe-MIL-100 for supercapacitor and the material performed better than its carbon counterparts. Elevated temperature (190°C) and pressure (60 bar) electrochemical method was also tested for Fe-MIL-100 [91].

3.2.5. Supercritical CO_2 (ScCO_2) synthesis

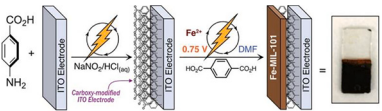
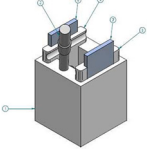
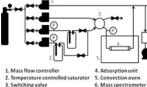
The ScCO_2 method is becoming increasingly used in the food, pharmaceutical, and textile industries as well as nanomanufacturing of different chemicals [92]. With this approach, CO_2 which is a cost-effective, innocuous, and nonflammable solvent, replaces organic solvents. ScCO_2 has unique qualities such as low viscosity, high diffusion rates, and the inability to condense that makes it desirable for the synthesis of porous materials [93]. Although ScCO_2 is popular in oxidation, hydrogenation and hydroformylation processes, it is yet to find popularity in precipitation reactions such as synthesis of MOFs. It is worth noting that many organic linkers are polar and have large molecular weights rendering them insoluble in CO_2 which poses a great challenge in the synthesis of MOFs. Several factors such as the lack of dipole moments, insufficient dielectric constant and low polarizability per unit volume, hinder the use of CO_2 as a solvent [94]. To circumvent this

challenge, mixed solvents (scCO_2 and organic solvents) that may dissociate both polar and nonpolar substances are added [95]. The use of ScCO_2 as a solvent was recently explained and employed in the synthesis of copper hexafluoroacetylacetonate-pyridine derivative adducts [96]. López-Periago et al. [97] extended this method to the synthesis of Fe-MIL-100, ZIF-8, and HKUST-1. For preparation of Fe-MIL-100, Fe (NO_3)₃ and H_3BTC in either 1-ethyl-3-methylimidazolium tetrafluoroborate (emimBF₄) or 1-ethyl-3-methylimidazolium bromide (emimBr) solution was placed in a stainless steel autoclave which was heated via resistance and pressurized using a syringe pump. The surface areas for these materials were found to be 650, 1156 and $1290 \text{ m}^2/\text{g}$ respectively, and these values are comparable to the conventionally obtained results. Fe-MIL-88B was prepared using Fe(NO_3)₃ and H_2BDC in the presence of 2 % v/v dioxane as cosolvent at 20 MPa and 60°C . The product needed intensive washing due to the presence of unreacted precursors. Although characterization by X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the formation of Fe-MIL-88B, the obtained surface area was very low at $60 \text{ m}^2/\text{g}$ [98]. In another study, Kubovics et al. [99] prepared Fe-MIL-100 and Fe(BTC) via ScCO_2 method with addition of dioxane at 70°C and 20 MPa and obtained surface area of 1542 and $1290 \text{ m}^2/\text{g}$ respectively for the MOFs. The prepared materials were used for loading of azelaic acid where Fe-MIL-100 exhibited a loading of $15 \pm 2.0 \text{ wt\%}$ and FeBTC a loading of $17 \pm 3.0 \text{ wt\%}$, respectively.

3.2.6. Spray-drying assisted synthesis

The idea behind spray drying method is simply the synthesis of precipitates from liquids or slurry precursors. Feed solution is atomized into microdroplets which are brought into contact by feed stream and suspended within hot air which evaporates the solvent [100]. The dried precipitates are then collected at the bottom of the gas-stream cyclone. This concept was extended to MOF synthesis where the precursor solutions are atomized into microdroplets which are injected at a certain feed rate and compressed gas at predetermined flow rate ensures contact amongst precursors. The precipitate is then rapidly dried into hollow spherical or compact structures [101]. Fe-BTC/MIL-100 was prepared through spray drying where a solution of Fe(NO_3)₃ and BTC in DMF was injected into the coil flow reactor at a feed rate of $2.4 \text{ mL}/\text{min}$ and temperature of 135°C . The pre-heated mixture was then spray-dried at a

Table 3
Summarized operational parameters and results of electrochemical prepared iron MOFs.

Product	Process conditions	Device	Surface area
Fe-MIL-101	0.5, 0.75, 1.0 or 1.25 V versus Ag/Ag^+ for 2, 6, 10, 14 or 18 h.		$2368 \text{ m}^2/\text{g}$
Fe-MIL-100	10 mA for 30 min at 110°C	 (1) PTFE cell block, (2) perforation in the cell block to situate the reference electrode, (3, 4) PTFE electrode holder masks and (6, 7) stainless steel electrode holders.	
Fe-MIL-100	$2\text{--}20 \text{ mA cm}^2$ for 55 min at $110\text{--}190^\circ\text{C}$	 1. Mass flow controller, 2. Temperature-controlled reservoir, 3. Gas inlet valve, 4. Activation unit, 5. Gas outlet valve, 6. Mass spectrometer	$1335 \text{ m}^2/\text{g}$

flow rate of 336 mL/min and temperature of 180 °C, and the obtained material exhibited surface areas of 1039 m²/g which is comparable to the commercial material Basolite F300 [102]. The obtained surface area of this material was better than the previously obtained surface area of 600 m²/g [103]. In the synthesis of Fe-MIL-88 A and Fe-MIL-88B using fumarate and iron(III) metal salt and terephthalic acid, the combination of the precursors at room temperature results in amorphous material. To overcome this challenge a three-fluid nozzle was adopted to atomize each precursor independently using Mini Spray Dryer B-290, a feed rate of 2 mL/min, a flow rate of 474 mL/min and an inlet air temperature of 180 °C [101].

3.2.7. Flow chemistry synthesis

This method offers an opportunity to commercialize and industrialize MOF synthesis due to it being continuous, rapid, feasible and cost-effective. The most attractive property of this approach is the high degree of precision in the delivery of precursor solutions and total control on synthetic conditions. Bagi et al. [104] looked at the techno-economic analysis of continuous flow chemistry of Zr-MOF-808 and deduced that residence time of 15 min results in productivity of 31,730 kg/m³/day with surface area of ~2000 m²/g. On another study, crystal size of Zr-MOF-808 with respect to flow rate was investigated. The fast rate (0.334 mL/min) in a 5 mL reactor resulted in small crystal sizes (~105 ± 22 nm) whereas slow rate (0.6 mL/min) in a 9 mL reactor resulted in large crystal sizes (~180 ± 19 nm) [105]. HKUST-1 was prepared using microfluidic device where CuO and H₃BTC were dissolved in 1-octanol and supplied into the microfluidic device [106]. The effect of temperature (55, 75, or 95 °C), residence time (60–600 s) and slug volume were investigated using segmented flow microfluidics in the fast synthesis of Fe-MIL-88B. It was observed that shorter residence time and low volume slug results in fine-tuned and narrow crystal sizes [107]. An in-droplet microfluidic method was used to fine-tune the hollow spheres of biocompatible Fe-MIL-88 A MOF. A solution of FeCl₃, poly(vinyl alcohol) and water named “aqueous phase” and one named “organic phase” made of fumaric acid, 1-octanol and tributylamine were separately introduced by two syringe pumps into a perfluoroalkoxyalkane capillary through T-junction into the microreactor coil at 40 °C for 20 min.¹⁰⁸ A copper loaded Fe-MIL-100 was prepared for selective adsorption of carbon monoxide using microwave-assisted continuous flow reactor. Two solutions of FeCl₃, water and DMF, and BTC, water and DMF were separately introduced into a coiled Teflon tubular reactor which was placed in a microwave oven at 250 W, using syringe pumps. The microwave prepared Fe-MIL-100 had better crystallinity, high porosity and surface area as compared to conventionally prepared material. The space time yield of 7717. kg/m³/day was obtained [109].

3.2.8. Dry gel synthesis

An interest in the synthesis of MOFs using gels stems from the flexible structures of the gel which assist in fine tuning of morphologies and porosities of MOFs [110]. The widely used steam assisted dry-gel conversion (DGC) facilitates the conversion of metal ions and organic linkers into crystalline porous materials. This method offers several advantages such as the least amount of waste generated, smaller reactor size, high concentration of precursors, and reduced synthesis durations [111]. Through this method, high crystalline and porous Fe-MIL-100 was prepared in the absence of acid and salt. The obtained material was done under shorter duration (4 days) as compared to the conventional heating method (10 days). The obtained surface area and pore volume were also higher [112]. Microwave-assisted dry-gel conversion was employed for the synthesis of Fe-MIL-100 which offered fast heating, minimal amount of solvent and shorter reaction times. Additionally, this method allows the recycling of the solvent without compromising the yield of the material [113]. In-situ synthesis of glass-fiber Fe-MIL-100 with improve surface area and pore volume was prepared through this method. Fe(NO₃)₃, BTC and water was stirred for 3 h followed by the immersion of glass-fiber into the solution for 1 min. Fe-BTC dry gel

material was evenly spread on the surface of the glass-fiber [114].

3.2.9. Ionothermal synthesis

Ionic liquids (IL) are defined as compounds that are entirely made of ions, with melting point below 493 K and have little to no vapor pressure. This method eliminates the need for sealed systems that can withstand the autogenous pressure generated by conventional solvents and reflux condensers [115]. Ionothermal synthesis is unique because the IL acts as a solvent and template for the synthesis of porous materials [116]. Many common IL are based on alkyimidazolium and pyridinium coordinated to inorganic anions such as bis[(trifluoromethyl)sulfonyl] amides (Tf₂N[−]), tetrafluoroborate (BF₄[−]), hexafluorophosphate (PF₆[−]) and trifluoromethanesulfonate (triflate, OTf). Another unique feature of this method is the elevated concentrations of ions which can be tuned to make new materials [117]. Fe₂X₂(dobdc) (where X = Cl, OH and dobdc = 2,5-dihydroxyterephthalic acid) was prepared through the ionothermal synthesis at 200 °C and 16 h and the obtained surface area were lower than the already reported data. This was attributed to the addition of extra species and increased molecular weight due to the added ions (Cl[−] and/or OH[−]) [118]. Yilmaz et al. [119] prepared Fe-MIL-53 via ionothermal synthesis using a deep eutectic solvent formed from choline chloride and urea at 110 °C for 3 h. The prepared materials were tested for the catalytic activity on esterification of acetic and butanol and 75.7 % conversion of acetic acid was achieved. Table 4 summarizes unconventional methods for Fe-MOF synthesis.

3.3. Machine learning-assisted synthesis

There are no generic synthesis routes for MOFs, even the known synthesis conditions of one MOF cannot be transferred to new MOFs. Several parameters such as solvent type, synthesis time and temperature must be taken into consideration for each MOF. If these parameters are taken as variables, one needs to explore complex chemical spaces constructed by these variables to find sets of synthesis conditions leading to the targeted MOF. This approach is costly and time consuming. To maximize the use of these materials, data science needs to be applied to design and modify synthesis conditions. In recent times, several research groups used MOF descriptors such as pore size, metal source, organic

Table 4

A summary table of unconventional methods for Fe-MOFs synthesis.

Technique	Type of MOF	Reaction conditions	Reference
Microwave	Fe-MIL-88A, -MIL-88B, -NH ₂ -MIL-88 and -MIL-101	150 °C, power: 200 W, 10 min, Yield: 35 %	[66–68,71,120]
Sonochemical	Fe-MIL-53, -MIL88 A and Cr-Fe-MIL-53	33 % of maximum power, 12 min, Yield: N/A	[75,76]
Mechanochemical	Fe-MIL-88A and -MIL-88B	Ball-to-powder ratio 10: 1, 500 rpm, 120 min, Yield: 49.6 %	[81–84]
Electrochemistry	Fe-MIL-101 and -MIL-100	Working electrode: ITO electrode, Reference: Ag wire, Counter: Pt Mesh, CPE: 0.75 V, 14 h, Yield: N/A	[89–91,121]
Supercritical scCO ₂	Fe-MIL-88B, and -MIL-100	200 bar, 65 °C, 10–72 h, Yield: 50 %	[97–99]
Spray-drying	Fe-MIL-100, -MIL-88 A, and -MIL-88B	Feed rate: 2.4 mL/min, flow rate: 336 mL/min, 180 °C, Yield: 78 %	[101,102]
Flow chemistry	Fe-MIL-88B, -MIL-88A, and -MIL-100	Residence time: 20–600 s, 55–90 °C, Yield: 0.6–6 %	[107–109]
Dry gel	Fe-MIL-100	3 h, 150 °C, 800 W, Yield: 81 %	[112,113]
Ionothermal synthesis	Fe-MIL-53	72 h, 110 °C, Yield: N/A	[122]

linker, and surface area to derive machine learning (ML) methods for gas adsorption predictions (see Fig. 4) [123–125].

Several conventional approaches such as the nonlinear or immense combinatorial processes have failed to solve complex problems, which can easily be solved by ML techniques. There are several ML techniques that have been employed in the field of chemistry such as regression, classification, clustering and neural networks. The ability to predict or learn numeric features is called regression in statistical literature and ML. Many real-life situations are modeled as regressions, hence the need for regression techniques. It estimates the independent variable due to the dependent variable [127]. It can be classified as simple linear regression or multiple linear regression. Simple regression is used to predict a response variable from known explanatory variable while multiple linear regression predicts the result of an answer variable, using several explanatory variables [128]. Clustering techniques identify similarities between data sets and groups them into clusters [129]. Neural networks (NNs) are designed to emulate the structure of the brain and have the ability to recognize underlying connections in a set of data. The structure of neural networks is stratified in such a way that neurons in one layer transmit data to several neurons in the next layer, and so on. NNs are designed in a way that, outputs are independent on inputs [130].

Organic and inorganic scientists have employed ML methods to overcome challenging synthesis routes. Ahneman et al. [131] predicted the reaction of C–N cross coupling using neural network ML methods. They further trained a random forest model to predict the performance of the Pd-catalyzed Buchwald-Hartwig reaction. ML methods were employed to predict the reaction outcomes for the crystallization of templated vanadium selenites using information of failed hydrothermal synthesis [132]. Neural networks method was used to predict organic chemistry reactions [133]. Up until recently, ML was used to optimize synthesis routes for HKUST-1 (HKUST = Hong Kong University of Science and Technology) and to determine the significance of different parameters [134]. In another study, Zhang et al. [135] trained ML techniques using 481 adsorption data sets obtained at room temperature and low pressure to predict H₂ adsorption of over 8000 MOFs at

cryogenic temperature (77 K) and high pressure (35 bar). To further confirm validity of the ML methods, H₂ adsorption prediction on four MOFs (namely: Cr-MIL-101, HKUST-1, Al-MIL-53 and OTIBUQ) was performed. The experimental adsorption of the MOFs differed by less than 1.5 % as compared to the predicted one.

While ML has many potential applications on MOF synthesis, the chemical synthesis of these materials is often complex, and the lack of readily available high-quality data and/or readable data makes it more difficult to use [136,137]. There exist some databases such as Cambridge Structural Database (CSD) MOF subset which provides information such as properties including the synthesis method, solvent, organic linker, metal precursor, and topology. The ab initio REPEAT charge MOF (ARC-MOF) database has some information on MOFs which have either been experimentally characterized or computationally generated [138]. Another challenge is the difficulty of interpreting ML models, making it difficult to understand the outcomes predicted by the ML technique [139].

4. Activation strategies

During preparation of MOFs, solvent molecules are normally enclosed in the pores of the structure, in some cases the organic linker is also entrapped. The entrapped molecules compromise the accessible porosity and surface area of the MOFs. To access the internal surface, entrapped molecules should be removed via a process named activation. Three activation methods suitable for Fe-MOFs are outlined, i.e., vacuum activation, supercritical carbon dioxide activation and activation by freeze drying. Fig. 5 represents a simplistic physical phenomenon of each activation. Removing these molecules by conventional heating may compromise the textual properties by collapsing the pore structure of the MOFs. The structure collapses due to high surface tension and capillary forces acting on the MOF structure during liquid-to-gas transformation by solvents with high boiling points.

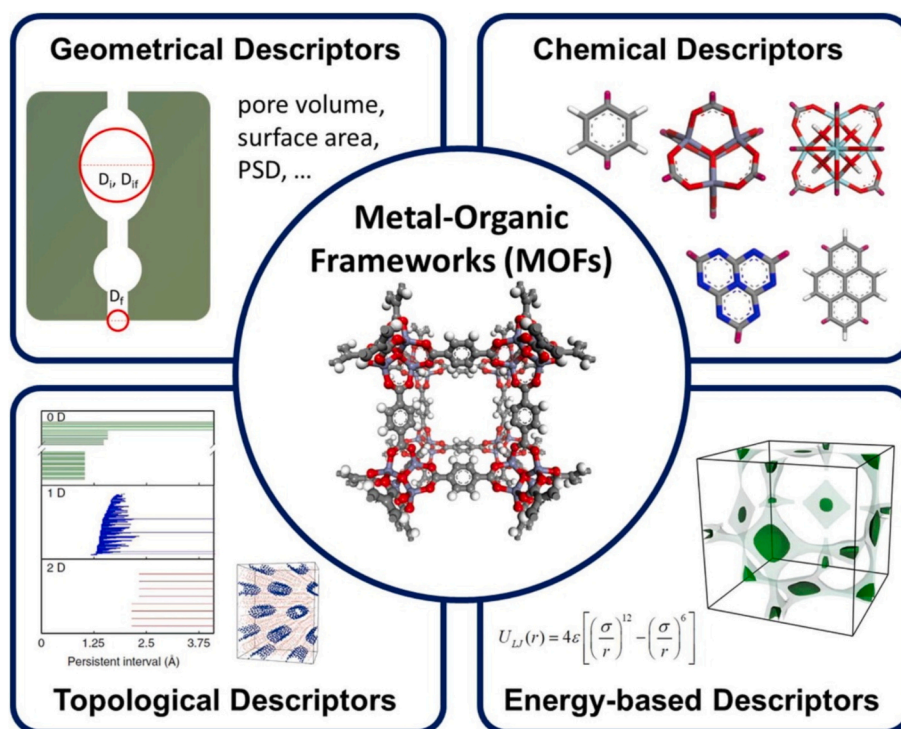


Fig. 4. Various input parameters that can be used for ML algorithms (reproduced with permission from ref.[[126]]).

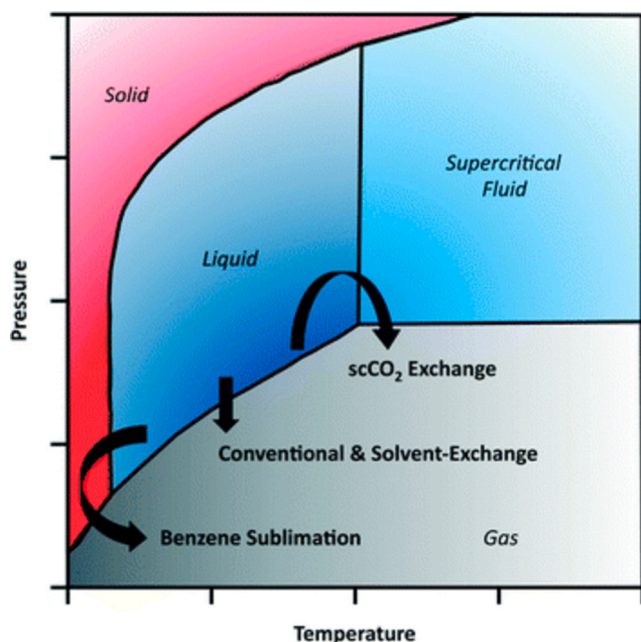


Fig. 5. Representation of phase diagram for activation methods (Reproduced from Ref. [140]) with permission from the Royal Society of Chemistry).

4.1. Vacuum activation

To address the challenge of the collapse of MOF pore structure during vacuum, high surface tension solvent must be exchanged with low surface tension and low boiling point followed by heating under vacuum. Low boiling points are generally attributed to weaker intermolecular forces which results in lower surface tension and capillary forces. Solvent exchange can be performed by soaking the sample or by reflux over prolonged periods. The operating temperature should be above the boiling point of the solvent but below the decomposition temperature of the MOF [140–142]. Yang et al. [143] used vacuum thermal activation on Fe-MIL-101 to evaluate the catalytic activity of the MOF on persulfate activation. Maksimchuk et al. [44] investigated vacuum drying of Fe-MIL-101 at 120 °C and showed that it enhances the catalytic activity of the MOF. Another study revealed that good styrene conversion (87.2 %) and epoxide selectivity (54.4 %) were achieved for vacuum dried Fe-MIL-101 [45]. A vacuum dried Ce-mediated Fe-MIL-101 was investigated for degradation of norfloxacin and shown promising results [144]. An enhanced H₂ adsorption (0.47 wt% at 298 K and 7 bar) was obtained for vacuum dried Fe-MIL-88B [145]. Ma et al. [69] investigated the effects of solvent exchange and vacuum drying on Fe-MIL-88B and NH₂-Fe-MIL-88B and observed shrinkage (20 % and 33 % respectively) of the structure upon evacuation of the solvents. Yoon et al. [146] observed that the removal of terminal water molecules by vacuum increases the Fe(III) coordinating unsaturated metal sites (CUS) thus increasing the catalytic activity of Fe-MIL-100.

4.2. Supercritical CO₂ activation

Vacuum activation requires elevated temperatures, which can be detrimental to MOFs with fragile frameworks. Supercritical CO₂ activation (ScCO₂) is more clement activation technique as compared to conventional heating and vacuum activation. This activation is environmentally friendly, cost effective and scalable, hence there is great interest in it. ScCO₂ does not go through the liquid-to-gas transition, which then eliminates the surface tension and capillary forces effects. Solvent exchange step is still required for ScCO₂ activation. Solvents (such as methanol and ethanol) that form a homogenous mixture with ScCO₂ and are compatible with the instrument are desirable for this

activation [140–142]. In this method, sample is placed in ScCO₂ drying vessel where the solvent is exchanged with CO₂ at pressures above 7.3 MPa and temperatures above supercritical temperature of CO₂ (31 °C). CO₂ can be purged after every hour and replaced with fresh CO₂ and this can be done in triplicate [147,148]. It is important to ensure that temperatures do not drop below zero as the adsorbed moisture can freeze thus increasing capillary forces and surface tension. Additionally, this method is advantageous as it reduces particle-to-particle agglomeration [149]. Nelson et al. [150] were the first to demonstrate the use of ScCO₂ activation on MOFs as this was inspired by activation done on aerogels. The MOFs of interest showed a dramatic increase in surface area, IRMOF-3 (IR = isorecticular) increased by 285 folds while IRMOF-16 increased by 4 folds. Matsuyama et al. [93] also obtained increased surface area for Fe-MIL-53 and Fe-MIL-100 via ScCO₂ activation.

4.3. Freeze drying

If the high boiling point, high surface tension and capillary forces solvents are replaced with low boiling points solvents (such as benzene) that can be evacuated by freeze drying, similar results to ScCO₂ can be obtained. If temperatures are set below the freezing point of the solvent under vacuum, then the solvent can be evacuated from the MOFs via sublimation process. Avoiding the liquid surface tension, increasing structural integrity of the MOF, thereby preserving the mesopores and micropores [140,151]. Zhang et al. [152] investigated activation of FIR-3 (FIR = Fujian Institute of Research) by freeze drying cyclohexane which is more ecofriendly as compared to the toxic benzene. Oven drying and freeze drying of shaped Fe-MIL-100 was reported and was found that surface area decreased significantly for oven dried samples as compared to freeze dried samples. [153] The 40 % MIL-100 (1265 m²/g) loaded shaped sample had decreased surface area of 846 m²/g while the oven dried sample had surface area of 32 m²/g. Fe-MIL-100 was tested as a HIV drug carrier, the drug loaded MOF was freeze dried and maintained similar textual properties as the heat dried samples [154].

5. Functionalization

MOFs are hybrid materials which consist of two or more constituents (i.e. metal ions and organic linker) and possess a high degree of tunability. Varying either the metal ion, organic linker or both, yields infinite possibilities to manipulate and control various properties such as pore size and pore volume [155]. MOFs can be functionalized in the same pot of synthesis by introduction of additives or other chemicals. The use of two or more linkers or metals has been proven to enhance the functionality and activity of MOFs. To achieve multi-metallic MOFs, metals of similar characteristics (ionic radii, coulombic charge and coordination geometry) must be used [156]. If these characteristics are ignored, an independent crystal with varying properties from the parent structure will arise. The large differences in geometry will lead to lattice disorder. The open unsaturated metal sites of the parent metal facilitate the incorporation of the secondary metal thus resulting in bimetallic MOFs [157]. Tanasaro et al. [158] investigated the addition of Fe(III) ion in synthesis of Cr-MIL-101 and Cr-MIL-88B. Fe(III) was added at varying percentages (5, 10, 15, 25, and 33 %), when iron content was below 15 %, the material preserved the octahedral MIL-101 morphology, however, at above 15 % the material was dominated by hexagonal MIL-88B morphology. Characterization by TEM/EDS proved that the prepared material were mixed metal MOFs (Cr-Fe-MOF) rather than individual Cr-MOF or Fe-MOF. Furthermore, Fe-MILs are only known to crystallize under DMF solvent and are amorphous under water as solvent. Mixed metal MOFs catalysts have gained great interest due to their synergistic effects. Hu et al. [159] prepared one pot synthesis of bimetallic MIL-101 construct from 2-amine-1,4-benzenedicarboxylate ligands and trimeric Al³⁺/Fe³⁺ octahedral clusters which afforded a mesoporous MIL-101-NH₂ series MOF framework. Higher catalytic activity was obtained for one-pot deacetalization-Knoevenagel

condensation reaction at relatively low temperature. Bimetallic Fe-Mg-MIL-88B was prepared for adsorption of arsenate from water. The material displayed exceptional absorption capacities, comparatively quick sorption rates, a wide pH operating range, robust anti-interference, extraordinary regeneration and structural stability, and a high degree of cycling stability, all of which point to their viability and enormous potential in the complex environmental water [160]. Several bimetallic MOFs have been reported for various applications, e.g., Fe₂Zn-MIL-88B for selectivity and detection of triclosan, FeAl-MOF for adsorptive removal of multiple dyes and FeMg-MOF for synthesis of xanthenes and removal of heavy metals [161–165].

On the other hand, synthesis of mixed-linker MOFs depends on the use of linkers with similar coordination geometries but different functionality. The parent morphology of the targeted MOF can be maintained while distribution of functional groups is not organized. Lammert et al. [166] reported a high throughput synthesis of single and mixed linker chromium MIL-101 derivatives. Mixed linker material of 2-bromoterephthalic acid and 2-nitroterephthalic yielded highly crystalline material. The effects of different metal sources (CrO₃, CrCl₃, Cr(NO₃)₃9H₂O) were also observed, where CrCl₃ showed better crystallinity. Fe-MIL-143 was prepared using mixed linkers, i.e. dicarboxylate linkers (1,4-benzenedicarboxylic acid - BDC or its amino functionalized derivative) and tricarboxylate linkers (4,4',4''-[1,3,5-triazine-2,4,6-triyl]tribenzoic acid - TATB or its nitro functionalized derivative). The prepared material exhibited high crystallinity [167]. Mixed linker microporous Fe-MIL-142 A and mesoporous MIL-143 have been synthesized using terephthalic acid and 1,3,5-benzenetrisbenzoic acid. [168] Additionally, functionalized linker may be used to modify the properties of the MOFs; however, the functional group must not interact with the metal clusters and should be compatible with the solvent used [169]. A large number of research groups [69,120,170–173] have employed the amine functionalized terephthalic acid linker for various applications. For instance, Van Tran et al. [174] used NH₂-MIL-88B for adsorption of oxytetracycline, the adsorption was facilitated by the hydrogen bonding from the amino group. Ha et al. [175] performed theoretical investigation about physisorption and chemisorption of CO₂ on Fe-MIL-88B and its derivatives (Fe-MIL-88B-X (X = -H, -OH, -CH₃, -F, -NH₂ and -CN)). It was shown that, the presence of X functional groups favors chemisorption of CO₂, but physisorption is more favorable for the introduction of cyanide.

Functionalization can also be introduced via post synthetic procedures whereby chemical modification is performed on the as-prepared materials rather than on the precursors. The functional groups and the reaction conditions need to be compatible with the targeted material. Functionalization can be directed to the organic linker or metal clusters via covalent bonding, dative bonding or post synthetic deprotection [176].

Covalent modification refers to the addition of the functional group via formation of covalent bond under either homogenous (in solution) or heterogenous conditions (solid-gas interaction). In these modifications, linkers with several substituents in the 2-position on the benzene ring are preferred. These substituents which are normally called “handles” or “tags” are vital for functionalization via covalent modification [177]. This method is advantageous since crystallinity of the materials is preserved and products can easily be analyzed using ¹H NMR. Lee et al. [178] used 1,3,5-tris(4-ethynylbenzonitrile) benzene with a pendant alcohol group in 2-position, connected to Ag(I) ions to construct MOF material. Trifluoroacetic acid anhydride vapors were used to functionalize the MOF via covalent bond formation on the pendant alcohol. Functionalization of Fe-MIL-101-NH₂ was achieved by formation of Schiff-base reaction with isatin and metalation with cobalt [179]. The activity of the prepared heterogenous catalyst was tested for Ullmann-type, Buchwald-Hartwig, Hirao, Hiyama and Mizoroki-Heck cross-coupling reactions. Attachment of Schiff base (2-pyridine carboxaldehyde (PyCHO)) on aminated Fe-MIL-101 was achieved by coordinating the pyridyl to nickel salt followed by imine condensation in the

presence of Ni(PyCHO)Cl₂ methanolic solution. The prepared material shown great efficiency on dimerization of ethylene to 1-butene [180]. Javanmardi et al. [181] modified Fe-MIL-101-NH₂ by covalently coordinating benzyl alcohol carbon to nitrogen of the amine group. A dative bond was also formed between the oxygen atom of the hydroxyl group of the alcohol and the vacant d orbitals of the metal (Fe). In another study, functionalization of Fe-MIL-NH₂ with long-chain amines (ethylenediamine (*en*) and 1,2-bis(3-aminopropylamino)ethane (*bap*)) for drug delivery systems was carried out [182]. The release of naproxen drug was studied on the functionalized MOFs, Fe-MIL-NH₂-*bap* showed lowest release at pH = 7.5 which was attributed to higher number of amine groups which formed hydrogen bond with the drug. Fe-MIL-88B-NH₂ was covalently modified using β-cyclodextrine for slow release of alendronate drug [183]. Fe-MIL-88-NH₂ functionalized with salicylaldehyde-supported lutidinium ionic liquid Schiff base was successfully employed for efficient removal of arsenic ions from aqueous effluents [184]. Table 5, shows the addition of functional groups on amine functionalized BDC.

Dative bond modification takes place when an additive (post modified agent) forms a dative bond with the organic linker/metal in homo- or heterogenous conditions. [185] A metal can be added to coordinate with the organic linker or organic linker added to coordinate with unsaturated metal sites at secondary building units. Chui et al. [186] found out that the aqua ligands in the pores of HKUST-1 can be replaced by pyridines. It was noted that this cannot be achieved via solvothermal methods, it can only be achieved post synthetically. The resulting MOF showed great crystallinity and thermal stability. Fe-MIL-101 unsaturated iron ions with cobalt or copper to activate persulfate for extraction of Orange 7 (AO7) in water [187]. The increase in wt% of the added transition metal resulted in decomposition of the MOF crystal structure. The adsorption of AO7 was low due to the decreased surface area.

Post synthetic deprotection involves the introduction of protected or “masked” functional on the organic ligand, then the ligand is coordinated to metal clusters under conventional solvothermal environment. To obtain the targeted functionalization, the protected group is removed via post synthetic conditions [176]. The termed “protection-complexation-deprotection” was first coined by Yamada and Kitagawa when insitu deprotection of organic ligand was observed [188]. The organic ligand, 2,5-dihydroxyterephthalic acid (H₂dhydbdc) was protected with 2,5-diacetoxyterephthalic acid (H₂dacodbdc) for synthesis of Zn(dhydbdc) (bpy)]₄DMF MOF. The acetoxy groups were deprotected resulting in dhydbdc ligand and MOF with unbound hydroxyl groups.

6. Applications

6.1. Fe-MOFs as catalysts

Catalysts provide an alternative reaction pathway by lowering the activation energy of the reaction, this significantly lowers the energy demands of several chemical reactions. Interest in Fe-MOFs as catalysts has escalated due to the abundance of unsaturated metal active sites, chemical stability, ease to separate and recyclability. Catalytic reactions by Fe-based MOFs can be classified into three groups, i.e. photocatalysis, Lewis acid catalysis and oxidation catalysis.

Photocatalysis is based on harvesting visible light and converting it into chemical energy. This is possible because Fe-based MOFs are made of light harvesting sites and catalytic sites. Photocatalysis follows the following summarized route: light is adsorbed by catalyst and converted into charge-separated excited state, followed by photogenerated electrons that move to the surface of the reactants which in turn leads to oxidative degradation of organic pollutants or reduction of CO₂ [189]. Organic linkers on Fe-Based MOFs show no activity towards visible light, thus making the oxo-iron (Fe—O) clusters responsible for photocatalytic activity. Laurier et al. [190] were the first to show the photocatalytic activities of Fe-based MOFs, they demonstrated that Fe-MIL-100, Fe-MIL-88B and Fe-MIL-101, as well as amino functionalized MIL-101 and

Table 5

Post synthetic covalent and dative functionalization of organic linkers of MIL-88B and MIL-101.

Organic linker	MOF type	Functionalization	Synthesis conditions	Reference
	MIL-101		isatin-Schiff-base + MIL-101-NH ₂ , Reflux in ethanol, 24 h (1) (1) + Co(OAc) ₂ 4H ₂ O, Reflux in ethanol 24 h	[179]
			NiCl ₂ + 2-pyridine carboxaldehyde + MIL-101-NH ₂ , r.t, 72 h	[180]
			benzyl alcohol + MIL-101-NH ₂ , reflux in CHCl ₃ , 72 h	[181]
			2-bis(3-aminopropylamino)ethane + MIL-101-NH ₂ , reflux in n-hexane, 80 °C, 12 h	[182]
			Ethylenediamine + MIL-101-NH ₂ , reflux in n-hexane, 80 °C, 12 h	
	MIL-88B		salicylaldehyde-supported lutidinium chloride + MIL-88B-NH ₂ , reflux in ethanol, 24 h	[184]

MIL-88B are all active for photocatalytic degradation of Rhodamine 6G. Fig. 6.a shows visible light photocatalytic activity of the unsubstituted Fe-MOFs with titanium dioxide (P25) and iron(III) oxide (Fe₂O₃) as reference materials. The amino-substituted material showed less activity at wavelength greater than 350 nm as compared to the unsubstituted MOFs (see Fig. 6.b). Oxidative degradation of tetracycline under visible light radiation using Fe-MIL-53, MIL-100 and MIL-101 as catalysts was reported. To test photocatalytic activity, tetracycline was first adsorbed by the MOFs in the absence of light followed by photocatalytic decomposition under visible light. MIL-101 had an excellent performance at 55.1 % adsorption and 87 % photodegradation, followed by MIL-100 with 44.1 % adsorption and minimal degradation, and finally 10.5 % adsorption and 30.2 % photodegradation by MIL-53. Although MIL-101 showed better activity, the degradation rate was very slow with only 10.8 % of tetracycline degraded after 1 h and total of 3 h to reach 87 % [191]. In recent study, comparison of amino-substituted Fe-MOFs (NH₂-MIL-101, NH₂-MIL-88B and NH₂-MIL-53) and un-substituted MOFs (MIL-101 MIL-88B and MIL-53) activity towards CO₂ reduction to formate (HCOO⁻) was performed under visible light (300 W, Xe lamp) and triethanolamine (TEOA) as sacrificial agent. The coordinated unsaturated Fe clusters of MIL-101 enhanced its catalytic activity as compared to the other MOFs. The amine-functionalized MOFs showed better activity due to the existence of dual excitation pathways, i.e., excitation of amine group followed by induced electron transfer to the

metal [192]. Ai et al. [193] also proved the photocatalytic activity of Fe-based MOF, when they showed degradation of RhB by Fe-MIL-53 in the presence of oxidizing agent (H₂O₂), under visible light irradiation (500 W, W lamp). The combination of MIL-53/H₂O₂/visible light completely degraded RhB (10 mg/L) at pH = 5. The increase in concentration of H₂O₂ from 5 to 20 mM increased degradation efficiency from 77 to 98 %. The effect of pH was also studied, the increase in pH from 5 to 9 showed a decrease in degradation which was attributed to instability of H₂O₂ in alkaline medium.

In the case of Lewis acid catalysts, accelerated chemical reactions are due to the UMCs which act as electron pair acceptors. Several studies on the use of Fe-based MOFs as Lewis acid catalyst on the conversion of organic molecules have been conducted. Zhang et al. [195] employed Fe-MIL-100 on acetalization of aldehydes and it showed better catalytic activity (85 % yield at 80 °C, 2 h) compared to commercial resin and zeolite. This activity was attributed to the Fe (III) Lewis acid sites. Yang et al. [196] used this as opportunity to employ Fe-MIL-101 as Lewis acid catalysts for reaction of benzaldehyde with methanol at 25 °C for 1 h to form benzaldehyde acetal. The benzaldehyde conversion reached 94 %, which was attributed to dispersion of active metal sites with mild acid strength and pore size, which accommodated the substrate. In another study, the removal of tetracycline hydrochloride from contaminated water in an ultrasound/Fenton process was reported [197]. Fe-MIL-101, Fe-MIL-53, Fe-MIL-88B and α-Fe₂O₃ were used as Lewis acid catalysts.

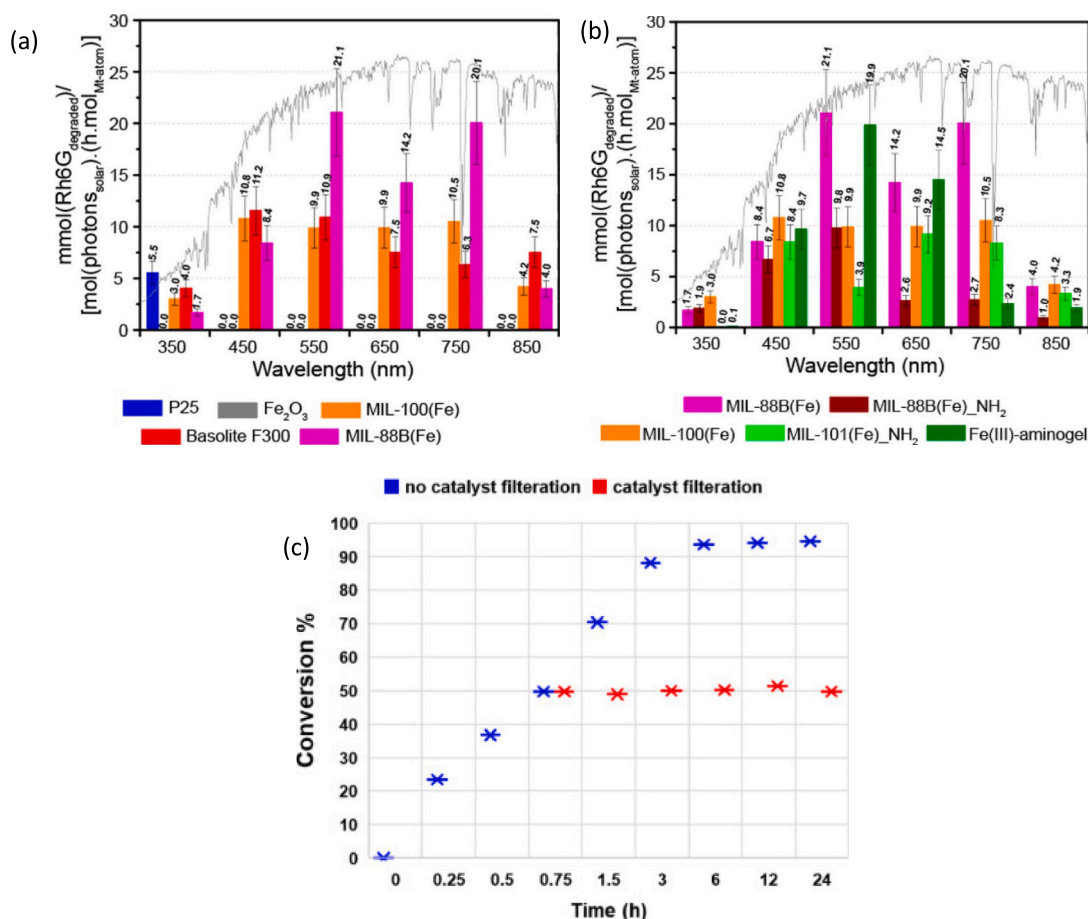


Fig. 6. Solar spectrum and photocatalytic degradation of Rh6G at different wavelengths (a) Fe-MOFs (b) Aminofunctionalized Fe-MOFs. (Reprinted (adapted) with permission from ref. [190] Copyright © 2013, American Chemical Society). (c) Fe-MOF catalytic conversion of benzyl alcohol as function of reaction time (blue) and after removal of catalyst (red). (Reprinted (adapted) with permission from ref. [194]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fe-MIL-88B had higher catalytic activity due to the high presence of Lewis acids sites as compared to the other MOFs studied in that work.

Oxidation catalysis by Fe-MOFs has been largely applied to Fenton oxidation of alcohols, alkanes and alkenes providing an alternative for transition metals and the use of peroxides as an oxidant. The Fe—O clusters, symmetry, pore dimensions and flexibility of organic linkers are responsible for the catalytic activity of MOFs. Ghasempour et al. [194] used Fe-MOF prepared from symmetrically incompatible building blocks (Fe_3O cluster) for oxidation of benzyl alcohols. The catalyst showed almost 100 % selectivity towards benzaldehyde and had high yield (91.9 %) in a short reaction time (3 h) (see Fig. 6.c). Selective oxidation of alcohols to ketones and/or aldehydes was investigated employing Fe-MIL-53-graphene nanocomposites as catalyst [198]. Selectivity of aldehydes or ketones was 99 % and the catalyst was recycled four times without loss of activity. Bhattacharjee et al. [199] investigated the effective catalysis of Fe-MOF-74 for oxidation of phenol towards catechol and hydroquinone. The heterogeneous catalysts had 60 % conversion of phenol and 68 % and 32 % selectivity towards catechol and hydroquinone respectively. Various Fe-MOFs were tested for oxidation of benzyl alcohol to 2-phenylquinazolin-4(3H)-one. Amongst the tested MOFs (MIL-88B, MIL-101, MIL-126, MOF-907, -908 and 909), MIL-100 showed the best performance for conversion of benzyl alcohol, which was attributed to high Fe-cluster active sites [200].

6.2. Fe-MOFs in biomedicine

MOFs have aroused a great interest in biomedicine due their ability

to load high amounts of drugs and capability of offering long release times (see Fig. 7) [58]. Although mesoporous silicas have been used extensively as drug carriers, MOFs surpass them by four folds in terms of drug loading and release times [201]. The compensating ions create strong electrostatic fields which in turn enhance interaction with the adsorbate leading to high drug delivery at low pressures [67]. MOFs are advantageous because of their flexible frameworks, ease of functionalization and narrow pore sizes. Ability to tune porosity allows control of drug release [202].

Férey et al. [204] were the first to prove drug delivery with MIL-based MOFs. MIL-100, MIL-101 and MCM-41 were investigated for Ibuprofen loading and release rate. Fe-MIL-101 drug loading was four times that of MCM-41 and releasing times were much slower (6 days as compared to 2 days). Compared to other metal-centered MOFs such as Cr-based MOFs, which are known to be toxic and not ideal for human consumption, Fe-based MOFs are more attractive due to their non-toxic nature. Bernini et al. [205] investigated adsorption and release of ibuprofen in Fe-MIL-53, Fe-MIL-100 and Fe-MIL-101 and compared it to other biocompatible MOFs such as CDMOF-1, MOF-74 and BioMOF-100, using Grand Canonical Monte Carlo simulations. Interaction of Ibuprofen and MIL-53 and MIL-101 is shown in Fig. 8. Fe-MIL-101 and Fe-MIL-101-NH₂ were tested for imaging and drug delivery and high loading of imaging contrast and anticancer drugs was demonstrated [66]. Furthermore Fe-MIL-53 nanocrystals were fabricated for loading and delivery of anticancer drug doxorubicin (DOX), and high loading and long release times (45 % released over 72 h) were observed [206]. Amino functionalized Fe-MIL-88B was prepared for detection of alpha-

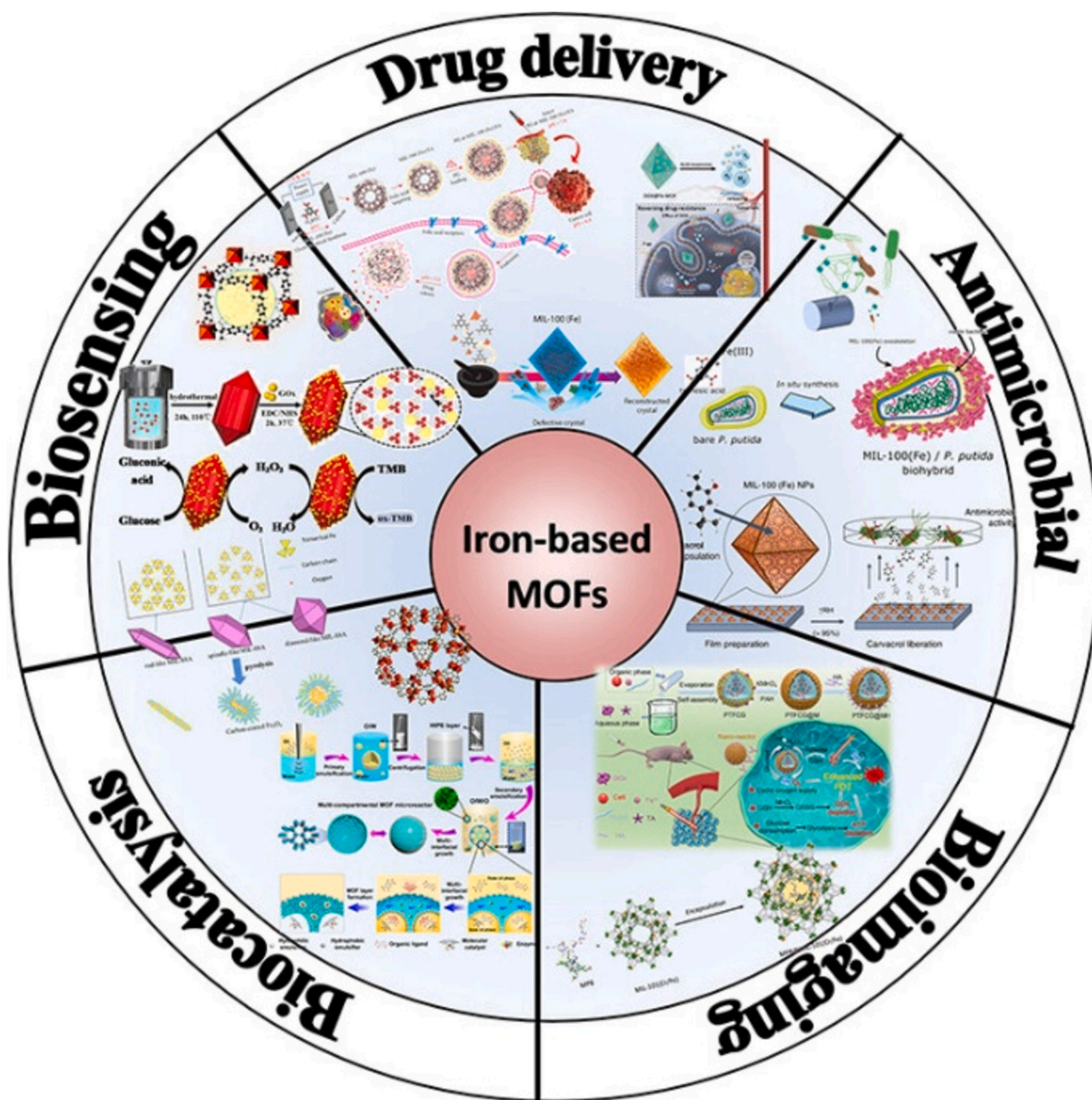


Fig. 7. Iron-based metal-organic frameworks applications in biomedicine (Reproduced from Ref. [203], Originally published by and used with permission from Dove Medical Press Ltd.).

fetoprotein in human serum and the obtained results were in agreement with those obtained by enzymes [207]. Wyszogrodzka-Gawel et al. [208] prepared Fe-MIL-101-NH₂ MOF for loading of isoniazid which was tested for tuberculosis treatment and magnetic resonance imaging. The use of functionalized MIL based MOFs has seen great interest as drug carriers and imaging agents. In this regard, Gao et al. [209] used a functionalized Fe-MIL-53-NH₂ as a carrier for anticancer drug 5-fluorouracil and further incorporated fluorescence imaging agent 5-carboxy-fluorescein and targeting reagent folic acid.

6.3. Fe-based MOFs for gas storage

There are traditional methods that have been used effectively for gas storage, methods such as high-pressure tanks and employing multistage

compressors for the storage system. However, these methods are not cost effective and often pose great danger to their surroundings [210,211]. There is a need for cheaper alternative solutions. Various porous materials such as zeolites and activated carbons have been tested for gas storage but they also fall short on several occasions. Although zeolites have well distributed pore diameters which is desirable for hydrogen storage, some researchers have related low hydrogen uptake of this material to their low surface areas and pore volume [212]. The wide pore size distributions of activated carbons and the low surface area in some cases renders them undesirable for gas storage [213].

MOFs have provided an edge over these materials since they have high surface areas, large pore volumes, ease of functionalization, tunable pore structures and structure flexibility. For MOFs to be applied in gas storage, they should have accessible internal pores, must be

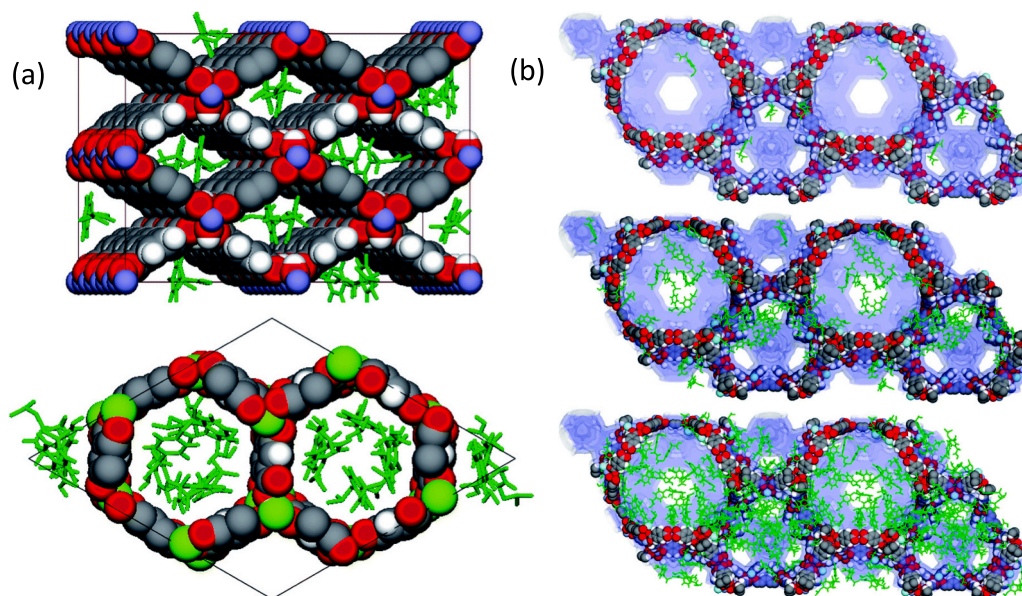


Fig. 8. Simulated interaction of ibuprofen with (a) Fe-MIL-53 and Mg-MOF-74 and (b) Fe-MIL-101 at varying loadings. Green sticks represent ibuprofen. (Reproduced from Ref. [205] with permission from the Royal Society of Chemistry). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

thermally stable and should interact with guest molecules via local polar adsorption sites on their inner surface [16]. Paz et al. [214] noted that organic linker plays a vital role in adsorbate interaction. Furthermore, it has been reported that UMCs provide binding sites for guest molecules [215].

Adsorption of methane (CH_4), carbon dioxide and hydrogen were tested on Fe-MOF-235, the material showed high adsorption of methane which was attributed to high pore volume and high number of open metal sites at 298 K and 10 bar [216]. Lee et al. tested adsorption of methane on Cr-MIL-100 and Fe-MIL-100 at 50 bar, and deduced that the chemical make-up of the material does not influence the adsorption of methane at high pressures as it is with hydrogen [217]. High pressure adsorption (65 bar) of CH_4 was recorded on Fe-pbpta (where $(\text{H}_4\text{pbpta} = 4,4',4'',4''')\text{-(1,4-phenylenbis(pyridine-4,2-6-triyl))\text{-tetrabenzoic acid}}$) with high surface area of $4937 \text{ m}^2/\text{g}$. The MOF exhibited a gravimetric uptake of $369 \text{ cm}^3/\text{g}$ at 35 bar and 298 K and volumetric capacity of $192 \text{ cm}^3/\text{cm}^3$ at 65 bar and 298 K, it was observed that lowering temperature

to 273 K showed a volumetric uptake increase from 116 to $167 \text{ cm}^3/\text{cm}^3$ which is the opposite to other MOFs such as HKUST-1, Ni-MOF-74 and NU-111 (where NU = Northwestern University) (see Fig. 9) [218]. Three Fe-MOFs, i.e. VNU-21, VNU-22 (where VNU = Vietnam National University) and Fe-NDC (where NDC = 2,6-naphthalene dicarboxylic acid) with 1D channels were tested for CH_4 storage. VNU-21 which had high surface area ($1440 \text{ m}^2/\text{g}$) and pore volume ($0.58 \text{ cm}^3/\text{g}$) exhibited high volumetric uptake of $182 \text{ cm}^3/\text{cm}^3$ at 65 bar and 298 K [219].

To understand adsorption at the molecular level, high-resolution powder x-ray diffraction (HR-PXRD) was used to show the interaction of CO_2 and $\text{Fe}_2(\text{BDP})_3$ (where $\text{H}_2\text{BDP} = 1,4\text{-bis(1H-pyrazol-4-yl)benzene}$) [220]. It was shown that at pressures below 1 bar and temperatures at 273 K and 298 K, the unit cell volume of the MOF tends to decrease by $\approx 0.4 \%$. When pressure is increased to 8 bar the unit cell volume increased by 0.26 % at 273 K and 0.16 % at 298 K. A stepwise adsorption of CO_2 in micropores and mesopores of PCN-53 was studied experimentally and computationally. The study showed that CO_2 first

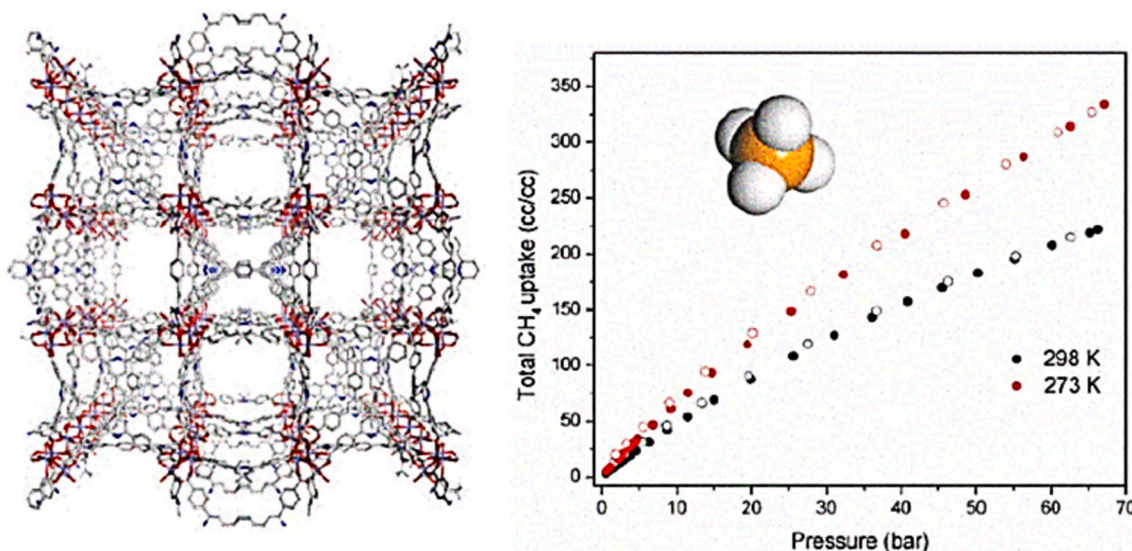


Fig. 9. Square-octahedron (soc) topology Fe-pbpta and volumetric uptake of methane. (adapted from ref. [218]).

fills the micropores then adsorb on the walls of the mesopores, and eventually fills in the mesopores [221]. IISERP-MOF30 (where IISERP = Institute of Indian Science Education and Research, Pune) exhibited CO₂ adsorption of 3.3 mmol/g at 298 K and 1 bar, with a CO₂/N₂ selectivity of ≈ 26 . The MOF also showed a 3.3 mmol/g uptake of CH₄ at 298 K and 10 bar and CH₄/N₂ selectivity of ≈ 4 [222]. Adsorptions done at different temperatures and adsorption cycles are shown in Fig. 10. Mahdipoor et al. [223] prepared three Fe-MOFs (i.e. Fe-MIL-53, Fe-MIL-101 and Fe-MIL-101-NH₂) and achieved 9.3, 8.6 and 13 mmol/g uptake of CO₂ respectively. The amino functionalized MOF had high adsorption due to addition of chemisorption of CO₂ to NH₂. SNU-64 (where SNU = Shaanxi Normal University) was used for purification of CH₄ from ethylene (C₂H₂), ethane (C₂H₄) and CO₂. Although the MOF adsorbs moderate amount of these gases, it showed great ideal adsorbed solution theory (IAST) adsorption selectivities for C₂H₂/CH₄ (35.8), C₂H₄/CH₄ (24.3), and CO₂/CH₄ (16.7) at room temperature [19].

Hydrogen storage in MOFs has aroused great interest, owing to the fact that it is a better energy carrier, and it is environmentally friendly since it only releases water upon combustion or when used in a fuel cell. A study on H₂ and Fe-MOF interaction by DFT showed that adsorption is facilitated by 1 σ of the H₂ molecule and d_{xz} orbital of the Fe-MOF cluster [224]. Intrigued by the 'breathing' effect of Fe-MIL-88B, Yurduşen et al. [145] optimized porosity of the crystals which then enhanced the adsorption of H₂ at room temperature. In a study by Lupu et al. [225] Fe-MIL-101 with surface area of 2823 m²/g had maximum H₂ adsorption of 5.1 wt% at 77 K and 100 bar. Huynh et al. [48] simulated H₂ adsorption by Fe-MIL-88(A/B/C/D) at pressures below 100 bar using grand canonical Monte Carlo simulations. MIL-88B showed high absolute and excess gravimetric uptake of 5.15 wt% and 4.03 wt% respectively at 77 K, and 0.69 wt% and 0.23 wt%, respectively at room temperature. Kinetics study of H₂ adsorption was performed on pelletized and composite pellets with aluminum on Cr-MIL-101, Fe-MIL-100, MOF-5, and HKUST-1. The study concluded that there is a correlation between the diffusivity of H₂ and the porosity of the material [226]. NU-1501-Fe MOF with ultra-high surface areas (7140 m²/g) and pore volume of

2.90 cm³/g showed H₂ adsorption of 13.2 wt% at 77 K and 100 bar [227]. Neutron diffraction data and inelastic neutron scattering spectroscopy were used to show the interaction of H₂ with the open metal sites (Fe²⁺) on Fe-BTT (where BTT = 1,3,5-benzenetris-tetrazolate)(see Figure 11.a). The open metal sites enhanced H₂ adsorption at room temperature and showed affinity towards CO₂ adsorption over N₂ (see Fig. 11.b,c for H₂ and CO₂ adsorptions) [228].

7. Challenges of transitioning MOFs towards industrial application

MOFs are very exciting porous materials owing to their unique properties and thousands of these materials have been synthesized. Nevertheless, very few have been applied industrially due to scale up difficulties and associated costs of synthesis. The industrial manufacturing of MOFs has been hampered by several issues, including the usage of large amounts of solvents (some very corrosive), extensive energy demands with prolonged reaction periods, and expensive precursors [229]. Additionally, MOFs are produced as powders which also hinders their industrial applications. Separation of powder from solvents require expensive centrifugation method [230]. Materials in powder form pose intrinsic safety hazards like those to respiratory health issues [231]. Shaping increases the costs of MOFs thus further hindering their industrial use.

The cost of MOF synthesis is mainly associated with the cost of metal salts and organic linkers, reaction vessels and post synthetic modifications [232]. In conventional synthesis, pressure-sealed reaction vessels with high chemical resistance and heating equipment (with precise temperature control) that must be in use for several days contribute to exorbitant costs. The autogenous pressure of the reaction vessels and hazards of precursors adds to the cost of safety. Filtration, washing and drying procedures further increase the cost of synthesis. The use of corrosive solvents such as DMF is detrimental to the equipment and respiratory health of the people. Apart from the initial cost of MOFs, economic viability, which includes things such as supply chains

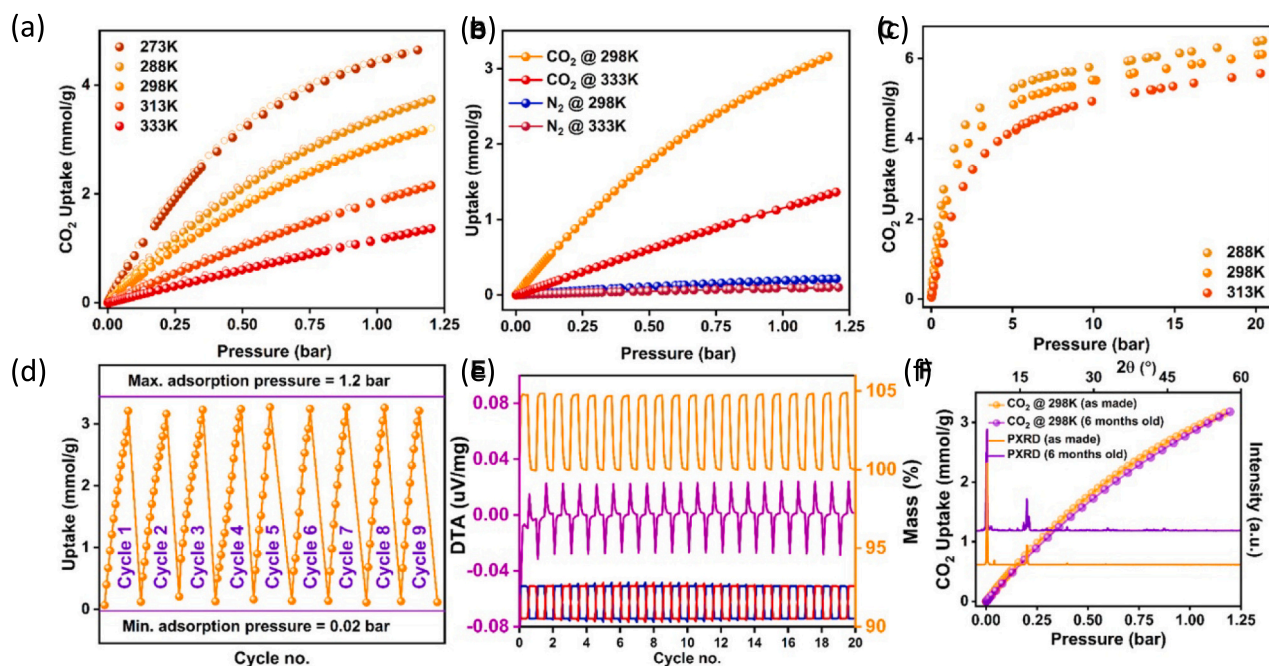


Fig. 10. (a) CO₂ adsorption of IISERP-MOF30 at various temperatures under standard pressure. (b) CO₂ and N₂ adsorption of IISERP-MOF30 at various temperatures under standard pressure. (c) Volumetrically measured high-pressure CO₂ adsorption isotherms. (d) Iso-cycling experiment showing the retention of working capacity on adsorption-desorption cycles. (e) TGA cycling showing the recyclability of IISERP-MOF30 up to 20 cycles. (f) PXRD and CO₂ adsorption of the fresh sample vs the 6-month-old sample showing no loss in the crystallinity as well as the working capacity of MOF. (Reprinted (adapted) with permission from ref. [222] Copyright © 2023, American Chemical Society).

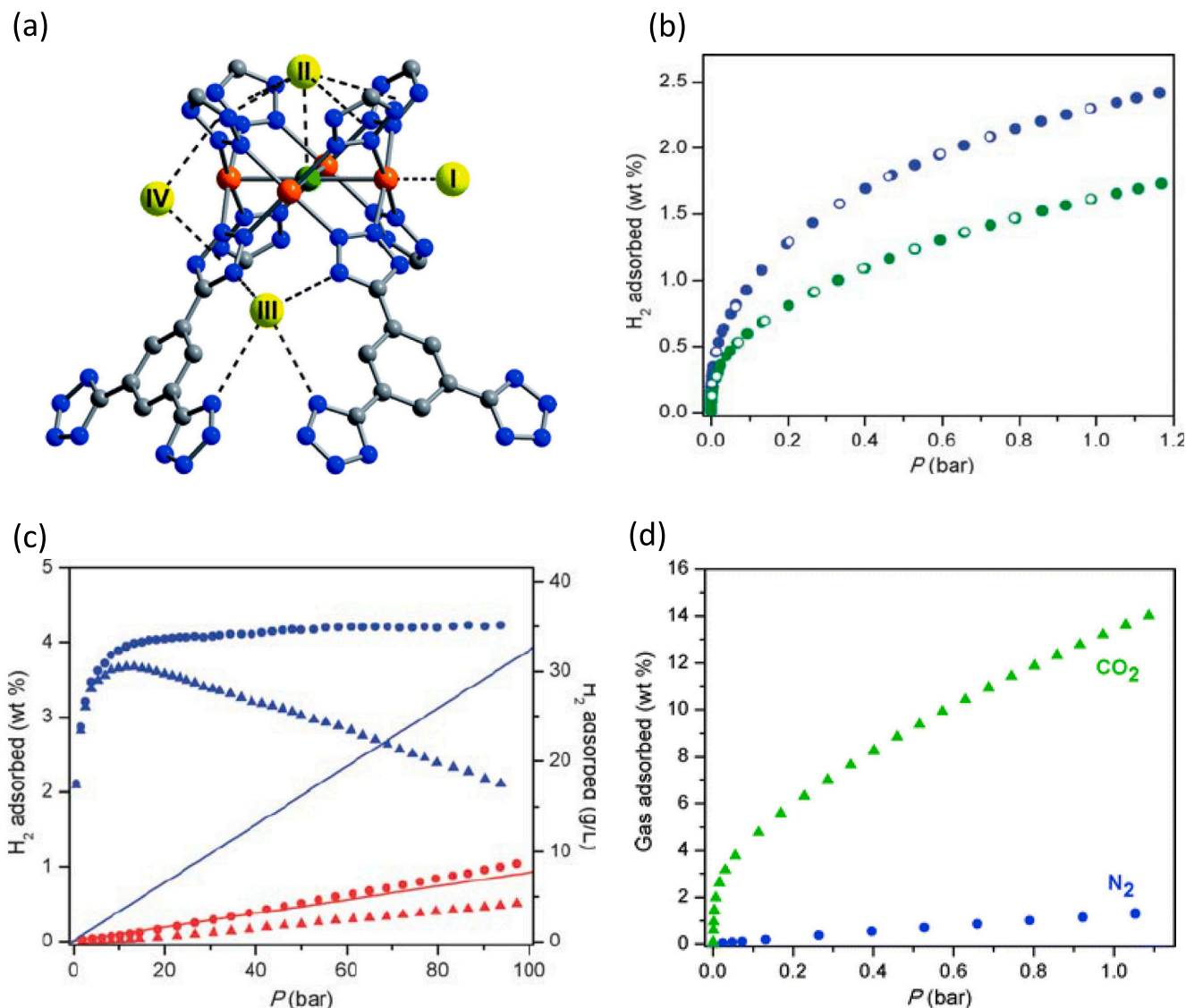


Fig. 11. (a) Four open metal metal sites from H₂ binding, (b) H₂ adsorption at 1 bar and 77 K (blue) and 87 K (green), (c) Hydrogen high pressures adsorption at 77 K (blue) and 298 K (red) and (d) CO₂ and N₂ adsorption at 1 bar and 298 K (All images Reproduced from Ref. [228] with permission from the Royal Society of Chemistry). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

logistics, energy consumption during production and market competition possesses another challenge. Many industries have established well-working industrial processes that may not readily adjust to new materials without significant modifications or capital investment in new technology. Therefore, it is imperative to overcome these challenges for the advancement of MOFs in practical applications. This will be beneficial for the progress of Fe-MOFs.

8. Remedial actions for Fe-MOF scale-up and commercialization endeavors

The production costs and scaling up issues for MOFs could be resolved by using waste materials, enabling industrial applications [233]. Recycling waste to create goods with added value has become a common goal, particularly in the chemical industry where a move towards green chemistry is essential. Organic precursors for MOF synthesis can be extracted from waste such as polyethylene terephthalate (PET) waste bottles while metal precursors can be obtained from battery waste (Cu, Co and Li), coal flyash (Al and Fe), and mine waters (Al, Fe, Ca, Mg etc) [234–237]. Iron-MOFs can be derived from PET-BDC linker and waste Fe metal source, which offer environmental preservation and

waste beneficiation. Previous studies have demonstrated that the quality of the material is not jeopardized when using inexpensive precursors produced from waste [238].

The cost of industrial MOF synthesis is majorly affected by the cost of organic linkers such as terephthalic acid (H₂BDC). BDC can be extracted from PET bottles, thereby reducing the cost of MOF synthesis and reducing the environmental effects of waste plastic [239]. Depolymerization of PET waste follows a typical procedure whereby PET flakes are mixed with ethylene glycol (EG) and H₂O then heated to temperatures above 200 °C [240]. Jung and co-workers prepared Fe-MIL-53 using PET-BDC, for synthesis of magnetic porous carbons [241]. The use of H₂BDC derived from PET waste to afford several MOFs, namely Al-Fum, Cr-MIL-101, Zr-Uio-66, Fe-MIL-101 and Fe-MIL-88B was investigated [242]. The as-prepared MOFs exhibited high surface areas, as well as enhanced water and heat adsorptions. Fe-MIL-88B was prepared by depolymerizing PET with water and NaOH followed by addition of iron salt and methanol. The obtained product contained Fe-MIL-88B crystals and PET derived H₂BDC [243]. The one pot synthesis of Fe/Cr-MIL-88B from PET waste and steel pickling wastewaters for adsorption of Zr(V) ions was reported [244].

Coal fly ash which is made up of mullite mineral (3Al₂O₃·2SiO₂) and

amorphous aluminosilicate glass has attracted attention on the synthesis of aluminum-based MOFs. Carbons derived from coal fly ash derived fumarate MOF were reported. The prepared fumarate MOF had surface area of 1236 m²/g and pore volume of 1.9 cm³/g which is comparable to the commercial MOF [236]. In another study Al-fumarate MOF prepared from coal fly ash was used for adsorption of CH₄ [245]. The prepared MOF adsorbed between 21.93 and 20.69 cm³/g at 298 K and 1.0 bar were comparable to commercial Al-FumMOF (22.13 cm³/g). Al-MIL-53 was prepared from coal fly ash for the removal of organic dyes from wastewater [246]. The use of aluminum from coal fly ash for value added products paves a way for the use of other metals that makes up this waste material to contribute to circular economy. Iron which is part of coal fly ash has potential to drive industrialization of iron-based MOFs.

8.1. Utilization of waste feedstocks for Fe-MOF synthesis

Several waste iron sources could be explored for Fe-MOF synthesis. Acid mine drainage waters (AMD) is a result of the reaction between sulfide-bearing minerals and oxygen and water. This process already happens naturally, but mining may accelerate it by exposing sulphide-bearing rocks to air and water [247]. Acidophilic bacteria called *Thiobacillus ferrooxidans* is known to catalyze the oxidation of sulphide bearing rocks thus accelerating AMD formation [248]. Calcium containing minerals would normally neutralize the acidic water, but in their absence, the acid percolate heavy metals from the waste deposit. Precipitation may then flush the acidic solution into groundwater, surface water and the environment in general [249]. There are over 120 coal and gold abounded mines in South Africa where their shafts have accumulated AMD. The Witwatersrand region (Gauteng province, South Africa) has shafts that decanted over 20 million liters of AMD per day on average and the amount can go up to 60 million liters per day on rainy seasons. As of 2023 approximately 12 million liters of AMD is partially treated while the rest flows into the surrounding areas [250]. The concentration of metals in AMD varies as per mining activities, Masindi et al. investigated the sustainability of AMD treatment in South Africa by collecting AMD from a coal mine, the collected AMD had 8000 mg/l of iron. On another study, AMD collected from tailings dams from a gold mine had 16,000 mg/kg of iron [251]. AMD is a risk to the environment because it contains high concentrations of metals like iron, aluminum, manganese, and other heavy metals. By precipitating with alkaline solutions, metals from AMD can be recovered as hydroxides. This technique allows for simple pH adjustment, is practical from an economic standpoint, and may be used for large operational units [252,253]. de Almeida Silva et al. [254] optimized selective precipitation of iron from AMD by using NaOH or NaHCO₃ to produce iron (III) as ferric hydroxide/oxyhydroxide. The pH was adjusted to 3.6 and Fe²⁺ oxidized to Fe³⁺ by compressed air. Iron and aluminum have also been precipitated from AMD via a two-step process [255]. Iron was precipitated at pH = 3.5–4, then filtered as hydroxide, the pH of the filtrate was then adjusted to 6–7 to precipitate aluminum. Three neutralizing agents, i.e. NaOH, Na₂CO₃ and Ca(OH)₂, were tested for recovery of Fe, Al, and Mn [256]. It was deduced that precipitation of the metals is independent of neutralizing agent used but dependent on the pH. High purity goethite, hematite, magnetite, and gypsum were prepared from selective precipitation of Fe^{2+/3+} from AMD [257]. This study proved the beneficiation of AMD into valuable products and how it can benefit circular economy. Hu et al. [258] investigated the pilot-plant study of the recovery of Fe³⁺ via the H₂O₂-NaOH process. Selective precipitation is the most common method used in the recovery of valuable metal ions from AMD, however, it has a tendency to produce large amounts of waste water [259]. Table 6, summarizes other methods used on recovery of valuable metals. Careful consideration of the economic value of the metals, their concentrations in AMD, and cost of machine operation should be applied before recovery. For context, electrochemical and membrane technologies are not feasible for metal extraction in large scales due to complicated

Table 6

Methods for selective recovery of Fe(II/III) ions from AMD.

Extraction methods	Description	References
Electrochemical reactions	Direct oxidation of Fe(II) on a graphite electrode immersed in quinone compounds (oxidizing agents) at 120 mA/L was performed successfully.	[262]
Ion exchange	Effective removal of sulphates, Fe, Al, Mg, Ca, and Zn by two-cell bioelectrochemical setup.	[263]
	Amberlite IRC-76 which is a macroporous acrylic resins, had good selectivity of Fe(III) over Cu(II), Ni(II) and Zn(II) in the pH range 2.0–2.3	[264]
	Faujasite zeolite prepared from coal fly ash and natural clinker has better selectivity for the removal of iron from AMD.	[265]
Membrane extraction	Mesoporous silica (SBA-15) was utilized on direct contact membrane distillation for the recovery of copper which also resulted in precipitation of Fe and Al	[266]
Solvent extraction	A copper free AMD was used for the extraction of iron using AliCy as extractant.	[267], [268]
Adsorption Extraction	Basic oxygen furnace sludge was employed as an adsorbent for heavy metals in AMD.	[269]

processes and high operating cost. Numerous studies have shown that recovered metals from AMD have potential to produce high quality products just as commercial grade metals. Leaching-hydrothermal method was used for extraction of iron for synthesis of mesoporous Fe-MIL-100 [260]. The prepared material with surface area of 1341 m²/g adsorbed 280.84 mg/g at 298 K of norfloxacin. However, AMD is an underexplored feedstock for MOF synthesis [261].

Spent pickling liquors (SPL) from steel industry contain high concentrations of heavy metals such as zinc and iron which pose environmental threat. SPL is generated when acids are used to remove iron oxides from the surface of the metal sheets, wires, strips and other arears [270]. To reduce the effects of this liquors several methods have been used to extract metals and/or acids such as diffusion dialysis, oxidation in fluidized bed, spray roasting, ion exchange, solvent extraction, and pyro-hydrolysis [271]. Solvent extraction is the most used method to recover acids and metal precipitates. Common solvents used to extract Fe³⁺ include methyl isobutyl ketone (MIBK), tri-n-butyl phosphate (TBP), di(2-ethylhexyl) phosphoric acid (D2EHPA), and amines [272]. Agrawal and Sahu [273], used Cyanex 923 in kerosene with different additives (NaCl, Na₂SO₄, (NH₄)₂SO₄, NaNO₃, and (NH₄)₂NO₃) for extraction of iron from chloride SPL. The addition of NaCl increased iron recovery to 79.9 % from 36.4 %. Sinha et al. [272] extracted iron and zinc from SPL by cosolvent of tri-isooctyl amine (TiOA) or tris(2-ethylhexyl) amine (TEHA), in the absence and presence of di-(2-ethylhexyl)phosphoric acid (HDEHP). Extraction of zinc and iron was done by Hu et al. using Cyanex 923 in isooctanol and sulfonated kerosene. Five extraction and stripping cycles were needed to achieve 92.50 % of zinc. SPL has high concentrations of iron which can be beneficial for synthesis of iron-based MOFs. It has potential to increase the chance of industrial applications of these materials.

The steel industry contains several waste materials that contain high concentrations of iron which can be beneficiated into valuable products. Shahrashoub et al. [274] recovered iron from direct reduction iron sludge via acid digestion and precipitation. The recovered iron was used for the synthesis of magnetic nanoparticles. Iron was recovered as iron hydroxide from iron ore tailings by acid digestion and precipitation for synthesis of magnetite [275]. Iron has also been extracted from mill scales through acid (sulfuric acid) digestion [276]. Recovery of iron from mill scales was performed by carbon monoxide reduction to obtain metallic iron [277]. There are many other iron wastes that can be explored for MOF synthesis.

9. Conclusions

Thousands of MOFs have been discovered to date, with Fe-MOFs making up a small number of these MOFs. The low toxicity, versatility and high abundance of iron are key reasons to further explore iron-based MOFs. The strategies for architectural design and synthesis of diverse Fe-MOFs still need much attention. This review provides a comprehensive overview of the rapid development of Fe-MOFs, covering their synthesis, activation, functionalization, selected applications, challenges, and remedial actions. Solvothermal and hydrothermal methods are the most common synthetic routes for Fe-MOFs, but unconventional methods have emerged due to their short duration, controlled crystal sizes, and potential industrial applications. MOF synthesis can further be enhanced by machine learning which offers an opportunity to design and predict material properties quickly by exploring out-of-sight data. Various properties such as porosity and surface areas of MOFs can be explored at very short time intervals.

Open pores are a key property of MOFs, and three activation methods: vacuum activation, supercritical carbon dioxide, and freeze drying have been explored to ensure permanent porosity. Vacuum activation has gained popularity due to its ease of use and cheap equipment, while ScCO₂ has allowed MOFs to reach unprecedented levels of porosity. The stability of Fe-MOFs under different solvents and temperatures needs urgent attention. That can be attained through functionalization, with efforts mainly directed at organic linker modifications and post-synthetic methods using UMCs (unsaturated metal centers) to improve hydrogen adsorption and thermal and hydro stability. Functionalization of these MOFs has further enhanced their applications in drug delivery, imaging and biomedicine. Several Fe-MOFs have shown great drug loading and suitable release times. Several studies have shown that PSM of UMCs and active organic linkers as well as impregnating open cavities with active metals can enhance catalytic efficiency. Although several studies have shown the catalytic activities of Fe-MOFs and their functionalized structures, advanced understanding of catalytic active sites at the atomic level is required.

There are a few challenges that hinder industrial applications of Fe-MOFs such as cost of synthesis, environmental and health concerns. The precursors, solvents, and industrial equipment contribute to the exorbitant cost associated with MOF synthesis. The amount and type of solvents used are of great concern to the environment and the equipment. Some solvents such as DMF are very corrosive thus limiting their use, other reagents such as hydrofluoric acid used in hydrothermal synthesis are very corrosive. Deriving MOFs from waste materials such as waste PET, spent lithium batteries, coal flyash have been demonstrated. This can contribute to alleviating the cost of synthesis of MOFs.

10. Future outlook

Sustainable chemistry focuses on designing products and processes that minimize environmental impact and enhance efficiency. This includes designing chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Designing processes that minimize waste production. Maximizing the incorporation of all materials used in the process into the final product and using safer and affordable solvents and avoiding synthesis conditions that use high temperatures and/or pressures. Recycling waste to generate organic linkers, use of iron waste and use of water as solvent provides a green chemistry solution. AMD and waste Fe sources from the steel industry have great potential in not only contributing to lessen the burden on the environment but also to produce value-added Fe-MOFs more cheaply.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Henrietta W. Langmi reports financial support was provided by South African Research Chairs Initiative (SARChI) of the Department of Science and Innovation (DSI). Nicholas M. Musyoka reports a relationship with Nottingham Ningbo China Beacons of Excellence Research and Innovation Institute that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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