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Synthesis of Metal Organic Framework (MOFs)

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Abstract

A significant class of materials for energy storage, CO_2 adsorption, alkane or alkene separation, and catalysis, the metal organic frameworks (MOFs) are porous crystalline materials of one-, two-, or three-dimensional networks made up of metal ions or clusters and multidentate organic linkers via coordination bonding. This paper provides a quick overview of the current MOF synthesis techniques in order to acquaint novices in the field of chemical engineering with the fast-growing MOF research projects. Microwave-assisted, mechanochemicals, Dry gel conversion, ionothermal, and microfluidic synthesis methods will be introduced, beginning with the traditional solvothermal or hydrothermal synthesis. Only exemplary MOF structures that may be created with common organic compounds of 1,4-benzenedicarboxylic acid and 1,3,5-benzenetricarboxylic acid in combination with metallic nodes of Zn^{2+}, Cu^{2+}, Cr^{3+}, Al^{3+}, Fe^{3+}, and Zr^{4+} will be included. Included is the synthesis of the extensively studied zeolite imidazole framework (ZIF) framework, ZIF-8. By carefully preparing stepwise manufacturing methods, MOF crystal formation can be regulated, and MOFs can be modified in hitherto unachievable ways. Over the past century, organic chemists have created a library of potent techniques that enable the complete synthesis and intricate modification of complex compounds. Our premise is that by developing comparable multistep methods, complete synthesis may likewise be achieved for customized porous materials. This will make it possible for MOFs to be designed rationally, which is one of the main objectives of numerous researchers in the field.

Keywords: Electrochemical Synthesis, Solvothermal or Hydrothermal Synthesis Microwave, Metal Organic Frameworks (MOFs), Zeolitic Imidazolate Frameworks (ZIFs), and Mechanochemical Synthesis

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1. Introduction

A family of crystalline organic and inorganic hybrid compounds known as MOFs (metal organic frameworks) is created by the coordination of metal clusters or ions with organic linkers, where frameworks with zinc, copper, chromium, aluminum, zirconium, and other elements are frequently formed using bivalent or trivalent aromatic acidic compounds or N-containing aromatics [1-2]. MOFs have become intriguing materials for a variety of applications in storage of energy [3-4] , CO_2 adsorption [5] , hydrocarbon adsorption/separation [5-6]. catalysis sensor [7] , magnetism [8] , delivery of drugs [9] , luminescence [9] , and others due to their high surface areas, high pore volumes in uniformly sized pores, and high metal content. Synthesis, characterization, surface modification, and applications have all been covered in recent in-depth review articles on MOFs [10] . Our goal is to offer more detailed, engineering-focused information about MOF material synthesis. Stock and Biswas review paper [11] is highly suggested for an improved understanding of the subject. Up until now, MOFs have typically been made using electrical heating in small-scale hydrothermal or solvothermal synthesis procedures, which can take hours to days to complete. The main focus was on creating excellent single crystals suitable for structural investigation under diluted liquid phase conditions. Other synthesis techniques, such as microwave- assisted [12-13] , sonochemical [14] , electrochemical [15] , and mechanical-chemical [16] , were later used in an attempt to reduce the synthesis time & create smaller, more homogeneous crystals.

Additionally, limited synthetic scale-up for industrial uses was carried out. In order to achieve a high yield of sturdy products for commercial uses, thorough research into the optimization were occasionally conducted the optimization of procedures to MOF synthesis in these investigations [17] . We look into MOF synthesis techniques documented in the freely available literature in this brief overview. Only the MOF structures shown in Scheme 1 are prepared using an organic ligand, such as H_2BDC (1,4-benzenedicarboxylic acid) and its functionalized form (H_2BDC-NH_2; 2-methyl-1,4-benzenedicarboxylic acid, H_2BDC-$(OH)_2$; 2,5-dihydroxy-1,4-benzenedicarboxylic acid) or H_3BTC (1,3,5-benzenetricarboxylic acid). Because of its strong open framework structure enabling permanent permeability and straightforward structure method for porosity management, MOF-5, that Yagi et al. described in Nature in 1999, garnered a lot of interest [18] . This sparked

active research into MOF applications to heterogeneous catalysis [19] and gas storage. But after its poor stability hydrothermal was discovered, focus turned to HKUST-1 [20] due to its superior thermal stability, strong stability against moisture, and relatively simple synthesis. MIL-101 appears to be the most widely used material for adsorption and catalysis at the moment. Ferey et al.'s MIL-101 ($Cr_3O(F/OH)(H_2O)_2[C_6H_4(CO_2)_2]_3$) is a strong MOF with a large surface area that is usually made hydrothermally with a chromium salt and H_2BDC is formed in an autoclave at autogenous conditions of pressure [21] .

MIL-101 is special because it is constituted of highly concentrated coordinately unsaturated Cr-sites that are accessible to catalysis and adsorption, and it shows remarkable stability towards moisture and other chemicals [22]. MIL-101 with a However, it is highly challenging to acquire BET with a surface larger than 4,000 m2/g because the impurities generated by unreacted H_2BDC or recrystallized H2BDC are present both inside and outside the MIL-101 pores. NH2-functionalization in MOF-5 results in IRMOF-3, that gives the MOF-5 framework basicity and increases CO_2 capture capacity [23]. It also offers sites of catalysis for the Knoevenagel condensation. Zeolitic imidazolate structures are a class of materials with micropores that a variety of neutral framing structures are formed by connecting Co or Zn atoms via Ditopic imidazolate's N atoms. Similar to the $(Al)SiO_2$ frameworks of (alumino) silicate zeolites, the frameworks of ZIF compounds can be represented by T(Im)2 (Im=imidazolate and its derivative, T=tetrahedrally coordinated metal ion); in particular, the T-Im-T angle of 145o is close to the Si-O-Si angle commonly found in zeolites. ZIFs materials can feature structures like rho, sod, gme, lta and ana that are similar to the typical zeolite topology. Because of its great thermal and chemical stability, ZIF-8 is the most studied structure among the ZIFs [24] . Its synthesis is also covered in this study.

2. MOF Synthesis Approaches

Metal-organic frameworks (MOFs) synthesis has considerably developed in the last twenty years, resulting in the establishment of rapidly expanding options of synthetic approaches to control crystal size, morphology, porosity, and scalability [25]. They can be generally divided into traditional solvothermal procedures and an array of alternative or non-conventional approaches that are aimed at the shortening of the synthesis period, enhancing the yield, and increasing the ability to control the material properties. Later, main synthesis routes of MOFs such as solvothermal synthesis, microemulsion-based, and microwave-assisted synthesis among others will be discussed with illustrative examples found in the literature.

2.1. Conventional Solvothermal Synthesis

MOFs have been produced solvothermal in vials on a limited scale using traditional electric heating. MOF-5 is made up of octahedral Zn_4O clusters connected by ditopic linear BDC. Its chemical formula is $Zn_4O\cdot(BDC)_3\cdot$guest molecules, which are produced at low yield using a diffusion synthesis process [18]. H_2BDC was deprotonated and reacted with Zn^{2+} ions when triethylamine diffused into a zinc nitrate solution and H_2BDC in chlorobenzene. It has been superseded by a high-yield solvothermal approach that produces crystalline MOF-5 by heating a $Zn(NO_3)_2\cdot4H_2O$ and the H2BDC in a DEF (N,N-diethylformamide) solution mixture at 105° C i [26]. IRMOF-3 within a closed vessel belongs to the isoreticular MOF structures, where BDC-NH_2 connects Zn_4O clusters. An intramolecular hydrogen bond between an aromatic amino hydrogen atom and a carboxylate oxygen atom stabilises the benzene ring's in-plane position with the Zn_4O ring, according to the geometry for IRMOF-3 [27] . Similar solvothermal conditions can be used to synthesise IRMOF-3: substrate mixture of Zn $(NO_3)_2\cdot6H_2O$ & H_2BDCNH_2 dissolved in DMF (N, N-dimethylformamide) or DEF, and the reaction mixture is heated in an oven at 9°C for 24 hours. at room temperature MOF177, HKUST-1) was also reported [28]. Synthesis of MOF-5 (and MOF-74) with high yield. Despite the numerous positive properties of Zn (II)-based MOFs, their limited industrial applications are probably due to their poor stability against moisture and protic solvents. This led to attempts to create frameworks that were more chemically resistant & long-lasting.

Ferey & colleagues have studied porous chromium-benzenedicarboxylate, also known as MIL-101 (MIL stands for Material of Institute Lavoisier) [42]. Frey and colleagues have studied MIL-101 (MIL stands for Material of Institute Lavoisier) [42]. MIL-101 is normally made hydrothermally using Cr salt, H_2BDC and a very small quantity of HF hydrothermally in an autoclave set at 220°C with autogenous pressure for 8 hours. MIL-101 is a solid MOF. It is composed of coordinately unsaturated Cr-sites in high concentration that are accessible for adsorption and catalysis, as well as uniform mesoporous accessible through two types of microporous windows. There have been numerous attempts to improve the MIL-101 product's purity by strict three step purification that includes temperature-programmed synthesis to create large residual carboxylic acid impurity crystals that are easier to isolate [29] the addition of tetraethyl ammonium hydroxide to encourage the dissolution of H_2BDC [30] , and double filtering through two distinct filters, solvent treatments using water and heated ethanol and, lastly, aqueous fluoride-ion NH_4F solutions [31] . Low product yields were also caused by the development of impurity phases [32].Therefore, in the near future, it would be very beneficial to develop a different synthesis technique for MIL-101 with a streamlined purification phase is known as a paddle-wheel unit [33]. Imidazolate-based compounds, now referred to as zeolitic imidazole frameworks (ZIFs), were added to the MOF family in 2002 [34] . In mixtures of DMF and DEF, nine imidazolate type linkers and mixtures of them interacted with zinc or cobalt nitrate at different concentrations and molar ratios of metal to linker between 65 and 150°C [24] . Most extensively studied structure among the products found is ZIF-8, that is Zn atoms coupled tetrahedrally with 2-methylimidazolate (HMeIm), resulting in formula $Zn(MeIM)_2$ [35]. ZIF-8 has a sod structure made up of ring ZnN_4 clusters with four and six members that are connected by 0.34 nm windows and have internal cavities with a diameter of 1.16 nm. ZIF-8 has been investigated for hydrogen storage and adsorption [36] and as a catalyst that is heterogeneous (Figure 1).

2.2. Microwave-Assisted Synthesis

For fast synthesis of Nano porous substances under hydrothermal conditions, microwave synthesis techniques have been often used [36]. In addition to quick crystallization, this method may have phase selectivity restricted distribution of particles by size & easy morphological control [37].

Commercial microwave equipment features fiber optic temperature & pressure controllers in addition to changeable power outputs. A combination of substrates in an appropriate solvent is moved to a Teflon vessel, sealed, and put in the microwave during microwave synthesis. unit, and heated at the designated temperature for the proper amount of time. The microwave method causes the liquid phase to heat up quickly by coupling an applied oscillating electric field with the permanent dipole energy of molecules within the medium of synthesis which causes rotations of molecules [38]. Cr-MIL-100 was the first MOF microwave synthesis to be published. The product was produced in 4 hours at 220 degrees Celsius with a yield of 44%, which is like that of traditional hydrothermal synthesis, which takes 4 days and 220 degrees Celsius. In comparison to the standard material synthesized using the traditional electrical heating approach, the author reported identical physicochemical and textural features after expanding this process to synthesize Cr-MIL-101 at 210ºC in less than 60 minutes.

Microwave irradiation was also used to synthesize MOF-5; increases in microwave irradiation time, power level, and substrate concentration beyond ideal conditions resulted in an acceleration in synthesis time at the expense of crystal. Microwave radiation was also used to synthesize MOF-5; rises in the amount of microwave radiation period, the degree of power, and substrate concentration beyond the ideal conditions resulted in a reduction in synthesis time at the price of crystal quality. The preferred technique for quickly manufacturing HKUST-1 crystals in the range of 10–20 μm in high yields ~90% over 1 hour has been found to be microwave-assisted heating. Microwave-assisted synthesis has been utilized to create Fe-MIL-53, Fe-MIL-101-NH_2, IRMOF-3 (H_2BDC-NH_2), & ZIF-8. A systematic microwave-assisted synthesis of Co-MOF74 has recently been published [28]. In this technique, 0.148 mmol of cobalt nitrate hexahydrate (Co $(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich) and 0.044 mmol of H4DHBDC were dissolved in 18 mL of a mixture of solvents sealed with placed in a microwave oven with a rubber septum. Recently, an organized synthesis of Co-MOF74 using microwave support was published. This method required dissolving 0.148 mmol of cobalt nitrate hexahydrate, and 0.044 mmol of H_4DHBDC in 18 mL of a mixture of solvents. The mixture was then covered with a rubber septum and placed in a microwave oven.

2.3. Microemulsion Synthesis Method

This technique has recently being utilized to the synthesis of MOFs and is frequently used in the creation of nanoparticles [39].The components of water microemulsions are nanoscale drops of water that get stuck by a surfactant on organic phase. The kinetics of nucleation and crystal formation are controlled by micelles of microemulsions, that serve as nanoreactors. By varying the type of surfactant and the ratio of water to surfactant, the microemulsion's micelle quantity and size can be varied. The method's main drawbacks are its excessive cost and the fact that practically all of the surfactants used are harmful to the environment, yet it is beneficial since the form of the materials at the nanoscale can be managed (Figure 2).

3. Alternative Synthesis Methods

1) Ionic liquids as a synthesis medium

As previously stated, MOFs typically occur in water or organic solvents, but more recently, they have also been made in ionic liquids. Because of their special qualities, including nearly zero vapor pressure, superior solvating features, ease of recycling, and impressive thermal stability, ILs are gaining interest as a solvent for chemical synthesis. [40] whereas ionic liquids derived from 1-alkyl-3-methylimidazolium have been the topic of numerous reports on MOF synthesis, deep eutectic solvents (DESs), that are mixtures of two or more compounds with a melting point lower than either of their constituents, are also known to exhibit solvent properties very similar to those of ionic liquids [41] and have been used for synthesis of the MOF. The properties of the sample were compared to those of the HKUST-1 produced via conventional ionothermal synthesis method in an oven, and the effects of various synthesis settings on the crystallization procedure of the HKUST-1 were analyzed.

2) MOF Synthesis by conversion of dry gel

Zeolites and zeolite membranes have been made using the widely used dry-gel conversion synthesis method, in which a dry amorphous aluminum silicate gel is converted to crystalline zeolite upon contact with water and volatile amine vapors. The dry gel conversion approach was further divided into two distinct methods: (i) the method of vapor-phase transfer (VPT), and the (ii) the steam-assisted crystallization (SAC) method, which crystallizes a dry gel containing a non-volatile amine in steam [42]. Dry gel is crystallized in the vapor of water and volatile amine. Reducing waste disposal, reducing reaction volume, and fully transforming gel into uniform crystals zeolites with a high yield are all obvious advantages of the dry gel conversion process. ZIF-8 and Fe-MIL-100 were recently made using the environmentally friendly dry gel conversion synthesis method. After reacting at 120ºC for 24 hours, the condensed composites dynamically rearrange to a ZIF-8 as the water steam penetrates the surface of eutectic mixtures of substrate (Zn $(OAc)_2 \cdot 2H_2O$ and HmIM) and excess HmIM. Fe-MIL-100 was obtained quickly. Water steam penetrates the surface of eutectic mixtures of substrate (Zn $(OAc)_2 \cdot 2H_2O$ and HmIM) and excess HmIM. After a reaction at 120ºC for 24 hours, the condensed composites continuously rearrange to a ZIF-8. Using metallic iron (Fe0) and H3BTC from the this method, Fe-MIL-100 was quickly produced at 165ºC for four days without the addition of acid or salts [43].

3) System of Microfluidic MOF Synthesis

For this reason, microfluidic synthesis of MOFs may be considered. To meet commercial and industrial needs, it would be necessary to create continuous, more rapid, and viable methods for MOF synthesis. A microfluidic device was recently used for studying the preparation of HKUST-1[44]. At first, two types of substrate mixes were made: the organic ligand solution was made by dissolving H3BTC in 1-octanol and heating it to 60 ºC, while the aqueous phase was made by combines Cu (OAc)2$\cdot H_2O$ and polyvinylacohol in water at the room temperature. Syringe pumps bring both immiscible liquids to a T-junction, where aqueous solution droplets form in continuous organic phase. As these droplets go through hydrophobic polytetrafluoroethylene tubing and gather in the ethanol, the HKUST-1 capsule shell develops at the liquid-liquid interface. By regularly changing supernatant

with new ethanol, residual 1-octanol was removed. Resulting HKUST-1 capsule walls had a macroporous structure on the outside and were around 4 mm thick, while interior layer of shell remained made up of separated crystallites (Table 1).

4. Activation of Metal–Organic Frameworks

The majority of metal-organic frameworks (MOFs) that are produced following the synthesis process are typically required to undergo an activation step to remove the remaining solvents or guest molecules trapped in framework that are not visible as porosity to form accessible pore space [45]. In the synthesis, the solvent molecules can usually enter the internal cavities of MOFs and coordinate with them weakly to metal sites, thus preventing the access of pores and leading to diminished surface area [46]. Activation is hence a vital post-synthetic step which directly affects properties of textual characteristics, adsorption capacity and general performance of MOFs in real world applications. Solvents exchange is the most widely used activation strategy where synthesis solvents that are high boiling point are substituted by lower boiling, less strongly binding solvents, such as ethanol, methanol, or acetone [47]. Thermal or vacuum treatment is usually used to follow this step and assist in the elimination of the remaining molecules of the guest in pore network [48]. As an example, several solvent exchange cycles are usually necessary before high BET surface areas could be obtained by MOFs like MIL-101 and HKUST-1.

But new hope to be introduced in the form of gas-flow activation, photothermal activation by using UV-visible light, and dimethyl ether (DME) activation to minimize the time and energy used in the activation process without impairing the structure [47]. Activation is however a major problem, especially in cases of MOFs that are not thermally or chemically stable. Too much heating or drastic vacuum conditions may cause collapse of the structure or loss of crystallinity or even breakdown of metal-ligand coordination bonds, particularly in Zn-based MOFs like MOF-5 [49]. Accordingly, recent progress in the softer activation methods has been taken up and these consist of supercritical CO_2 drying, freeze-drying, and solvent-free mechanochemical directions which primarily seek to maintain framework integrity without compromising pore opening efficiency [50]. The translation of MOFs in the scope of the laboratory synthesis to the industrial one requires efficient and scalable activation modes because development of low-energy, environmentally friendly activation strategies also represents one of the research directions to enhance the commercial capabilities of MOF-based materials [25].

5. Applications for MOFs

High porosity, crystallinity, thermal resistance, and a large surface area are the usefulness of the pores and structure are just some of the structural features of MOFs which make them promising materials to be used as metal ions, catalysts, sensors, and dangerous gases absorbers in biomedical and environmental applications.

5.1. Gas Adsorption, Separation, and Storage for Energy and Environmental concerns

The use of MOFs in gas storage has been extensively investigated. For instance, the transportation sector still faces difficulties in properly using H_2 and CH_4, which represent alternate energy sources for future cars. Environmental protection depends extensively on the elimination of SO_2 and NOx from flue gas as well as the capture of harmful industrial gases like NH_3 and H_2S volatile hydrocarbons like benzene. The separation of gas mixtures, such as CO_2 capture and CO_2/CH_4, CO_2/N_2 separation, O_2 purification, and so on, is an essential technology in the chemical sector. Most significant greenhouse gas, CO_2, accountable for both water acidification and global warming. The magnesium alternative of MOF-74, MOF-74-Mg, has a highest CO_2 uptake capacity of 228 and 180 $cm^3 \cdot g^{-1}$ at 273 and 298 K and 1 bar, respectively [51]. The increased ionic nature of the Mg-O bond, enabling extra uptake beyond weight effects while conserving reversibility of adsorption, is responsible for MOF. In the initial phases of MOF development, alternatives for H2 storage and its possible use as renewable fuel for automotive applications were thoroughly investigated. The necessary materials must satisfy the U.S. Department of Energy's (DOE) standards, which call for 100 bars maximum pressure and a 5.5 weight percent H_2 gravimetric capacity that can be achieved in temperature range of −40 to 60 °C. The significant CO_2 absorption capacity of MOFs, including MOF-5, MOF-177, and UiO-66, is shown by H_2 uptake of 5 weight% (77 K, 90 bar), 7.5 weight % (77 K, 80 bar), & 4.2 weight % (77 K, 60 bar), respectively [52]. Recent achievements include the synthesis of a number of Pd-doped MIL-101 samples with varying Pd contents that impact their H_2 storage performances; Pt nanoparticles on outer surface of MOF-5 and subsequent coating it with hydrophilic micro pores carbon black which exhibits 41% greater H_2 absorbance than MOF-5; the formation of polarize organic units into MOFs to raise H_2's energy for binding (Figure 3).

5.2. Applications of Sensing

Because of their large surface area, which increased the sensitivity of agents, specific structural features, which support Selection, host-guest interactions, and adaptive porosity, which able to the reversible releasing and consumption of biomolecules, cations, and anions, as well as very small molecules, and so forth, MOFs have particular appeal as creative materials enabling sensing. Visible changes, such as a shift in the emission spectrum in addition to change in intensity of fluorescence, such as "turn-on" and "turn-off" processes, can be due to the guest molecules. High selectivity for Eu3+ ions at low concentrations in aqueous solutions is shown by a thermoplastic Mg-based MOF, [Mg(pdda)(dmf)] (H_2pdda = 4,4′-(pyrazine-2,6-diyl) dibenzoic acid), which has nanoholes and non-coordinating nitrogen atoms inside the hole walls [53]. [Me_2NH_2] [Tb(bptc)] is a luminous Ln-MOF. Despite the organic ligand's achiral nature, (H_4bptc = 3,3′,5,5′-tetracarboxylic acid) reveals uncommon chiral helical channels. It is a possible chemosensor for Fe^{3+} ions as luminescent experiments have established a highly selective fluorescence quenching response to Fe^{3+} ions in a liquid suspension [54]. In polluted natural fluids, a bimetallic Eu-Tb MOF with 1,4-benzenedicarboxylate ligand established Pb^{2+} selectivity. By doping the MOFs with various Tb/Eu ratios, the luminous Ln-MOFs' color could be altered from green to red. When Pb^{2+} is present, the MOFs' emission color changes from bright red to green, which is detectable to the untrained eye [55]. For the reason of sensing biological molecules such as human blood albumin, bacterial endospores, and cancer cell apoptosis, core-shell nanocomposites containing a MOF core have been

constructed. Luminescent MOFs have advantages over other biomolecule sensing materials in terms of structural diversity, high sensitivity, and biodegradability. They are also efficient at detecting RNA, DNA, protein, and other biomolecules. In order to attain in vivo sensing, compatible and non-toxic metallic clusters must be generated [56]. By adapting emission spectrum or altering luminescent intensity, MOFs based on guest-dependent luminescent responses can effectively detect volatile organic compounds and hazardous materials [57].

5.3. Biomedical Applications

Because of their outstanding physicochemical properties, MOFs and the materials made from them have been investigated more as transmitter of pharmaceuticals, biological imaging agents, and therapeutic agents. Most known drug carriers, including liposomes, nanoparticles, and micelles, indicate fast drug release and low drug loading. Porous structures with significant drug loadings are therefore taken into consideration for delivery applications. High drug loads, drug release control, matrix degradation control, and low toxicity are all required for efficient drug carriers. Drugs can be introduced into MOFs by physisorption, non-covalent encapsulation into the MOF, subsequent modification of the organic ligands after the MOF has been produced, applying the drugs as organic ligands in the building process of the MOFs, and attaching the drugs to the MOF's subunits [58].

The drugs can be loaded into MOFs through non-covalent encapsulation through physisorption, subsequent modification of organic ligands following the MOF's synthesis, using drugs as organic ligands during the MOF's development, or attaching the drugs to the MOF's subunits. MOFs have been considered as antifungal and antibacterial agents. For example, BioMIL-5, which is formed from Zn(II) and azelaic acid, has a 3D nonporous form and has remarkable antibacterial and dermatological characteristics against the Gram-positive bacteria S. aureus and S. epidermidis [Zn(hzba)2].Ag(I)-MOFs were tested against S. aureus and E. coli and exhibited significant antibacterial activity 2.4H2O (hzba = 4-hydrazinebenzoate) inhibited the growth and metabolic activity of Staphylococcus aureus and first antibacterial Co-MOF, Co-TDM (TDM = tetrakis[(3,5-dicarboxyphenyl)-oxamethyl]methane), inactivates the Gram negative bacteria E. coli [59].

5.4. Applications of Analytics

MOFs, such as MIL-53 for polycyclic aromatic hydrocarbons and drugs; MIL-101(Cr) for PAHs, bichlorinated biphenyls (PCBs), organic volatile compounds (VOCs), drugs, herbicides, and pesticides; ZIF-8 for PAHs and VOCs; MIL-100(Fe) and UiO-66-NH2 for PCBs and pesticides. One of the most successful methods is the solid phase extraction of microscopic molecules from biological fluids by using MOFs as sorbents. For the successful solid phase extraction of low abundance peptides, phosphopeptides clycopeptide, nucleic acids, and proteins from biological fluids, including human plasma, urine, serum, saliva, egg white, and milk, well-known and extensively studied MOFs and composites, such as MIL-53, MIL-100, MIL-101, and MIL101(Cr)-NH_2. In addition, MOFs can be used as absorbents to prepare samples of food matrices, as milk, drinks, meat, fish, and Material 2021, 14, 310 22 of 32 chicken items, before being examined using spectrometric and chromatographic methods (Table 2) [60].

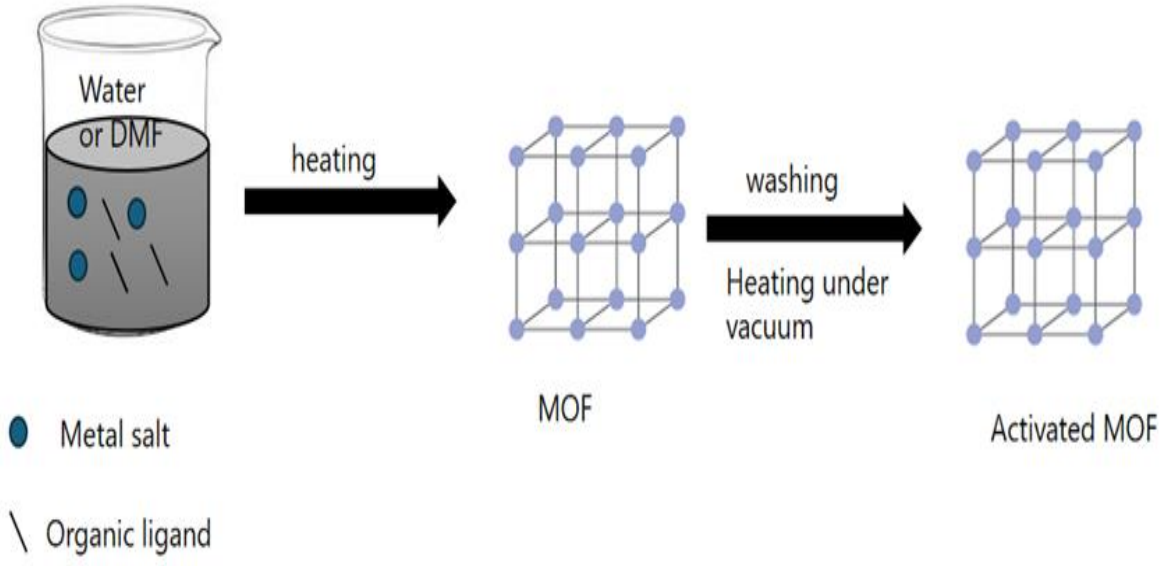

Figure 1. Schematic representation of MOF synthesis and activation process.

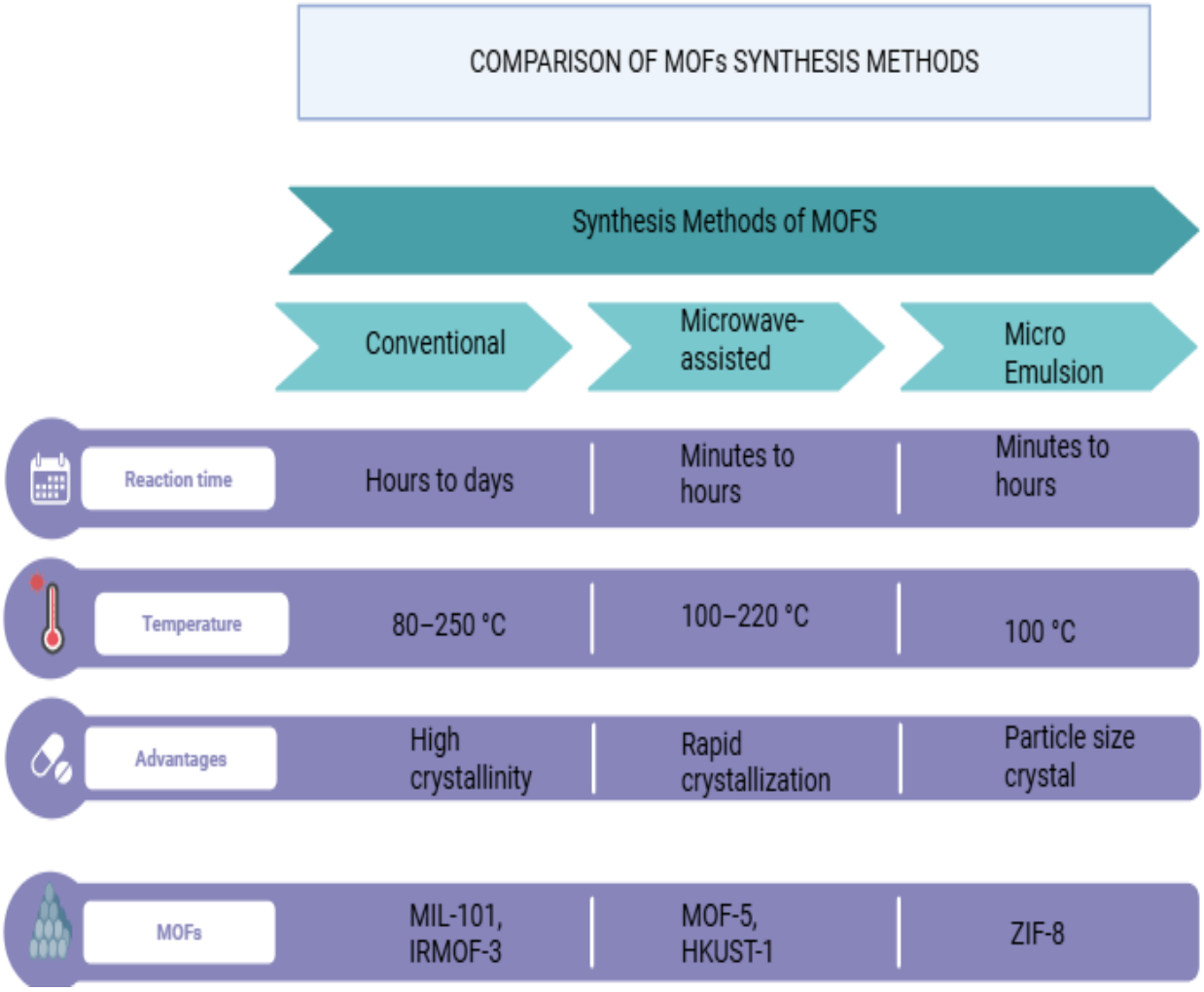

Figure 2. Comparison of synthesis method of MOFs

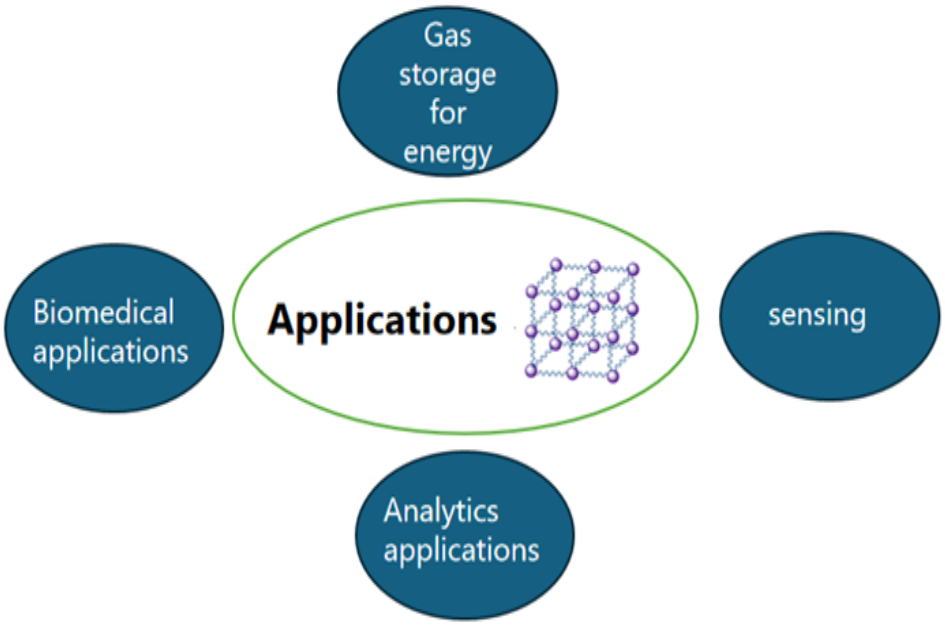

Figure 3. Major applications of metal–organic frameworks (MOFs) in energy, sensing, biomedical, and analytical fields.

Table 1: Comparison of major metal–organic framework (MOF) synthesis methods highlighting reaction conditions, advantages, limitations, and representative materials reported in the literature [48].

Synthesis method	Typical temperature	Reaction time	Key advantages	Main limitations	Representative MOFs
Conventional solvothermal / hydrothermal	80–250 °C	Hours to days	High crystallinity; well-defined structures; widely established	Long reaction time; high solvent consumption; limited scalability	MOF-5, HKUST-1, MIL-101, IRMOF-3
Microwave-assisted synthesis	100–220 °C	Minutes to hours	Rapid crystallization; reduced synthesis time; uniform particle size	Requires specialized equipment; possible crystal defects at high power	MOF-5, HKUST-1, ZIF-8, MIL-101
Mechanochemical synthesis	Room temperature to mild heating	Minutes	Solvent-free; environmentally friendly; high yield	Limited control over crystal morphology; scale-up challenges	ZIF-8, HKUST-1
Microemulsion synthesis	Room temperature to 100 °C	Minutes to hours	Excellent control over particle size and morphology	High cost; use of toxic surfactants; difficult purification	Nano-MOFs, ZIF-8
Dry-gel conversion	120–200 °C	Hours to days	Reduced solvent usage; high yield; environmentally benign	Limited to specific MOFs; requires precise humidity control	ZIF-8, Fe-MIL-100
Ionothermal synthesis (ionic liquids / DES)	100–200 °C	Hours to days	Low vapor pressure; recyclable solvent; improved thermal stability	High cost of ionic liquids; viscosity issues	HKUST-1
Microfluidic synthesis	Ambient to moderate	Minutes	Continuous production; precise control; scalable potential	Complex setup; limited throughput	HKUST-1 capsules

Table 2: Summary of representative metal–organic frameworks (MOFs), their structural components, and key application areas as reported in previous studies.

MOF material	Metal node	Organic linker	Key applications	Reference
MOF-5	Zn^{2+}	1,4-Benzenedicarboxylate (BDC)	H_2 storage, CO_2 adsorption, heterogeneous catalysis	[18-23-45]
HKUST-1	Cu^{2+}	1,3,5-Benzenetricarboxylate (BTC)	Gas separation, catalysis, sensing	[20-32]
MIL-101 (Cr)	Cr^{3+}	1,4-Benzenedicarboxylate (BDC)	Gas adsorption, catalysis, drug delivery	[21-22-51]
ZIF-8	Zn^{2+}	2-Methylimidazolate	Gas separation, sensing, membrane applications	[24-34-35]
MOF-74 (Mg)	Mg^{2+}	2,5-Dihydroxyterephthalate	CO_2 capture, gas storage	[44]
UiO-66	Zr^{4+}	1,4-Benzenedicarboxylate (BDC)	Gas adsorption, catalysis, water stability	[45]
Ln-MOFs (Eu/Tb)	Eu^{3+} / Tb^{3+}	Polycarboxylate ligands	Luminescent sensing of metal ions	[46–48]
BioMIL-5	Zn^{2+}	Azelaic acid	Antibacterial and biomedical applications	[52]

6. Conclusions

At present MOFs are receiving explosive concentration because of their incredible textural characteristics and different post synthesis organic alterations are possible. For these MOFs synthesis, scaling up in solvothermal orhydrothermal synthesis also attempts at alternative synthesizing techniques acquire additional optimization. This analysis introduced a brief overview of recently available MOFs synthesis techniques now in use that chemical engineers may find useful. ZIF8, MIL-101, MOF-5, HKUST-1 are those that can produce by simple organic ligands of commercial terephthalic acids, 1,3,5-benzenetricarboxylic acid, and 2-methylimidazole combined with metal nodes of Zn^{2+}, Cu^{2+}, and Cr^{3+}. commencing the traditional hydrothermal synthesis, microwave-assisted, dry-gel conversion, ionothermal, and micro fluid synthesis techniques were discussed with examples. The following conclusions about MOFs engineering applications can be drawn from brief review. The reported synthesis of MOFs is often inadequate and limited to very incredibly small scales that are adequate for the study of crystal structure.

Accurate methods for synthesis of suitable amount of MOF material are greatly desirable, like those accessible for mesoporous silica and zeolites. For optimizing and cost-effective MOFs materials to be used in industries as catalyst, adsorbent and template for more complicated materials more synthesis scaling experiments need to be conducted. ideal temperature or pressure conditions leads to high product yield. MOFs often require high vacuum and solvent exchange for activation; these should be replaced to a more-mild activation method. The development of new materials for clean and emerging technologies in the automotive sector, energy production, clean air and water, and health is greatly influenced by the versatile nature of MOFs and associated composite materials. Startups in the US and Europe have already introduced MOF-based commercial products for carbon capture, storage of extremely hazardous gases in the semiconductor industry, extraction of water from humid air, selective lithium ions separation for electric vehicles, removal of toxic metals and ions from water, and adsorbent nanomaterials. The "heart" of smart materials needs to advance the fourth industrial revolution of our century is MOFs and alternative materials.

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