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# A review on zeolite imidazole frameworks: synthesis, properties, and applications

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## Abstract

Zeolitic imidazolate frameworks (ZIFs) consist of transition metal ions (Zinc or Cobalt) and imidazolate (Im) linkers in tetrahedral coordination surrounded by nitrogen atoms from the five-membered imidazole ring serving as a bridging linker, i.e. a link connecting the metal centres in the three-dimensional framework. The crystal structures of ZIFs share the same topologies as those that can be found in aluminosilicate zeolites. ZIFs have advantages over zeolites such that the hybrid framework structures are expected to have more flexibility in surface modification. Due to their interesting properties such as high porosity, high surface area, exceptional thermal and chemical stability, ZIFs are very attractive materials with potential applications including gas sorption, gas separation, and catalysis. Over a decade tremendous work has been carried out to develop ZIFs in synthesis and its various applications. In this review, we have briefly composed the different methods for the synthesis of ZIFs such as solvent-based and solvent-free methods. In addition, its thermal and chemical properties and potential applications in the field of adsorption, separation, catalysis, sensing, and drug delivery have been summarized.

**Keywords** ZIFs · Synthesis methods · Properties · And applications

## 1 Introduction

Due to the vital properties such as high surface areas, large pore volumes, and tunable pore sizes, ZIF has become an area of interest for researchers. ZIFs are a sub-family of Metal–organic framework (MOF) compound that incorporates M-Im-M (where M stands for Zinc and Cobalt and Im stands for imidazolate linker) fashioned by a self-assembly approach [1]. The crystal structure of ZIF has an identical topological structure as those found in aluminosilicate zeolites. The framework of zeolite is composed of tetrahedral silicon or aluminium connected by oxygen atoms. In ZIFs, the tetrahedral silicon or aluminium atoms bridged by oxygen are replaced by transition metals such as (Zn or Co) and Im as linkers [2]. They have advantages over zeolites because the mixed framework structure is expected to have greater flexibility in surface modification. Zeolites are aluminosilicates based three-dimensional framework compounds; it is commonly used as water softeners and as a catalyst in petroleum refining. Framework adaptable structures are such that the metal atoms and the organic moieties can be varied to enhance the structural properties and applications [3, 4].

ZIFs are porous co-ordination polymers with uniform micropores and large void associated by small windows made up of tetrahedral building blocks in which each bivalent metal cation $M^{2+}$ (M = Co and Zn) combines four Im-derived ligands to generate neutral open framework structures $[M^{2+}(Im)_2]$ with zeolitic topologies [5]. As shown in Fig. 1, ZIF-8 has a sodalite structure, with four and six-member ring Zn-N4 clusters with internal cavities measuring 1.16 nm in diameter and 0.34 nm windows connecting them as confirmed by thermogravimetric analysis (TGA) or by examining the X-ray diffraction (XRD) pattern of the material [6]. The five-member Im ring serves as the bridging unit between the Zn(II), Co(II), or In(III) centres and imparts an angle of 145° throughout the frameworks via coordinating nitrogen atoms in the 1,3-positions of the ring [7–9].

During the intensive study and the development period of MOFs, successfully synthesized MOF-5 and its analogs were found to be chemically reactive with water and thus

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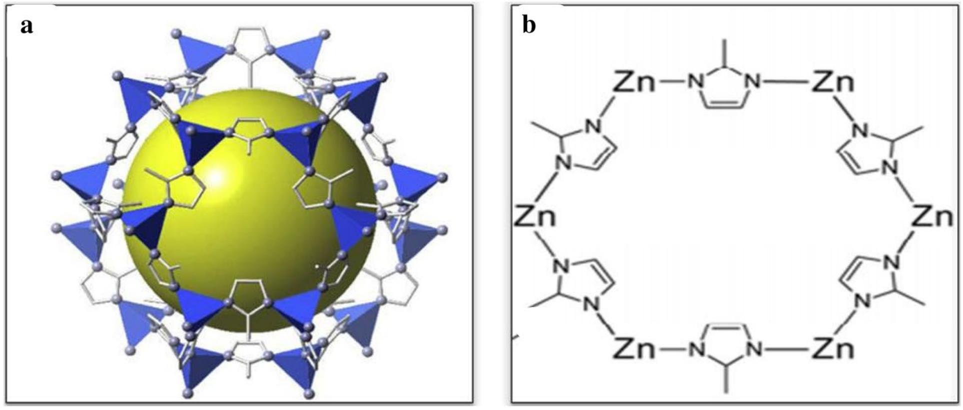



**Fig. 1** **a**. Crystal structures of ZIF-8: Zn (polyhedra), N (sphere), and C (line). The massive sphere represents the largest Van der Waals spheres that would fit in the cavities without touching the framework. All hydrogen atoms were omitted to clear the crystal structure of ZIF-8 and reproduced from reference number 6. **b**). Structure of framework ZIF-8. They are reproduced from reference number 7

undergo decomposition easily. This was primarily attributable to their Zn–O bonds, which support the framework to be broken under humid conditions [10, 11]. Researchers, by focusing more on hydrolytic stability, new MOFs were developed. In 2012, by protecting the Zn–O bond with functional groups of the ligand, the water stability of the MOF-n series was improved [12]. In addition, ZIFs were found to be highly stable at hydrothermal conditions, withdrawing the hydrolysis remark on MOFs. MOFs need to exhibit good stiffness, rigidity, and robustness to retain their structural integrity under high-pressure environments. ZIFs are promising materials for many industrial utilities such as gas adsorption and gas storage [13, 14], solvent separation [15], chemical sensing [16], catalysis [17], biomedical imaging [18], and drug delivery [19].

The primary building unit of ZIFs is made of T-Im-T (T = tetrahedrally coordinated metal ion, Im = imidazolate, and its derivative) with a bond angle of $145^0$, which is analogous to the Si–O–Si angle in zeolites. ZIF materials can have structures analogous to standard zeolite with a topology, such as sod, rho, gme, lta, and ana, employing a different Im ligand as shown in Fig. 2. The structure adopted by a given ZIF depends primarily on the type of Im and solvent used [20, 21] and greater structural diversity in ZIFs is possible using functionalized Im ligands in their synthesis. MOFs with zeolitic structures have been synthesized in a large number. Among them, ZIFs have recently gained curiosity among researchers. Some of the examples of ZIFs are mentioned below in Fig. 3.

Several review articles have recently been published, covering framework design and functionalities, synthesis, and applications of ZIFs and their composites and ZIF-based separation membranes and functional films [22, 23]. They are proven to be potential candidates for carbon dioxide adsorption due to their large surface area with porous structures [24]. ZIFs have exceptional chemical and thermal stability [25] that makes ZIFs capable of numerous applications like gas storage, heterogeneous separation, catalysis, and chemical sensing. The combination of high porosity with tunable pore chemistry from metal ions and ligand functional groups leads to potential applications in gas sorption, gas separation, and catalysis. Indeed, these applications are cost-sensitive; greatly promote the large-scale production of ZIFs for industrial applications.

## 2 Novelty and justification

In this review, we focus on the various synthesis methods, the chemical and thermal properties, and the applications of ZIF compounds that have been uniquely discussed, some of the chemical and thermal properties of ZIF compounds are summarized. We discussed some of the major applications in detail such as drug delivery, sensing, separation, catalysis and adsorption. Further, we offer some remarks at the end of the review for further development in the research of ZIF compounds. Hopefully, this review will help the researchers with the basic ideas in the area of ZIFs in the future.

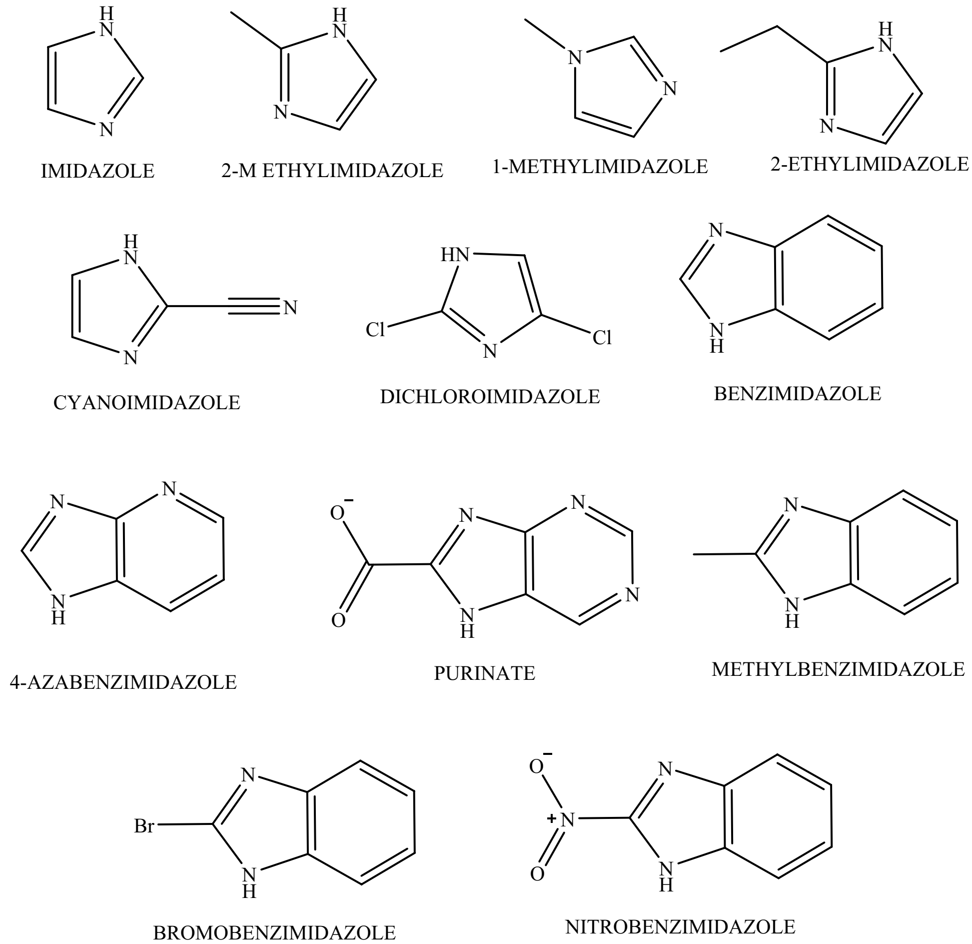
To further develop new synthesis strategies and explore the potential applications of ZIFs, it is vital to take advantage of the knowledge and experience gained from other research fields such as those in zeolites. Undoubtedly, much research is needed to explore those fast developing and emerging fields. With the effort from scientists in relevant fields, novel synthesis approaches for ZIF materials that are low-cost, scalable and reproducible will emerge in the near future. Even though vast advancement have made in the synthesis and applications of ZIF-based materials, certainly more innovative synthesis strategies of ZIFs and implementation in various fields will emerge in the future.

## 3 Different methods for the synthesis of ZIFs

### 3.1 Solvent-based Synthesis

As shown in the above classification Fig. 4 there are various methods for the synthesis of ZIFs. In Solvent-based

**Fig. 2** Some of the examples of Im linker




synthesis, methanol, ethanol, water, dimethylformamide, diethyl formamide, etc., are used as a solvent. Further, based on the solvent used they were many strategies like solvothermal, hydrothermal, microwave, ionothermal, and sonochemical methods.

### 3.1.1 Solvothermal method

During the early stage of ZIF synthesis, the solvothermal method was widely used. Later, Chen's group for the first time developed polyhedral crystals of zeolites framework in methanol and ammonia using zinc and Im as precursors in a 1:2 ratio [26]. In this synthesis method, metal and excess ligands are placed in Teflon-lined autoclaves at 120 °C for 24 h. A sequence of framework compounds was synthesized by Yaghi et al. in 2006 from ZIF-1 to ZIF-12, through solvothermal synthesis using organic solvents such as methanol, ethanol, isopropyl alcohol, dimethylformamide, and diethyl formamide [7]. Particles up to 40 nm were found and had better stability with solvothermal synthesis. Other ZIF compounds were also synthesized using the same solvents such as ZIF-60 to ZIF-71, ZIF-78, ZIF-82, ZIF-90, ZIF-95, and ZIF-100. However, synthesis methods were later modified using some bases such as triethylamine, pyridine, sodium hydroxide, sodium formate, and n-butylamine [3, 27, 28] to deprotonate the Im linker which increases the rate of reaction and gives high yield product. Janosch Cravillon et al., experimented with the synthesis of ZIF-8, using methanol as a solvent along with the addition of sodium formate as the competitive ligand in the presence of Im linker [29]. The experimental analysis reveals that sodium formate acts as a more deprotonating agent than a competitive ligand. His experiment also reveals that large and scattered particles have appeared with the increase in the concentration of ammonium hydroxide. Thereby, the morphology and the structural properties can be varied by controlling the concentration of ammonia.

### 3.1.2 Hydrothermal synthesis

Hydrothermal synthesis refers to any homogeneous or heterogeneous chemical reaction in the presence of an aqueous or non-aqueous solvent higher than the room temperature and at pressure more than 1 atmospheric in a closed system [30]. In this one-step process, the precursors are heated in an aqueous mixture in a sealed stainless steel

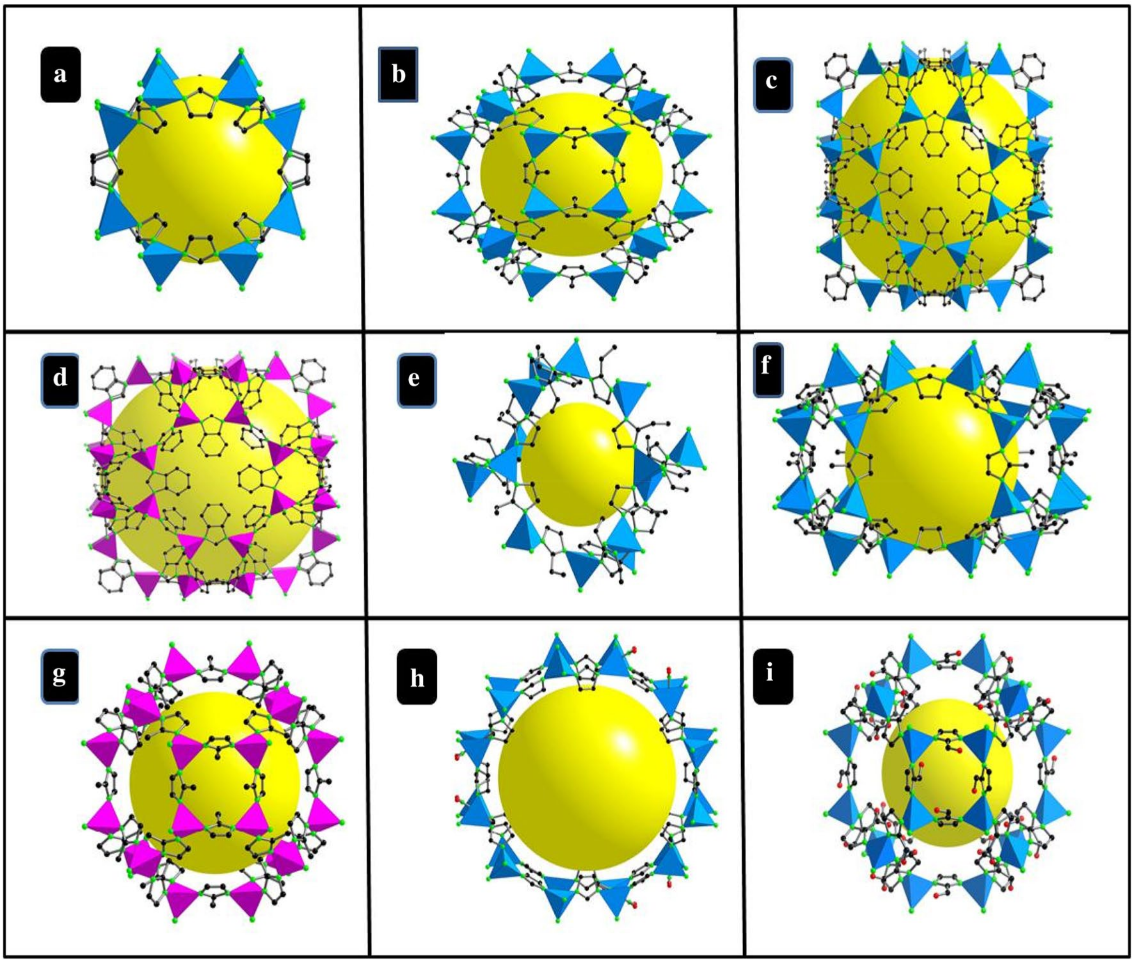



**Fig. 3** Some of the examples of ZIF compounds**. a**) ZIF-3. **b**) ZIF-8. **c**) ZIF-11**. d**) ZIF-12. **e**) ZIF-14. **f**) ZIF-60. **g**) ZIF-67 h) ZIF-70 **i**) ZIF-90. Reproduced from reference number 3

autoclave beyond the boiling point of water, which results in a drastic increase in the pressure above atmospheric pressure; consequently, highly crystalline materials are produced without the need of post-annealing treatments.

Undoubtedly, the use of organic solvents is economically costly, toxic to human health, and not environmentally friendly. Hence, substantial research is done to develop a productive, green method for syntheses of ZIF materials. The reactants often play a major role in the formation of ZIF compounds with different morphologies. In 2010, Pan et al. synthesized nanocrystals of ZIF-8 in a pure aqueous medium with a higher yield than organic solvents in a short duration of 5 min but required a more amount of linker [31]. Then, many researchers put efforts to propose the green method for the synthesis of ZIFs. For example, Junfeng Qian et al. successfully synthesized the nanocrystals of ZIF-67 in an aqueous medium. Upon dilution, the mean particle size of ZIF-67 can be varied from 689 nm to 5 µm [32].

Some modifications were initiated in hydrothermal synthesis to decrease the reaction rate for example, by adding some deprotonating agents such as triethylamine [33], ammonium hydroxide [34] etc. These deprotonating agents not only reduce the use of ligands but also enhance the rate of reaction. Also, by the inclusion of surfactants in the ZIF synthesis solutions reduce the usage of solvent and organic ligand significantly.

Several surfactants have also acted as structure-directing agents in the ZIF synthesis processes, which have proved effective in tuning the ZIF crystal size and shapes. For example, Pan and his research team controlled the morphology and size of ZIF-8 crystals in an aqueous solution using cetyltrimethylammonium bromide (CTAB) and precisely adjusted the particle size 100 nm to 4 mm. However, CTAB is not effective as a capping agent in organic solvents [35] and the SEM images in Fig. 5 clearly show the uniform dispersion of ZIF-8 nanoparticles. Various other parameters can high impact the emergence of these crystalline zeolites,

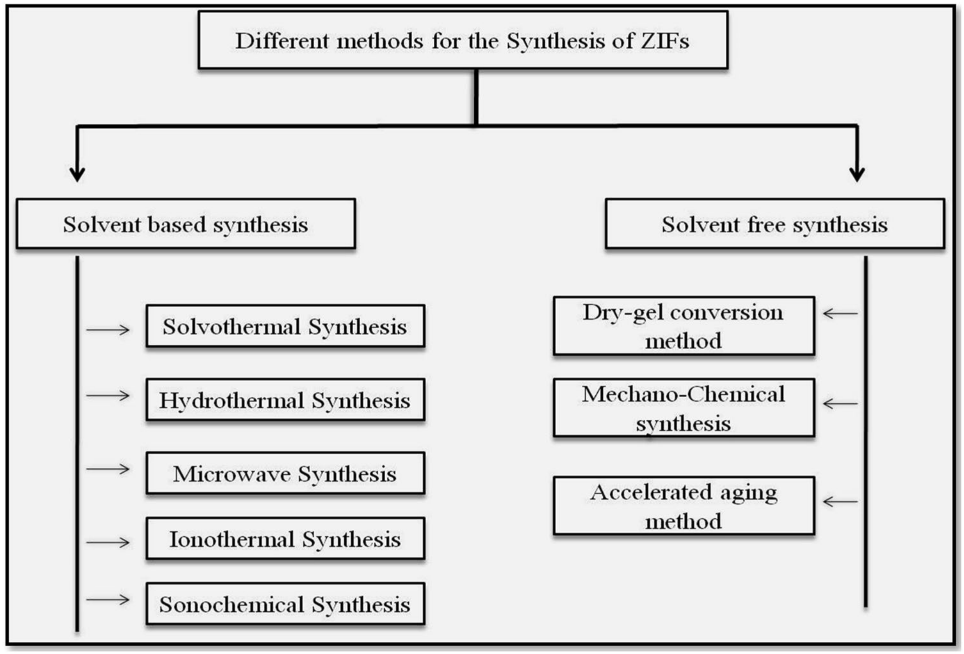



**Fig. 4** Different methods for the synthesis of ZIFs

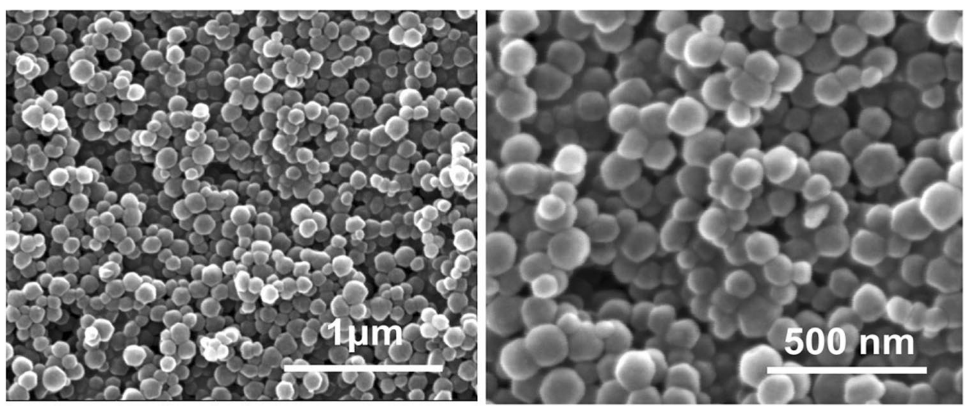



**Fig. 5** SEM images of ZIF-8 nanoparticles. Reproduced from reference number 43

such as the surfactant alkyl chain's length, the surfactant's concentration, the precursor ratio, and the temperature at which reaction is maintained produces hierarchically porous ZIF crystals for improved adsorption properties [36].

Moreover, a polymer such as polyvinylpyrrolidone (PVP) is used as a surfactant promoting porous ZIF compounds' formation due to electro statistical attraction to the metal ions [37]. Polymers play a crucial role in controlling morphology by adding PVP;for example; Nune et al. show that 1% high molecular weight poly (diallyldimethylammonium) chloride plays a key role in controlling the morphology of nanoparticles [38]. Ironically, ZIF compounds could be prepared using the stoichiometric ratio of metal ions and MIm in the presence of other additives such as triblock copolymers poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (PEO-PPO-PEO) and PVP in an aqueous system. For instance, both ZIF-8 and ZIF-67 were synthesized from the stoichiometric metal ions and 2-methylimidazolate linker in a diluted ammonia system containing triblock copolymer surfactant in the presence of PEO groups [39], where it was assumed that surfactant could assist the formation of porous ZIF-8 and ZIF-67 because of electrostatic attraction to the metal ions [40]. For example, Shieh et al. also found that ZIF-90 microcrystals could be synthesized using a hydrothermal technique in the presence of PVP. Besides, PVP was believed to rule the morphology of crystals and suppress the accumulation of crystals [37].

#### 3.1.3 Microwave synthesis

Microwave synthesis is a new type of heating technology, which is widely used in many chemical syntheses. It has been acknowledged that Microwave synthesis is an easy, swift, and economically feasible route for the synthesis of MOF compounds as shown in Fig. 6. Compared to the conventional heating method, the microwave irradiation method is a green and more promising method, which can remarkably quicken the reaction rate [41]. The microwave method notably shortens the synthesis time, produces a higher yield, considerably reduces the number of ligands, and extinguishes the use of deprotonating agents. The researcher proposed many synthetic techniques to produce ZIF-8, despite not all of them leading to the material possessing a high specific surface. Fast synthesis often results in Brunauer–Emmett–Teller Nitrogen adsorption specific surface areas not higher than 1000 $m^2 g^{-1}$ and the molar ratio between zinc salt and linker is optimized. In 2013, Bux and his coworkers for the first time reported the synthesized ZIF-8 using microwave irradiation [42]. Vera V. Butova, et al. in 2016 successfully reported a new fast (15 min) microwave-assisted hydrothermal method for the synthesis of ZIF-8 with a high specific surface area of 1419 $m^2 g^{-1}$. The starting materials were zinc nitrate hexahydrate, 2-methyl imidazole, dimethylformamide, and triethylamine [43].

#### 3.1.4 Ionothermal synthesis

Ionothermal synthesis is a new method for synthesising porous materials such as ZIF which includes green, recyclable ionic liquids and eutectic mixtures as solvents. The synthesis can be carried in an open system due to the non-flammability and negligible vapor pressure of ionic liquids. They also act as templates to avoid competitive interaction between the solvent and template framework as in hydrothermal synthesis. Morrison and co-workers for the first time synthesized ZIF using an ionic liquid such as 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfanilamide [44]. Yang and his team synthesized stable ZIF-8 with regular morphology using 1-butyl-3-methyl-imidazolium

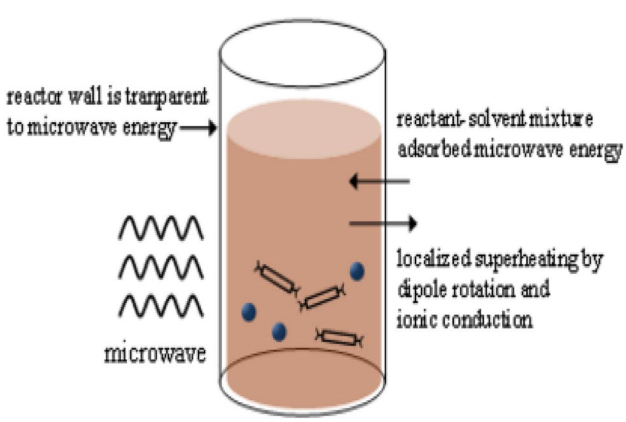



**Fig. 6** Microwave synthesis of ZIFs. Reproduce from the reference number 04

tetrafluoroborate as an ionic liquid; this acts as a structure-directing agent under microwave irradiation in a short time of 60 min [45].

#### 3.1.5 Sonochemical synthesis

Compare to standard conventional synthesis methods; the sonochemical method promotes the formation of nucleation due to the disintegration of acoustic cavitations generated by ultrasonic waves. Consequently, crystallization time decreases accompanied by significant crystal size reduction. Sonocrystallization products also result in smaller crystals with a narrower size distribution than conventional crystallization due to the advancement of the nucleation process in solution [46, 47]. Different SEM images using the sonochemical method are shown in Fig. 7.

### 3.2 Solvent-free synthesis

In this group of methods, a new strategy of solventless synthesis methods was put forth. Since the solvents are not environmentally friendly and economically costly, thus these methods are green methods for synthesizing ZIFs compounds. Some examples of such methods are steam assisted conversion method (dry gel conversion method) [48], accelerated aging method [49], and mechano-chemical synthesis method (Ball milling method) [50].

The dry gel conversion method involves a reaction between amorphous gel powder with water vapors or vapors of amines resulting in the formation of zeolite crystals. Using the dry gel conversion method Ningyue Lu, et al. successfully synthesized ZIF-8 [51], MIL-100(Fe) [52], and MIL-101(Cr) UIO-66 [48] without using acid or salt. Shi et al. successfully synthesized highly porous ZIF-8 and ZIF-67 using the steam-assisted conversion method (dry-gel conversion method) [53]. This method is environmentally friendly and avoids the use of harmful solvents and is cost-efficient for the preparation of porous compounds. Concurrently, the synthesized compounds show excellent catalytic activity, high stability, and reusability in the esterification reaction.

Also, mechanochemical is an efficient and easy method for the synthesis of porous materials [54]. Patrick J. Beldon et al. did comparable studies between mechanochemical and microwave-assisted methods for the synthesis of ZIF at room temperature [50]. In the mechanochemical method, the reaction was completed within 30 min whereas, in microwave-assisted methods, reactants gave a mixture of products at low conversion after a few hours. The illustration of the ball milling method is seen in Fig. 8. Furthermore inspired by geological biomineralization, Friscic et al. proposed the environmentally friendly age-accelerating method is also used to prepare ZIFs, which is different from solvent-based or

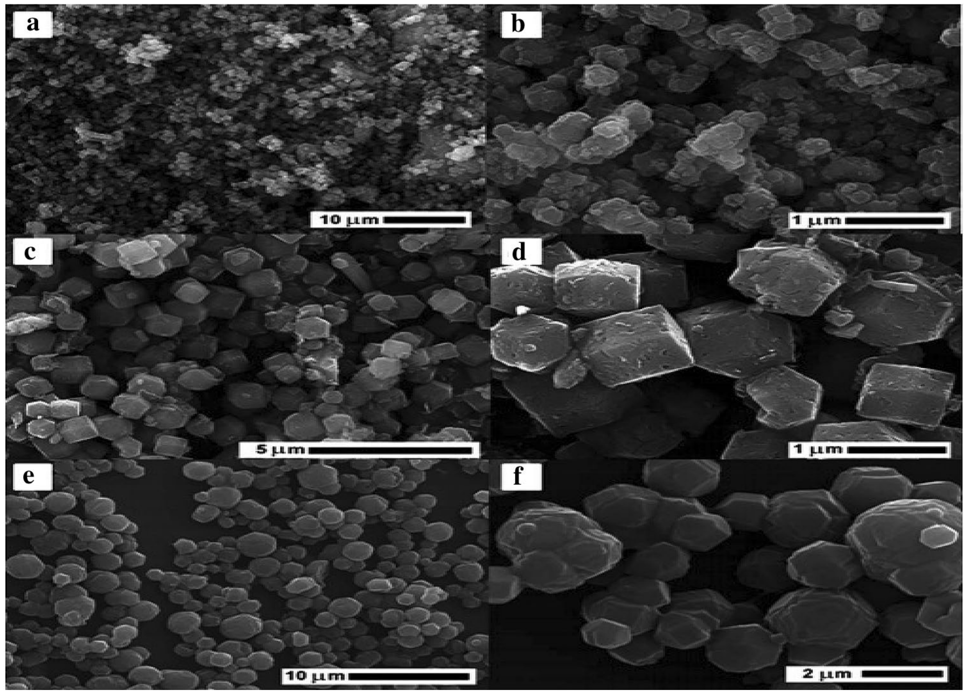



**Fig. 7** SEM images of ZIF-8 (**a** and **b**), ZIF-11 (**c** and **d**), and ZIF-20 (**e** and **f**) using sonocrystallization. Reproduced from reference number 49

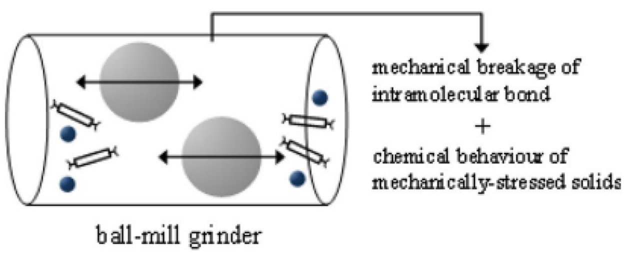



**Fig. 8** Ball-mill grinding method for the synthesis of ZIFs. Reproduced from reference number 04

other solvent-free synthesis methods [55]. The proton transfer mechanism was also proposed by Friscic et al. Where the catalytic salts could induce and accelerate the transformation of a metal oxide into a ZIF material.

Compare to other methods, solvent-free synthesis has emerged as an eco-friendly method with potential advantages such as fast, reduced waste or toxic disposal, minimum usage of templates, and uninterrupted formation of products.

## 4 Summary for the synthesis methods of ZIFs

We have discussed various methods for the synthesis of ZIFs. Undoubtedly, all the methods have their advantages and disadvantages. Among solvent-assisted methods such as hydrothermal, solvothermal, ionothermal, microwave, and sonochemical methods. These novel approaches offer reproducibility, scalability, and high surface area in a short period. But excessive usage of linker and solvent makes these methods inefficient. Further, Solvent-free synthesis methods have their credits and drawbacks. These methods are cost-effective and skip the use of solvents which correspondingly reduces the impurity or solvent molecules trapped in the pores of the crystal.

## 5 Thermal and chemical properties of ZIFs

### 5.1 Thermal properties

Using TGA under an inert atmosphere it was reported that ZIFs are thermally highly stable up to 450–550 °C [56]. Later, using various characterization techniques it was studied that ZIF-8 undergoes partial carbonization in inert, oxidizing, and reducing atmospheres to form an imidazole–Zn–azirine structure above 300 °C [57]. Remarkable degradation of ZIF-8 was observed above 300 °C under different atmospheres using static TGA. It is also claimed that the size of a particle and the synthesis condition plays a vital role in the thermal stability of a particle of ZIFs [58]. Comprehensively, it suggests that 200 °C is the standard operating temperature at any atmospheric temperature [7]. In Fig. 9, it is seen that the ZIF-8 is stable till 300 °C and then slow decomposition starts further.

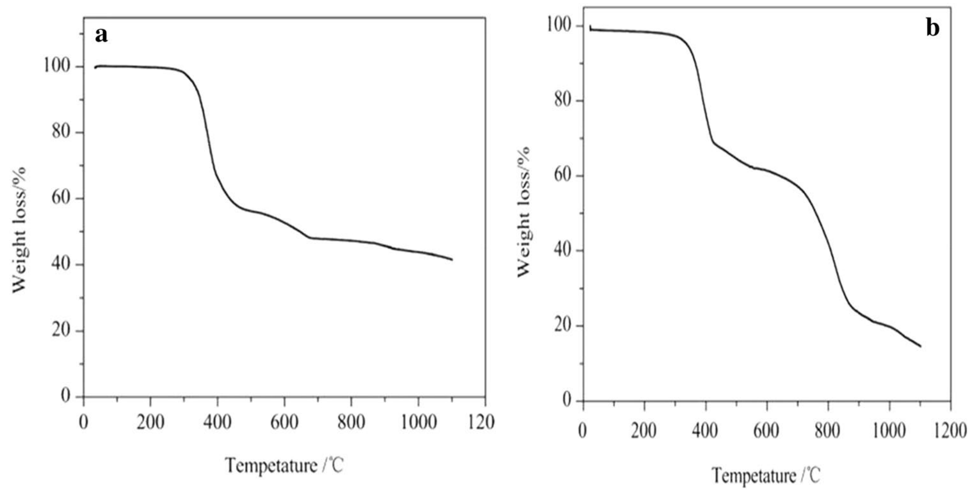



**Fig. 9** Thermo-gravimetric curves of ZIF-8 synthesized using different heating methods: (**a**) 72 h of reaction time by conventional heating; (**b**) 60 min of reaction time by microwave heating. Reproduced from reference number 48

## 5.2 Chemical properties

The invention of highly stable ZIFs in hydrothermal conditions overcomes the major drawback of MOFs, Thus strengthening the desirability of MOF compounds [58]. The chemical stability was profoundly studied by Kyo Sung Park and Co-workers, the ZIF samples (ZIF-8 and ZIF-11) were submerged in the desired solvents such as boiling water, methanol, benzene, and aqueous sodium hydroxide for 1–7 days at 50 °C. The experiment was continuously under observation under a microscope and found that to be remaining inert in each condition [7]. Figure 10 shows the XRD patterns and the SEM images of ZIF-8 kept in methanol for some days to study the chemical reactivity of ZIF-8.

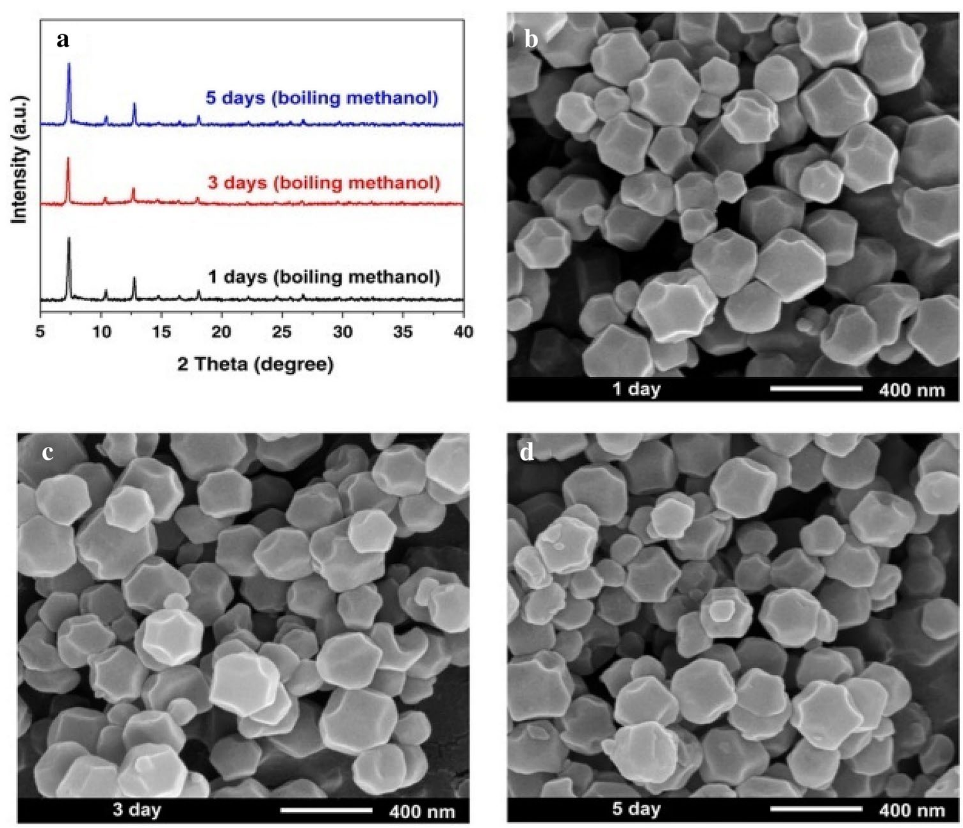



**Fig. 10** **a**. XRD patterns and **b–d** SEM pictures of synthesized ZIF-67 nanocrystals immersed in boiling methanol for 1–5 days. Reproduced from reference number 64

### 5.3 Surface area

Surface area is the major parameter for characterizing porous materials. ZIFs have a high surface area which is measured using BET. Sometimes the reason for the low surface area is low or partial activation of samples [59]. Nitrogen adsorption/desorption, Langmuir and Brunauer–Emmett–Teller (BET) analysis are the major analysis for evaluating.

Specific surface area and recorded in ($m^2$/g). The highest SSA recorded was determined by the BET method as 2490 $m^2$/g. The SSA ranges from 6.050 to 2490 $m^2$/g. The finer the particle size, the larger the surface area thus the more availability of active binding sites for pollutants. The pore diameter ranges from 0.34 to 2350 nm [60]. The reduction in the surface area may be due to the guest molecules or unreacted species struck in the pore of the compounds. Hence, the samples should be heated to a high temperature above 200 °C to eliminate the trapped molecules [61].

## 6 Applications

### 6.1 Adsorption

Adsorption is a highly favorable method due to its low cost and high efficiency. MOFs are multi-skilled components for contaminated groundwater. Meipeng Jian et al. showed that adsorption on ZIF-8 at different pH. Arsenic [62], humic acid [63], phthalic acid [64], benzotriazoles [65] and antibiotics like tetracycline (TC) and oxytetracycline (OTC) with high adsorption capacity of 122.0 and 149.3 mg $g^{-1}$, respectively using ZIF-8 [66]. ZIFs are the efficient compounds for the adsorption of most organic dyes, such as methyl blue [67], malachite green [68], and rhodamine B [69]. Adsorption is the basic principle in the synthesis of styrene carbonate from $CO_2$ and styrene oxide using ZIF-8 as the catalyst. In ZIF-8, Lewis acid metal (II) sites and the nitrogen basic moieties from the imidazole linker in the ZIF-8 framework promoted the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate [70]. For adsorption applications, ZIFs should exhibit excellent rigidity and robustness to retain their structural integrity under high-pressure environments. Pores are driven by the interaction between acid and base, electrostatic interactions, π bonds stacking, co-ordination interactions, and hydrogen bonding [3], which helps to preferentially adsorb molecules that fit in tightly inside the pores and they exclude the molecules that are too large or too small [71]. Adsorption mechanism of Malachite green on ZIF-67 is illustrated in Fig. 11. The adsorption of malachite green on ZIF-67 is consider to be significantly involved in the chemical interaction with ZIF-67 gleaned from exploration of the kinetics, adsorption isotherm and thermodynamics [68]. The imidazole ring in 2-methylimidazole contain two double bonds and a pair of electrons from the pronated nitrogen, which all interact on the planar surface of the imidazole ring. Therefore, the imidazole ring can be considered as an aromatic compound which can interact with other aromatic compounds via the π–π stacking interaction [68].

### 6.2 Separation

Separation technique has emerged as one of the frontier applications with the rapid increase of global issues such as natural gas purification, carbon dioxide capture, hydrogen separation, etc. In 2015, air separation experiences huge market value approximately around \$4 billion and it was predicted by 2022 that it will reach around \$6 billion [72]. Hence, making it economically less expensive is essential because of the main components like $O_2$ and $N_2$. Oxygen is essential due to its medical applications, gasification combined cycle for power generation, oxy-fuel combustion, and many more. Nitrogen has its own importance in the industries such as in petroleum industries. Separation using cryogenic distillation and pressure swing adsorption are high energy-consuming and expensive methods. Thus, another method for efficient and economical gas separations is membrane-based approaches. So far, membranes for this separation are held either by low selectivity (polymeric membranes) or high sensitivity that results in cracking (ion transport membranes) [73, 74].

ZIFs membranes have evolved as particularly remarkable because they require less energy to synthesize and have relatively short synthesis time and they are chemically

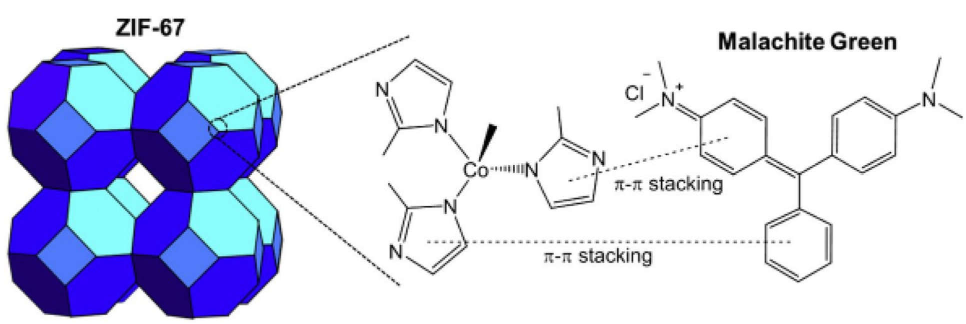



Fig. 11 Proposed mechanism for the adsorption of malachite green using ZIF-67. Reproduced from the reference number 74

and thermally stable and can achieve low defect fraction compared to zeolites [75]. Moreover, they exhibit outstanding performance in kinetic-driven gas separations because they can sieve molecules with size less than 1 Å. Figure 12 summarizes the applications of ZIFs for the many different separation. It is quite advisable to develop eminent ways for effective separation to maintain a clean eco-friendly environment. Since ZIF exhibits physical dimensions proportional to that of natural zeolites, it is an excellent plan to incorporate ZIF in these applications. Pure ZIF and modified forms of ZIF have a great validity for the exposure of gas separation.

Based on data gathered from Citation Index from 2009 to the end of 2020, ZIF-8 gains 70% of the entire number of papers published in sorption/separation with ZIFs. ZIF-8 is an ideal selectivity for He/$CH_4$, $H_2$/$CH_4$, $O_2$/$N_2$, $CO_2$/$CH_4$, and $CO_2$/$N_2$ as shown in Fig. 13 [76]. Adsorption-based gas separation processes by nanoporous materials are widely used because of their low energy demands and environmentally friendly nature. As depicted in the Fig. 14 adsorption capacity in ZIF-67 is greater for $CO_2$ than $CH_4$, $N_2$, and $H_2$ [77].

Nature and content of the target gas, variety of ZIF and mode of operation, physical conditions all together affect the efficiency of separation. By introducing organic linkers to ZIF, paves a pronounced compatible way when compared with other forms. This also helps to equilibrate the processing of polymers. In addition to this gas separation, the present research studies have shown clearly that ZIF materials can be served in vapor separation, biofuel recovery, etc. It is advisable to note that the flexibility of ZIFs and their modified forms under sarcastic conditions are on the way in research [78].

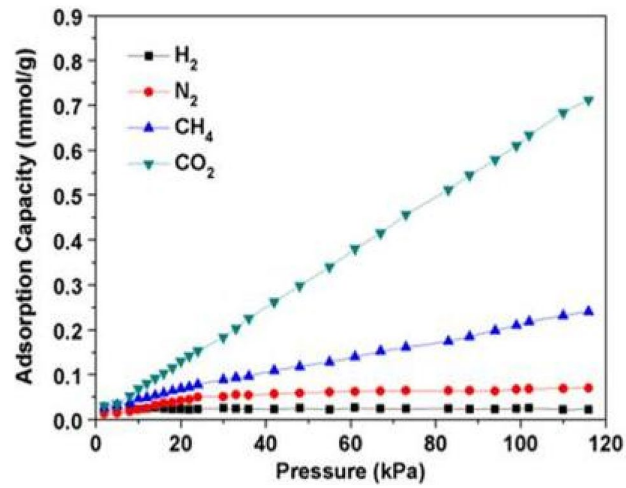
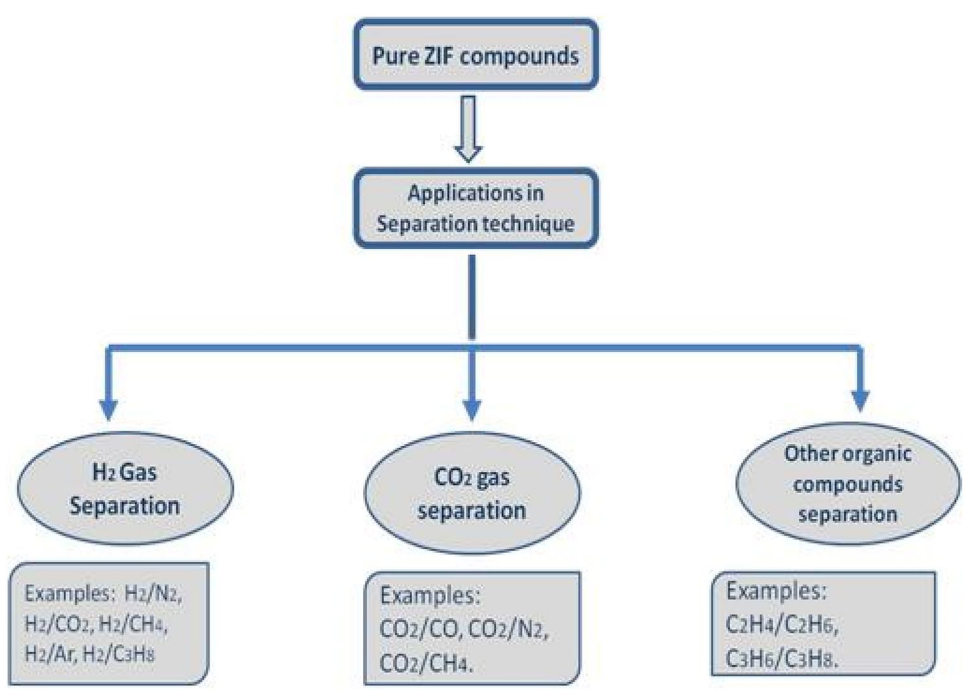



**Fig. 13** Gas adsorption isotherms of ZIF-67 nanocrystals at room temperature. Reproduced from reference number 84

## 6.3 Sensing

The sensing of hazardous and inflammable gases is important for health and environmental welfare. A few decades early, many metal oxide-based sensors were developed such as $SnO_2$, ZnO, $In_2O_3$, and NiO film [79]. Since surface area plays an important role in absorbing more gases, inorganic metal oxide has a low surface area and requires a high temperature for the gas sensing process [3]. Since ZIFs are

**Fig. 12** Summary of gas separation on both pure ZIFs and ZIF-based compounds



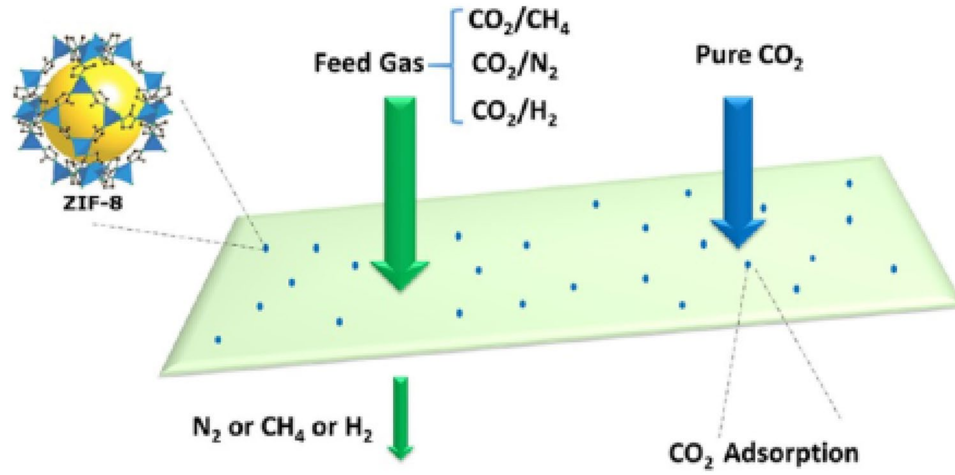



**Fig. 14** ZIF-8 based membranes as gas separation membranes. Reproduced from the reference 83

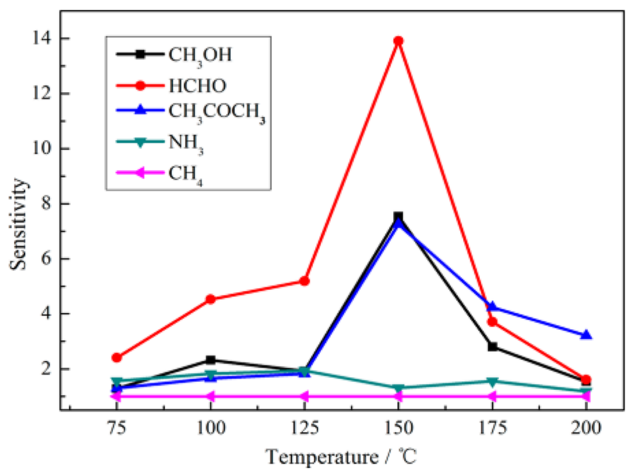



**Fig. 15** Sensitivity of the ZIF-67 sensor to different 100 ppm gases measured between 75 and 200 °C. Reproduced from reference number 90

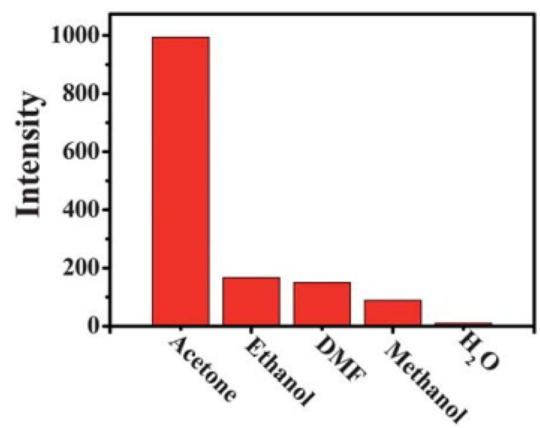



**Fig. 16** The effect of different solvents on the intensity of luminescence. Reproduced from the reference number 91

materials with high surface area and good thermal stability, Hupp and co-workers came up ZIF materials as sensors and developed a ZIF-based sensing device for chemical vapors and gases called Fabry P'erot [80]. They found that ZIFs are excellent candidates as sensing materials due to their unique properties of water-resistant and high porosity. Inspired by the idea of Hupp et al. many researchers put forth their work with promising approaches [81].

One such approach by Er-Xia Chen et al. by employing ZIF-67 as a formaldehyde gas sensor at 150 °C with low concentration as low as 5 ppm. ZIF-67 has shown good sensitivity towards detecting various gases like formaldehyde, methanol, acetone, ammonia, and methane between the ranges between 75 and 200 °C [82]. It is worth noting that ZIF-67 shows maximum response to formaldehyde and least response to ammonia and methane as shown in Fig. 15.

Also, ZIF-8 has strong selectivity towards detecting small molecules and ions such as Copper and Cadmium ions [83].

In Fig. 16 it is depicted the effect of different solvents on the intensity of luminescence. It is clearly shown that the intensity of luminescence largely depends upon the solvent molecules. Also, it is noted that the luminescence property of ZIF-8 increases with an increase in the concentration of acetone.

## 6.4 Catalysis

Many researchers have devoted a lot of joint efforts to studying high-performance, low-cost, and highly stable catalysts. ZIFs are synonymous with a porous material such as aluminosilicate zeolites. They serve as both homogenous and heterogeneous catalysts, but the latter is quite prominent than the former. They are one of the most prominent and economically placed catalytical materials for many reactions as depicted in Fig. 15 such as Knoevenagel condensation [84], Friedel–crafts acylation [85], Sonogashira coupling reaction [86], Suzuki cross-coupling reaction [87], synthesis of Styrene carbonate [70], synthesis of cyclic carbonates from carbon dioxide and epoxides [88], for the conversion of glucose to fructose and 5-hydroxymethyl furfural [89], aminocarbonylation [90], hydrogenation of 1,4-butanediol [91], reduction of alkenes such as 1-hexene and 1- hexyne [92, 93]. ZIF compounds not only exhibit great stability in the cyclo-addition reactions but also can be reused up to ten times in condensation reactions without losing their properties [94]. ZIFs can also be imposed in oxidation and epoxidation reactions. For instant, ZIF-9 has been successfully used in the anaerobic oxidation of tetralin. Also, ZIF-9 is shown to be an efficient heterogeneous catalyst for the Knoevenagel reaction between benzaldehyde and malononitrile to form benzylidene malononitrile as the principal product. Excellent conversions, high yield, and efficiency were achieved even without needing an inert atmosphere and can be reused as catalyzed without significant degradation [95]. With only 2%–6% catalytic amount of ZIF-8, aromatic compounds with acid chlorides are converted into aryl ketones which are well-known as Friedal craft acylation reaction. It is a predominant process in the production of pharmaceuticals, agrochemicals, and fragrances. ZIFs used as a catalyst in many reactions are summarized in Table 1. The solid catalyst can be easily separated from the reaction mixture by simple centrifugation or filtration and can be reused without significant degradation in catalytic activity [96, 97].

Even reactions that are difficult to handle can also be carried out at room temperature with the help of ZIFs. Since natural ZIFs are used in many reactions, the modified ones also exhibit a large surface area and changeable pore size. Henceforth, it can be integral support for the introduction of different metals or oxide nanoparticles with eminent physical and chemical properties [98, 99] (Fig. 17).

In addition, ZIFs with nanomaterials have shown an increase in photocatalytic efficiency. Photocatalysis is a gifted method that aids to degrade toxic organic molecules, to purify water and air [100, 101]. Tayirjan et al. incorporated $TiO_2$ nanotubes with Pt/ZIF-8 and found a remarkable increase in the photodegradation of phenol. Wherein ZIF-65 with molybdenum oxide was demonstrated the photocatalytic property towards the degradation of methyl orange and orange II dye under visible light [102, 103]. Interestingly, they can be easily separated from the reaction mixture and reused without any major changes to catalytic activity. Yi Feng et al. synthesized ZIF-8 and studied the adsorption of methyl orange, concluded that ZIF-8 has a high adsorption capacity than most adsorbents. The maximum adsorption capacity of ZIF-8 was found to be 2500 mg $g^{-1}$. The adsorption capacity does not decrease even after three cycles [67].

ZIF-67 derivatives such as CoP/g-$C_3N_4$ show excellent photocatalytic activity for hydrogen production. A high photocatalytic hydrogen production rate of 201.5 μmol $g^{-1}$ $h^{-1}$ was obtained, which was almost 23 times higher than that of bulk g-$C_3N_4$ [104]. Co-ZIF-67 dodecahedron was controllably carved via the different ways for

**Table 1** Summary of catalytical applications of ZIF or ZIFs based composites

| Pure ZIF or ZIF composites | Applications | Reference |
|---|---|---|
| ZIF-8 | Photocatalytic degradation of Methylene blue | [111] |
| ZIF-8 | Conversion of Glucose to fructose and 5-hydroxy methyl furfural | [89] |
| ZIF-8 | Monoglycerine synthesis | [112] |
| ZIF-8 | Friedal-craft acylation | [85] |
| ZIF-8/Ni/Pd | Sonogashira coupling reaction | [86] |
| ZIF-8/ Pd NPs | Aminocarbonylation | [90] |
| ZIF-8/ PVP-Pd | Hydrogenation of 1,4-butynediol | [91] |
| ZIF-8/Pd NPs | Hydrogenation of Cinnamaldehyde | [113] |
| ZIF-8/Pd/Au | Ullmann Homocoupling reaction | [114] |
| ZIF-8/Pd/Ag | Dehydrogenation of formic acid | [100] |
| ZIF-8/Ir NPs | Hydrogenation of cyclohexene and phenylacetylene | [115] |
| ZIF-8/Ru | Dehydrogenation of dimethylamine-borane | [116] |
| ZIF-8/Ru | Asymmetric hydrogenation of acetophenone | [117] |
| ZIF-8/Cu | Cyclo-addition reaction | [118] |
| ZIF-9 | Knoevenagel Condensation | [84] |
| ZIF-9/Co | Hydrogen production from $NaBH_4$ hydrolysis | [119] |
| ZIF-67 | Synthesis of quinazolines | [120] |
| ZIF-67/Co | Synthesis of benzimadazoles | [121] |
| ZIF-67/Pd | Heck Reaction | [122] |
| ZIF-95 | Synthesis of cyclic carbonates from $CO_2$ and epoxides | [88] |
| ZIF-8/ZIF-67 | Fischer–Tropsch synthesis | [123] |

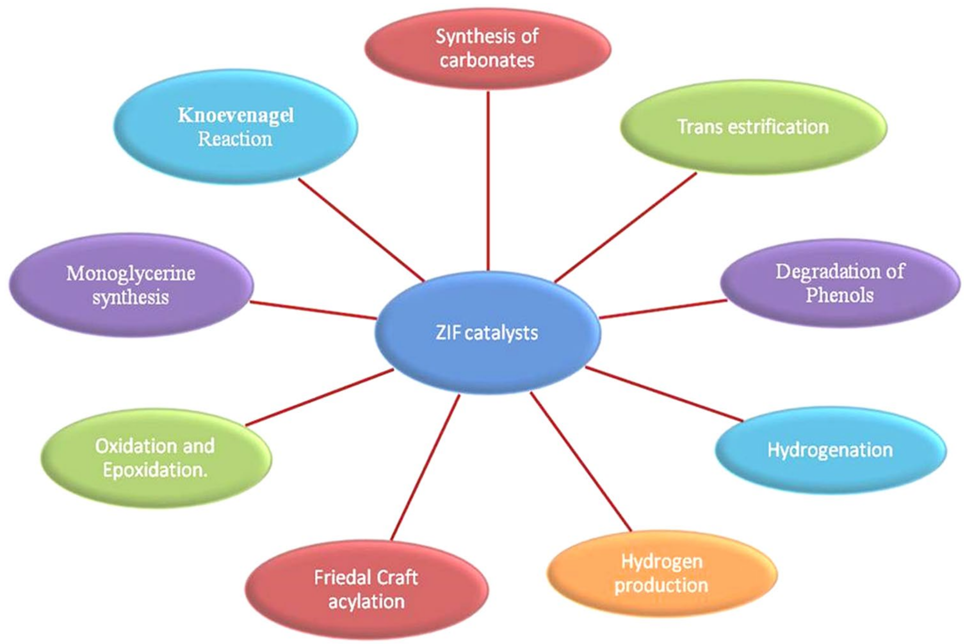



**Fig. 17** Some of the applications ZIFs as catalysts in organic reactions

efficiently boosting the photocatalytic property of hydrogen evolution. The mechanism of hydrogen evolution of ZIF-67-derived P-ZIF-67 concave polyhedron showing a more excellent photocatalytic performance in the EY sensitization system was investigated as shown in Fig. 18 [105].

## 6.5 Drug delivery

The classical drug delivery system made from organic or inorganic-based materials has a major setback due to the consequences resulting from uncontrolled drug release, biocompatibility, and cytotoxicity, etc. It is not an easy task to bring a drug into the market from synthesis, altogether it takes decades of research. At last, they suffer from high side effects, minimum efficiency, and non-specific delivery with high cytotoxicity [106]. To overcome this drawback, precise and targeted delivery of drugs without affecting the healthy cells to the maximum extent is in great need for existence. Thus as such ZIF is one of the excellent systems for the controlled release of drug molecules as seen in Fig. 19; it is because of the excellent physical and chemical dimensions, high loading capacity, low toxicity, pH-sensitive degradation, stabilities, and tunable properties. The well-defined pores of ZIFs play an important role in drug delivery because a substantial quantity of drugs can be fit within the framework to accomplish the targeted drug delivery. Even the changed materials of ZIF have evolved mutually of the potential frontiers during this field. $Zn^{2+}$, organic linkers, and target molecules were mixed, forming a consistent system as illustrated in figure seventeen. At the side of the

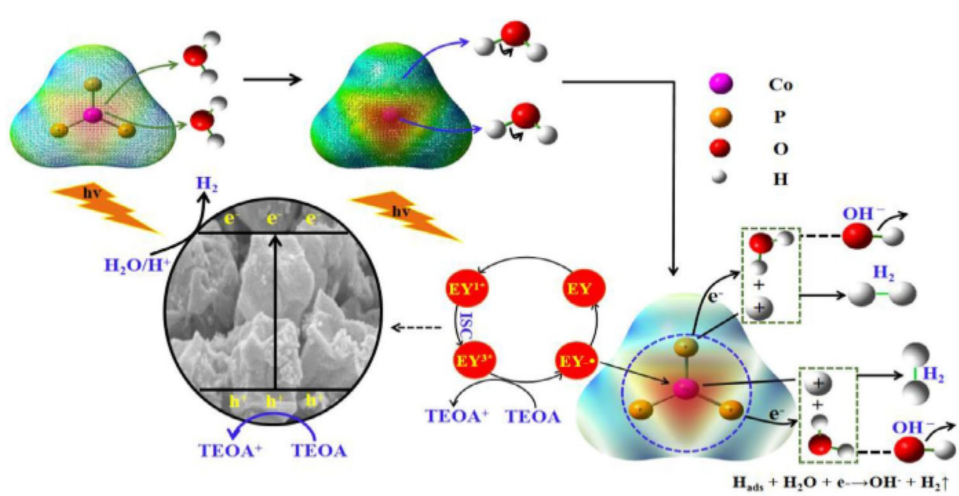



**Fig. 18** Schematic representation of hydrogen evolution mechanisms. Reproduced from reference number 112

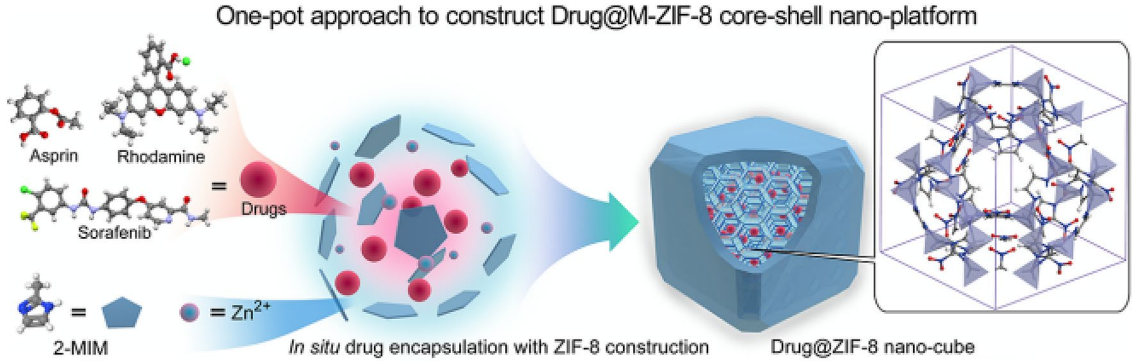



**Fig. 19** Preparation of Drug@M-ZIF-8 Nano-Platform. Reproduced from the reference number 131

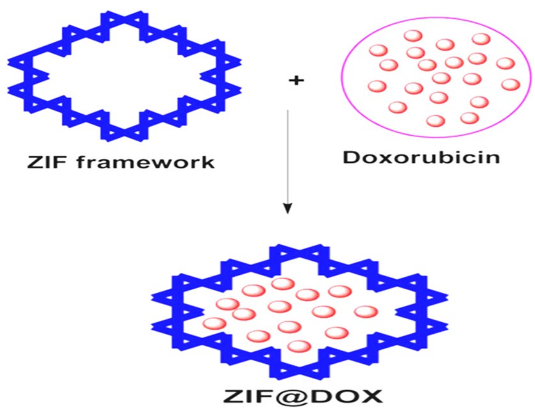



**Fig. 20** Encapsulation of DOX inside ZIFs Framework. Reproduced from reference number 133

coordination between $Zn^{2+}$ and linkers, target molecules were in place encapsulated at intervals ZIF-8, forming drug-containing ZIF-8 cores (denoted as drug@ZIF-8) [107].

Romy Ettlinger et al. successfully loaded arsenite (As) in the ZIF-8 nanopores with a loading capacity as high as 74 µg of as per 1 mg of ZIF-8. Studies suggest that As is released thoroughly in acidic conditions at pH whereas at neutral conditions only partial As is released due to the decomposition of nanocarrier ZIF-8 at acidic conditions [108].

So far many works have carried out, especially for the safe delivery of anticancer drugs. ZIF-8 has emerged as one of the potential candidates for its site-specific approach of anticancer drug—doxorubicin [109]. This being sustained to pH changes and shell-life is appreciable. As far as the best of our knowledge is considered, attempts are being made to construct hybrid nanocomposites for serving as drug delivery vehicles. Work has been done to build a ZIF-based material that can serve as a carrier for simultaneous fluorescence imaging and pH-responsive drug delivery to cancer cells as shown in Fig. 20. DOX is step by step discharged upon the buildup of DOX@ZIF-8in tumour sites. The distinct unleash property of DOX@ZIF-8 makes it significant as a pretty pH-responsive drug delivery system for tumor treatment.

ZIF-8 also exhibits excellent drug delivery capacity for anticancer drug 5-fluorouracil (5-FU) with 600 mg loading. Thus ZIF-8 proves to be an effective drug delivery agent. It was noted that in acidic condition drug are released much faster than in neutral conditions, thus ZIF-8 tends to be a pH-responsive drug delivery system [110].

## 7 Conclusion

Over a decade tremendous work is distributed for the event of ZIFs in synthesis, characterization, and style of applications attributable to its versatile crystalline porous materials with nice potential in a very sizable amount of applications, ZIFs can emerge within the future. There are a variety of synthesis methods available for the preparation of a large number of ZIFs and ZIF-based composites using solvent-based and solvent-free methods.

Due to their unique exceptional chemical, thermal, and structural properties. There is explosive growth in the research and development in ZIFs from an application point of view more work is indeed going on. The Classical applications such as adsorption, separation, drug delivery, and sensing, utilization of ZIFs have been a long journey, most recently modified. Both ZIF and ZIF- based materials have been flourished as versatile tools in many fields, even their combinations forming composites have been extensively used. Despite these many advantages and distinct properties, some challenges need to be overcome to meet the potential needs of commercial application and large-scale production.

Moreover, different varied approaches like mechanochemical synthesis methods, dry-gel, or steam-assisted conversion methods have been custom-made to prepare ZIFs. On the other hand, thus to bring ZIFs from laboratory studies to business applications, it's crucial to develop abundant on-market synthesis methods that unit of measurement cost-effective and consistent with producing ZIFs on an outsized scale to satisfy the potential industrial application desires. So lot of work needs to be done to take advantage of ZIF for environmentally friendly sustain. ZIFs and ZIF-based materials, new applications of the distinctive fast growing materials, and even a lot of new opportunities for additional exploring ZIFs and ZIF-based materials can still emerge within the future. To Further develop new methods, executions, mode of approach, permutations, and mixtures, analysis are needed for the event of this branch and to profit a man.

## 8 Limitations

No doubt, ZIFs are excellent compounds with distinguish properties such as high surface area, tunable pore size and volume, high thermal and chemical stabilities which leads to new opportunity. Perhaps the most important property is the ZIFs' hydrophobic properties and water stability. However, ZIFs tend to be expensive to synthesize. Synthesis methods with long reaction periods, high pressures, and high temperatures, which aren't methods that are easy to scale-up. Their use and study has been restricted to the bench top due to which significant amounts of information are missing.

## 9 Recommendation

Finally, we recommend for future work regarding different parameters such as temperature, pressure, time, and pH which can play an important role in controlling the shape and morphology of ZIF materials. Besides, more important environmental issues should be taken into account before using these materials for any applications.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported.

## References

1. Anh Phan, Christian J. Doonan, Fernando J. Uribe-Romo, Carolyn B. Knobler, Michael O'keeffe, and Omar M. Yaghi., Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks. Acc. Chem. Res. (2009). https://doi.org/10.1021/ar900116g
2. S. Tanaka, K. Kida, M. Okita, Y. Ito, Y. Miyake, Size-controlled synthesis of zeolitic imidazolate framework-8 (ZIF-8) crystals in an aqueous system at room temperature. Chem. Lett. **41**, 1337–1339 (2012)
3. B. Chen, Z. Yang, Y. Zhu, Y. Xia, Zeolitic imidazolate framework materials: recent progress in synthesis and applications. J. Mater. Chem. A **2**, 16811–16831 (2014)
4. S. Bhattacharjee, M.-S. Jang, H.-J. Kwon, W.-S. Ahn, Zeolitic imidazolate frameworks: synthesis, functionalization, and catalytic/adsorption applications. Catal. Surv. Asia **18**, 101–127 (2014)
5. Yongyong Zhang, Ying Jia, Ming Li, Li'an Hou., Influence of the 2-methylimidazole/zinc nitrate hexahydrate molar ratio on the synthesis of zeolitic imidazolate framework-8 crystals at room temperature. Sci. Rep. **8**, 1–7 (2018)
6. H.-Y. Cho, J. Kim, S.-N. Kim, W.-S. Ahn, High yield 1-L scale synthesis of ZIF-8 via a sonochemical route. Microporous Mesoporous Mater. **169**, 180–184 (2013)
7. Kyo Sung Park, Zheng Ni, Adrien P. Côté, Jae Yong Choi, Rudan Huang, Fernando J. Uribe-Romo, Hee K. Chae, Michael O'Keeffe, Omar M. Yaghi, Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. Proc. National Acad. Sci. **103**, 10186–10191 (2006)
8. Li Sze Lai, Yin Fong Yeong, Noraishah Che Ani, Kok Keong Lau, Azmi Mohd Shariff, Effect of synthesis parameters on the formation of zeolitic imidazolate framework 8 (ZIF-8) nanoparticles for CO2 adsorption. Part. Sci. Technol. **32**, 520–528 (2014)
9. Kumari Shalini, Pramod Kumar Sharma, Nitin Kumar, Imidazole and its biological activities: A review. Der. Chemica. Sinica. **1**, 36–47 (2010)
10. Jesse LC. Rowsell, Omar M. Yaghi, Metal–organic frameworks: a new class of porous materials. Microporous Mesoporous Mater. **73**, 3–14 (2004)
11. N. Stock, S. Biswas, Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites. Chem. Rev. **112**, 933–969 (2012)
12. G.E. Cmarik, M. Kim, S.M. Cohen, K.S. Walton, Tuning the adsorption properties of UiO-66 via ligand functionalization. Langmuir **28**, 15606–15613 (2012)
13. Y.-S. Li, F.-Y. Liang, H. Bux, A. Feldhoff, W.-S. Yang, J. Caro, Molecular sieve membrane: supported metal–organic framework with high hydrogen selectivity. Angew. Chem. **122**, 558–561 (2010)
14. W. Morris, B. Leung, H. Furukawa, O.K. Yaghi, N. He, H. Hayashi, Y. Houndonougbo, M. Asta, B.B. Laird, O.M. Yaghi, A combined experimental− computational investigation of carbon dioxide capture in a series of isoreticular zeolitic imidazolate frameworks. J. Am. Chem. Soc. **132**, 11006–11008 (2010)
15. Johan van den Bergh, Canan Gücüyener, Evgeny A. Pidko, Emiel JM. Hensen, Jorge Gascon, Freek Kapteijn, Understanding the anomalous alkane selectivity of ZIF-7 in the separation of light alkane/alkene mixtures. Chem. A Eur. J. **17**, 8832–8840 (2011)
16. G. Lu, J.T. Hupp, Metal− organic frameworks as sensors: a ZIF-8 based Fabry− Pérot device as a selective sensor for chemical vapors and gases. J. Am. Chem. Soc. **132**, 7832–7833 (2010)
17. JeongYong Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Metal–organic framework materials as catalysts. Chem. Soc. Rev. **38**, 1450–1459 (2009)
18. C.G. Jones, V. Stavila, M.A. Conroy, P. Feng, B.V. Slaughter, C.E. Ashley, M.D. Allendorf, Versatile synthesis and fluorescent labeling of ZIF-90 nanoparticles for biomedical applications. ACS Appl. Mater. Interfaces. **8**, 7623–7630 (2016)
19. C.-Y. Sun, C. Qin, X.-L. Wang, G.-S. Yang, K.-Z. Shao, Y.-Q. Lan, Su. Zhong-Min, P. Huang, C.-G. Wang, E.-B. Wang, Zeolitic imidazolate framework-8 as efficient pH-sensitive drug delivery vehicle. Dalton Trans. **41**, 6906–6909 (2012)

20. Bo. Wang, A.P. Côté, H. Furukawa, M. O'Keeffe, O.M. Yaghi, Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs. Nature **453**, 207–211 (2008)
21. F. Fu, B. Zheng, L.-H. Xie, Du. Huiling, Du. Shuangming, Z. Dong, Size-controllable synthesis of zeolitic imidazolate framework/carbon nanotube composites. Curr. Comput.-Aided Drug Des. **8**, 367 (2018)
22. J. Yao, M. He, H. Wang, Strategies for controlling crystal structure and reducing usage of organic ligand and solvents in the synthesis of zeolitic imidazolate frameworks. CrystEngComm **17**, 4970–4976 (2015)
23. N. Rangnekar, N. Mittal, B. Elyassi, J. Caro, M. Tsapatsis, Zeolite membranes–a review and comparison with MOFs. Chem. Soc. Rev. **44**, 7128–7154 (2015)
24. Z. Zhang, Z.-Z. Yao, S. Xiang, B. Chen, Perspective of microporous metal–organic frameworks for $CO_2$ capture and separation. Energy Environ. Sci. **7**, 2868–2899 (2014)
25. Bouëssel du Bourg, Aurélie U. Lila, Anne Boutin Ortiz, François-Xavier. Coudert, Thermal and mechanical stability of zeolitic imidazolate frameworks polymorphs. APL Mater. **2**, 124110 (2014)
26. X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, Ligand-directed strategy for zeolite-type metal–organic frameworks: zinc (II) imidazolates with unusual zeolitic topologies. Angew. Chem. Int. Ed. **45**, 1557–1559 (2006)
27. A.F. Gross, E. Sherman, J.J. Vajo, Aqueous room temperature synthesis of cobalt and zinc sodalite zeolitic imidizolate frameworks. Dalton Trans. **41**, 5458–5460 (2012)
28. T. Yang, T.-S. Chung, Room-temperature synthesis of ZIF-90 nanocrystals and the derived nano-composite membranes for hydrogen separation. J. Mater. Chem. A **1**, 6081–6090 (2013)
29. J. Cravillon, C.A. Schröder, H. Bux, A. Rothkirch, J. Caro, M. Wiebcke, Formate modulated solvothermal synthesis of ZIF-8 investigated using time-resolved in situ X-ray diffraction and scanning electron microscopy. CrystEngComm **14**, 492–498 (2012)
30. Kullaiah Byrappa, Masahiro Yoshimura, *Handbook of hydrothermal technology* (William Andrew, Norwich, 2012)
31. Y. Pan, Y. Liu, G. Zeng, L. Zhao, Z. Lai, Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system. Chem. Commun. **47**, 2071–2073 (2011)
32. J. Qian, F. Sun, L. Qin, Hydrothermal synthesis of zeolitic imidazolate framework-67 (ZIF-67) nanocrystals. Mater. Lett. **82**, 220–223 (2012)
33. N.A.H.M. Nordin, A.F. Ismail, A. Mustafa, P.S. Goh, D. Rana, T. Matsuura, Aqueous room temperature synthesis of zeolitic imidazole framework 8 (ZIF-8) with various concentrations of triethylamine. RSC Adv. **4**, 33292–33300 (2014)
34. Imran Ullah Khan, Mohd Hafiz Dzarfan. Othman, A.F. Asim Jilani, Haslenda Hashim Ismail, Juhana Jaafar, Mukhlis A. Rahman, Ghani Ur Rehman, Economical, environmental friendly synthesis, characterization for the production of zeolitic imidazolate framework-8 (ZIF-8) nanoparticles with enhanced $CO_2$ adsorption. Arab. J. Chem. **11**, 1072–1083 (2018)
35. Y. Pan, D. Heryadi, F. Zhou, L. Zhao, G. Lestari, Su. Haibin, Z. Lai, Tuning the crystal morphology and size of zeolitic imidazolate framework-8 in aqueous solution by surfactants. CrystEngComm **13**, 6937–6940 (2011)
36. W.-W. Xiong, Q. Zhang, Surfactants as promising media for the preparation of crystalline inorganic materials. Angew. Chem. Int. Ed. **54**, 11616–11623 (2015)
37. B. Chen, Z. Yang, Y. Zhu, Y. Xia, Zeolitic imidazolate framework materials: recent progress in synthesis and applications. J. Mater. Chem. **A2**, 16811–16831 (2014)
38. S.K. Nune, P.K. Thallapally, A. Dohnalkova, C. Wang, J. Liu, G.J. Exarhos, Synthesis and properties of nano zeolitic imidazolate frameworks. Chem. Commun. **46**, 4878–4880 (2010)
39. J. Yao, M. He, K. Wang, R. Chen, Z. Zhong, H. Wang, High-yield synthesis of zeolitic imidazolate frameworks from stoichiometric metal and ligand precursor aqueous solutions at room temperature. CrystEngComm **15**, 3601–3606 (2013)
40. T. Xing, Y. Lou, Q. Bao, J. Chen, Surfactant-assisted synthesis of ZIF-8 nanocrystals in aqueous solution via microwave irradiation. CrystEngComm **16**, 8994–9000 (2014)
41. Z. Ni, R.I. Masel, Rapid production of metal-organic frameworks via microwave-assisted solvothermal synthesis. J. Am. Chem. Soc. **128**, 12394–12395 (2006)
42. H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. J. Am. Chem. Soc. **131**, 16000–16001 (2009)
43. V.V. Butova, A.P. Budnik, E.A. Bulanova, A.V. Soldatov, New microwave-assisted synthesis of ZIF-8. Mendeleev Commun. **1**, 43–44 (2016)
44. Gesley AV. Martins, Peter J. Byrne, Phoebe Allan, Simon J. Teat, Alexandra MZ. Slawin, Yang Li, Russell E. Morris, The use of ionic liquids in the synthesis of zinc imidazolate frameworks. Dalton Trans. **39**, 1758–1762 (2010)
45. L. Yang, Lu. Huimin, Microwave-assisted ionothermal synthesis and characterization of zeolitic imidazolate framework-8. Chin. J. Chem. **30**, 1040–1044 (2012)
46. B. Seoane, J.M. Zamaro, C. Tellez, J. Coronas, Sonocrystallization of zeolitic imidazolate frameworks (ZIF-7, ZIF-8, ZIF-11 and ZIF-20). CrystEngComm **14**, 3103–3107 (2012)
47. W.-J. Son, J. Kim, J. Kim, W.-S. Ahn, Sonochemical synthesis of MOF-5. Chem. Commun. **47**, 6336–6338 (2008)
48. Imteaz Ahmed, Jaewoo Jeon, Nazmul Abedin Khan, Sung Hwa Jhung, Synthesis of a metal–organic framework, iron-benezenetricarboxylate, from dry gels in the absence of acid and salt. Crystal Growth Design **12**, 5878–5881 (2012)
49. M.J. Cliffe, C. Mottillo, R.S. Stein, D.-K. Bučar, T. Friščić, Accelerated aging: a low energy, solvent-free alternative to solvothermal and mechanochemical synthesis of metal–organic materials. Chem. Sci. **3**, 2495–2500 (2012)
50. Patrick J. Beldon, László. Fábián, Robin S. Stein, A. Thirumurugan, Anthony K. Cheetham, Tomislav Friščić, Rapid room-temperature synthesis of zeolitic imidazolate frameworks by using mechanochemistry. Angew. Chem. **122**, 9834–9837 (2010)
51. Kyo Sung Park, Zheng Ni, Adrien P. Côté, Jae Yong Choi, Rudan Huang, Fernando J. Uribe-Romo, Hee K. Chae, Michael O'keeffe, Omar M. Yaghi, ZIFs-first synthesis. Proc. Natl. Acad. Sci **103**, 10186–10191 (2006)
52. N. Lu, F. Zhou, H. Jia, H. Wang, B. Fan, R. Li, Dry-gel conversion synthesis of Zr-based metal–organic frameworks. Ind. Eng. Chem. Res. **56**, 14155–14163 (2017)
53. Qi. Shi, Z. Chen, Z. Song, J. Li, J. Dong, Synthesis of ZIF-8 and ZIF-67 by steam-assisted conversion and an investigation of their tribological behaviors. Angew. Chem. **123**, 698–701 (2011)
54. Stuart L. James, Christopher J. Adams, Carsten Bolm, Dario Braga, Paul Collier, Tomislav Friščić, Fabrizia Grepioni et al., Mechanochemistry: opportunities for new and cleaner synthesis. Chem. Soc. Rev. **41**, 413–447 (2012)
55. C. Mottillo, Lu. Yuneng, M.-H. Pham, M.J. Cliffe, T.-O. Do, T. Friščić, Mineral neogenesis as an inspiration for mild, solvent-free synthesis of bulk microporous metal–organic frameworks from metal (Zn, Co) oxides. Green Chem. **15**, 2121–2131 (2013)
56. J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber, M. Wiebcke, Rapid room-temperature synthesis and characterization of nanocrystals of a prototypical zeolitic imidazolate framework. Chem. Mater. **21**, 1410–1412 (2009)

57. Yang Liu, Zhifeng Liu, Danlian Huang, Min Cheng, Guangming Zeng, Cui Lai, Chen Zhang et al., Metal or metal-containing nanoparticle@ MOF nanocomposites as a promising type of photocatalyst. Coord. Chem. Rev. **388**, 63–78 (2019)
58. K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O′ Keeffe, OM Yaghi. Proc. National Acad. Sci. USA **103**, 10186 (2006)
59. H. Wang, L.R. Grabstanowicz, H.M. Barkholtz, D. Rebollar, Z.B. Kaiser, D. Zhao, B.-H. Chen, D.-J. Liu, Impacts of imidazolate ligand on performance of zeolitic-imidazolate framework-derived oxygen reduction catalysts. ACS Energy Lett. **4**, 2500–2507 (2019)
60. Joshua O. Ighalo, Selvasembian Rangabhashiyam, Comfort Abidemi Adeyanju, Samuel Ogunniyi, Adewale George Adeniyi, Chinenye Adaobi Igwegbe, Zeolitic Imidazolate Frameworks (ZIFs) for Aqueous Phase Adsorption–A Review. J. Ind. Eng. Chem. (2021). https://doi.org/10.1016/j.jiec.2021.09.029
61. Y.-R. Lee, M.-S. Jang, H.-Y. Cho, H.-J. Kwon, S. Kim, W.-S. Ahn, ZIF-8: A comparison of synthesis methods. Chem. Eng. J. **271**, 276–280 (2015)
62. M. Jian, B. Liu, G. Zhang, R. Liu, X. Zhang, Adsorptive removal of arsenic from aqueous solution by zeolitic imidazolate framework-8 (ZIF-8) nanoparticles. Colloids Surf. A **465**, 67–76 (2015)
63. Surendra Sasi Jampa, Ashish Prabhudas Kumar, Rajesh Vanshpati Unnarkat, Sivakumar Pandian, Manish Kumar Sinha, Swapnil Dharaskar, Adsorption and recyclability aspects of humic acid using nano-ZIF-8 adsorbent. Environ. Technol. Innov. **19**, 100927 (2020)
64. Nazmul Abedin Khan, Beom K. Jung, Zubair Hasan, Sung Hwa Jhung, Adsorption and removal of phthalic acid and diethyl phthalate from water with zeolitic imidazolate and metal–organic frameworks. J. Hazard. Mater. **282**, 194–200 (2015)
65. J.-Q. Jiang, C.-X. Yang, X.-P. Yan, Zeolitic imidazolate framework-8 for fast adsorption and removal of benzotriazoles from aqueous solution. ACS Appl. Mater. Interfaces. **5**, 9837–9842 (2013)
66. Na. Li, L. Zhou, X. Jin, G. Owens, Z. Chen, Simultaneous removal of tetracycline and oxytetracycline antibiotics from wastewater using a ZIF-8 metal organic-framework. J. Hazard. Mater. **366**, 563–572 (2019)
67. Yi. Feng, Yu. Li, Xu. Minying, S. Liu, J. Yao, Fast adsorption of methyl blue on zeolitic imidazolate framework-8 and its adsorption mechanism. RSC Adv. **6**, 109608–109612 (2016)
68. K.-Y. Lin, H.-A. Chang, Ultra-high adsorption capacity of zeolitic imidazole framework-67 (ZIF-67) for removal of malachite green from water. Chemosphere **139**, 624–631 (2015)
69. Yanfang Li, Xinlong Yan, Hu. Xiaoyan, Rui Feng, Min Zhou, Trace pyrolyzed ZIF-67 loaded activated carbon pellets for enhanced adsorption and catalytic degradation of Rhodamine B in water. Chem. Eng. J. **375**, 122003 (2019)
70. M. Zhu, D. Srinivas, S. Bhogeswararao, P. Ratnasamy, M.A. Carreon, Catalytic activity of ZIF-8 in the synthesis of styrene carbonate from $CO_2$ and styrene oxide. Catal. Commun. **32**, 36–40 (2013)
71. P.A. Jacobs, E.M. Flanigen, J. C., *Jansen, and Herman van Bekkum* (Elsevier, Introduction to zeolite science and practice, 2001)
72. Qilei Song, S.K. Nataraj, Mina V. Roussenova, Jin Chong Tan, David J. Hughes, Wei Li, Pierre Bourgoin et al., Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation. Energy Environ. Sci. **5**, 8359–8369 (2012)
73. Haiqian Lian, Eryue Song, Bin Bao, Yu. Wenhe Yang, Yichang Pan Yang, Ju. Shengui, Highly steam-stable CHA-type zeolite imidazole framework ZIF-302 membrane for hydrogen separation. Sep Purif Technol (2021). https://doi.org/10.1016/j.seppur.2021.119875
74. Y. Zhang, Y. Tong, X. Li, S. Guo, H. Zhang, Xi. Chen, K. Cai, L. Cheng, W. He, Pebax mixed-matrix membrane with highly dispersed ZIF-8@ CNTs to enhance CO2/N2 separation. ACS Omega. **6**, 18566–18575 (2021)
75. P. Krokidas, S. Moncho, E.N. Brothers, I.G. Economou, Defining new limits in gas separations using modified ZIF systems. ACS Appl. Mater. Interfaces. **12**, 20536–20547 (2020)
76. Víctor Manuel. Melgar, Jinsoo Kim Aceituno, Mohd Roslee Othman, Zeolitic imidazolate framework membranes for gas separation: A review of synthesis methods and gas separation performance. J. Ind. Eng. Chem. **28**, 1–15 (2015)
77. G. Zhong, D. Liu, J. Zhang, The application of ZIF-67 and its derivatives: adsorption, separation, electrochemistry and catalysts. J. Mater. Chem. A **6**, 1887–1899 (2018)
78. X. Gong, Y. Wang, T. Kuang, ZIF-8-based membranes for carbon dioxide capture and separation. ACS Sustain. Chem. Eng. **5**, 11204–11214 (2017)
79. Prabakaran Shankar, John Bosco Balaguru. Rayappan, Gas sensing mechanism of metal oxides: The role of ambient atmosphere, type of semiconductor and gases-A review. Sci. Lett. J. **4**, 126 (2015)
80. G. Lu, J.T. Hupp, Metal- organic frameworks as sensors: a ZIF-8 based Fabry- Pérot device as a selective sensor for chemical vapors and gases. J. Am. Chem. Soc. **132**, 7832–7833 (2010)
81. S.T. Meek, J.A. Greathouse, M.D. Allendorf, Metal**-** organic frameworks: A rapidly growing class of versatile nanoporous materials. Adv. Mater. **23**, 249–267 (2011)
82. E.-X. Chen, H. Yang, J. Zhang, Zeolitic imidazolate framework as formaldehyde gas sensor. Inorg. Chem. **53**, 5411–5413 (2014)
83. S. Liu, Z. Xiang, Hu. Zan, X. Zheng, D. Cao, Zeolitic imidazolate framework-8 as a luminescent material for the sensing of metal ions and small molecules. J. Mater. Chem. **21**, 6649–6653 (2011)
84. Lien TL. Nguyen, Ky. K.A. Le, Hien X. Truong, Nam TS. Phan, Metal–organic frameworks for catalysis: the Knoevenagel reaction using zeolite imidazolate framework ZIF-9 as an efficient heterogeneous catalyst. Catal. Sci. Technol. **2**, 521–528 (2012)
85. Lien TL. Nguyen, K.A. LE Ky, T.S. Nam, A zeolite imidazolate framework ZIF-8 catalyst for friedel-crafts acylation. Chin. J. Catal. **33**, 688–696 (2012)
86. Y. Wang, Y. Zeng, Wu. Xingchun, Mu. Manman, L. Chen, A novel Pd-Ni bimetallic synergistic catalyst on ZIF-8 for Sonogashira coupling reaction. Mater. Lett. **220**, 321–324 (2018)
87. M. Zhang, Ya. Gao, C. Li, C. Liang, Chemical vapor deposition of Pd (C3H5) (C5H5) for the synthesis of reusable Pd@ ZIF-8 catalysts for the Suzuki coupling reaction. Chin. J. Catal. **36**, 588–594 (2015)
88. Kyung Mi Bhin, Jose Tharun, Kuruppathparambil Roshith Roshan, Dong-Woo. Kim, Yongchul Chung, Dae-Won. Park, Catalytic performance of zeolitic imidazolate framework ZIF-95 for the solventless synthesis of cyclic carbonates from $CO_2$ and epoxides. J. CO2 Util. **17**, 112–118 (2017)
89. Ryan Oozeerally, Shivendra DK. Ramkhelawan, David L. Burnett, Christiaan HL. Tempelman, Volkan Degirmenci, ZIF-8 metal organic framework for the conversion of glucose to fructose and 5-Hydroxymethyl furfural. Catalysts **9**, 812 (2019)
90. Tuan T. Dang, Yinghuai Zhu, Joyce S. Y. Ngiam, Subhash C. Ghosh, Anqi Chen, Abdul M. Seayad, Palladium nanoparticles supported on ZIF-8 as an efficient heterogeneous catalyst for aminocarbonylation. ACS Catal. **3**, 1406–1410 (2013)
91. M. Zhang, Y. Yang, C. Li, Q. Liu, C.T. Williams, C. Liang, PVP–Pd@ ZIF-8 as highly efficient and stable catalysts for selective hydrogenation of 1, 4-butynediol. Catal. Sci. Technol. **4**, 329–332 (2014)

92. P. Wang, J. Zhao, X. Li, Y. Yang, Q. Yang, C. Li, Assembly of ZIF nanostructures around free Pt nanoparticles: efficient size-selective catalysts for hydrogenation of alkenes under mild conditions. Chem. Commun. **49**, 3330–3332 (2013)
93. C. Avci, M.L.D. Marco, C. Byun, J. Perrin, M. Scheel, C. Boissière, M. Faustini, Metal–organic framework photonic balls: single object analysis for local thermal probing. Adv. Mater. **33**, 2104450 (2021)
94. Wenjuan Wang, Shuang Chen, Eduardo Guisasola Cal, Marta Martínez Moro, Sergio Moya, Emerson Coy, Changlong Wang, Jean-René. Hamon, Didier Astruc, ZIF-8-based vs. ZIF-8-derived Au and Pd nanoparticles as efficient catalysts for the Ullmann homocoupling reaction. Chem. Front Inorg (2020). https://doi.org/10.1039/D0QI00831A
95. K. Alkanad, A. Hezam, G.C. Sujay Shekar, Q.A. Drmosh, A.L.A. Kala, M.Q.A. AL-Gunaid, N.K. Lokanath, Magnetic recyclable α-$Fe_2$ $O_3$–$Fe_3O_4$/$Co_3O_4$–CoO nanocomposite with a dual Z-scheme charge transfer pathway for quick photo-Fenton degradation of organic pollutants. Catal. Sci. Technol. **11**, 3084–3097 (2021)
96. Rashmi Veeranna, Pramila Shivamurthy, Mallikarjunaswamy Chandrashekaraiah, Nithin Kundachira Subramanni, Sangamesha Madanahalli Ankanathappa, Shaukath Ara Khanum, Lakshmi Ranganatha Venkataravanappa, Metal nanoparticles as emerging catalysts: A mini review. Int. J. Nano Dimens Spring. **12**, 90–97 (2021)
97. Ranganatha, V. Lakshmi, K. S. Nithin, Shaukath Ara Khanum, G. Nagaraju, and C. Mallikarjunaswamy. "Zinc oxide nanoparticles: A significant review on synthetic strategies, characterization and applications." In AIP Conference Proceedings, vol. 2162, no. 1, p. 020089. AIP Publishing LLC, 2019.
98. Salma Kouser, Abdo Hezam, K. Byrappa, Shaukath Khanum., Sunlight-assisted synthesis of cerium (IV) oxide nanostructure with enhanced photocatalytic activity. Optik **245**, 167236 (2021)
99. Khaled Alkanad, Abdo Hezam, Qasem Ahmed Drmosh, Sujay Shekar Ganganakatte. Chandrashekar, Abeer A. AlObaid, Ismail Warad, Mohammed Abdullah Bajiri, Lokanath Neratur Krishnappagowda, Construction of Bi2S3/TiO2/MoS2 S-scheme heterostructure with a switchable charge migration pathway for selective CO2 reduction. Solar RRL (2021). https://doi.org/10.1002/solr.202100501
100. H. Dai, B. Xia, L. Wen, Du. Cheng, Su. Jun, W. Luo, G. Cheng, Synergistic catalysis of AgPd@ ZIF-8 on dehydrogenation of formic acid. Appl. Catal. B **165**, 57–62 (2015)
101. G.C.S. Shekar, K. Alkanad, A. Hezam, A. Alsalme, N. Al-Zaqri, N.K. Lokanath, Enhanced photo-Fenton activity over a sunlight-driven ignition synthesized α-$Fe_2O_3$-$Fe_3O_4$/$CeO_2$ heterojunction catalyst enriched with oxygen vacancies. J. Mol. Liq. **335**, 116186 (2021)
102. T.T. Isimjan, H. Kazemian, S. Rohani, A.K. Ray, Photocatalytic activities of Pt/ZIF-8 loaded highly ordered $TiO_2$ nanotubes. J. Mater. Chem. **20**, 10241–10245 (2010)
103. C. Dey, R. Banerjee, Controlled synthesis of a catalytically active hybrid metal-oxide incorporated zeolitic imidazolate framework (MOZIF). Chem. Commun. **49**, 6617–6619 (2013)
104. X.-J. Sun, D.-D. Yang, H. Dong, X.-B. Meng, J.-L. Sheng, X. Zhang, J.-Z. Wei, F.-M. Zhang, ZIF-derived CoP as a cocatalyst for enhanced photocatalytic H 2 production activity of gC 3 N 4. Sustain. Energy Fuels **2**, 1356–1361 (2018)
105. Yanbing Li, Zhiliang Jin, Tiansheng Zhao, Performance of ZIF-67–Derived fold polyhedrons for enhanced photocatalytic hydrogen evolution. Chem. Eng. J. **382**, 123051 (2020)
106. L.R.M. Ferraz, A.É.G.A. Tabosa, D.D.S.S. Nascimento, A.S. Ferreira, V.A.W. Sales, J.Y.R. Silva, S.A. Júnior, L.A. Rolim, J.J.S. Pereira, P.J. Rolim-Neto, ZIF-8 as a promising drug delivery system for benznidazole: development, characterization, in vitro dialysis release and cytotoxicity. Sci. Rep. **10**, 1–14 (2020)
107. Huaiyuan Zhao, Hengshu Ye, Jun Zhou, Guping Tang, Zhaoyin Hou, Hongzhen Bai, Montmorillonite-enveloped zeolitic imidazolate framework as a nourishing oralnano-platform for gastrointestinal drug delivery. ACS Appl. Mater. Interfaces **12**, 49431–49441 (2020)
108. Romy Ettlinger, Natalia Moreno, Dirk Volkmer, Kornelius Kerl, Hana Bunzen, Zeolitic imidazolate framework- 8 as pH- sensitive nanocarrier for "arsenic trioxide" drug delivery. Chemistry (Weinheim an der Bergstrasse, Germany) **25**, 13189 (2019)
109. C. Adhikari, A. Das, A. Chakraborty, Zeolitic imidazole framework (ZIF) nanospheres for easy encapsulation and controlled release of an anticancer drug doxorubicin under different external stimuli: a way toward smart drug delivery system. Mol. Pharm. **12**, 3158–3166 (2015)
110. M. Gomar, S. Yeganegi, Adsorption of 5-fluorouracil, hydroxyurea and mercaptopurine drugs on zeolitic imidazolate frameworks (ZIF-7, ZIF-8 and ZIF-9). Microporous Mesoporous Mater. **252**, 167–172 (2017)
111. H.-P. Jing, C.-C. Wang, Y.-W. Zhang, P. Wang, R. Li, Photocatalytic degradation of methylene blue in ZIF-8. RSC Adv. **4**, 54454–54462 (2014)
112. Lik H. Wee, Tristan Lescouet, Jayashree Ethiraj, Francesca Bonino, Roxana Vidruk, Eva Garrier, Dirk Packet et al., Hierarchical zeolitic imidazolate framework-8 catalyst for monoglyceride synthesis. ChemCatChem **5**, 3562–3566 (2013)
113. D. Zhang, B. Wang, L. Yan, Lu. Ruixiao Gao, Z.X. Liu, X. Yan, Y. Li, L. Chen, Selective hydrogenation of cinnamaldehyde over magnetic flower-like carbonaceous Pd catalysts. New J. Chem. **44**, 20367–20374 (2020)
114. Wenjuan Wang, Shuang Chen, Eduardo Guisasola Cal, Marta Martínez Moro, Sergio Moya, Emerson Coy, Changlong Wang, Jean-René. Hamon, Didier Astruc, ZIF-8-based vs. ZIF-8-derived Au and Pd nanoparticles as efficient catalysts for the Ullmann homocoupling reaction. Inorg. Chem. Front. **7**, 3945–3952 (2020)
115. M. Zahmakiran, Iridium nanoparticles stabilized by metal organic frameworks (IrNPs@ ZIF-8): synthesis, structural properties and catalytic performance. Dalton Trans. **41**, 12690–12696 (2012)
116. M. Yurderi, A. Bulut, M. Zahmakiran, M. Gülcan, S. Özkar, Ruthenium (0) nanoparticles stabilized by metal-organic framework (ZIF-8): Highly efficient catalyst for the dehydrogenation of dimethylamine-borane and transfer hydrogenation of unsaturated hydrocarbons using dimethylamine-borane as hydrogen source. Appl. Catal. B **160**, 534–541 (2014)
117. M. Liu, B. Fan, X. Shi, R. Li, Ru/ZIF-8 with a chiral modifier for asymmetric hydrogenation of acetophenone. Catal. Commun. **42**, 20–24 (2013)
118. Jingze Sun, Liya Semenchenko, Woo Taik Lim, Maria Fernanda Ballesteros. Rivas, Victor Varela-Guerrero, Hae-Kwon. Jeong, Facile synthesis of Cd-substituted zeolitic-imidazolate framework Cd-ZIF-8 and mixed-metal CdZn-ZIF-8. Microporous Mesoporous Mater. **264**, 35–42 (2018)
119. K.-Y. Lin, S.-Y. Chen, Catalytic reduction of bromate using ZIF-derived nanoscale cobalt/carbon cages in the presence of sodium borohydride. ACS Sustain. Chem. Eng. **3**, 3096–3103 (2015)
120. Thanh Truong, Tam M. Hoang, Chung K. Nguyen, Quynh TN. Huynh, Nam TS. Phan, Expanding applications of zeolite imidazolate frameworks in catalysis: synthesis of quinazolines using ZIF-67 as an efficient heterogeneous catalyst. Rsc Adv. **5**, 24769–24776 (2015)
121. Viet D. Nguyen, Chung K. Nguyen, Kien N. Tran, Thach N. Tu, Tung T. Nguyen, Ha. V. Dang, Thanh Truong, Nam TS. Phan, Zeolite imidazolate frameworks in catalysis: Synthesis of

benzimidazoles via cascade redox condensation using Co-ZIF-67 as an efficient heterogeneous catalyst. Appl. Catal. A Gen. **555**, 20–26 (2018)
122. A. Zhou, R.-M. Guo, J. Zhou, Y. Dou, Ya. Chen, J.-R. Li, Pd@ ZIF-67 derived recyclable Pd-based catalysts with hierarchical pores for high-performance heck reaction. ACS Sustain. Chem. Eng. **6**, 2103–2111 (2018)
123. B. Lü, W. Qi, M. Luo, Q. Liu, L. Guo, Fischer–Tropsch synthesis: ZIF-8@ ZIF-67-Derived cobalt nanoparticle-embedded nanocage catalysts. Ind. Eng. Chem. Res. **59**, 12352–12359 (2020)