**INVESTIGATION OF METAL-ORGANIC FRAMEWORK**

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**Abstract:**

The metal organic framework (MOF) family includes zinc imidazole framework-8, often known as ZIF-8. Zinc metal is properly coupled with an organic ligand or fragment in ZIF-8's chemical structure, creating a cage-like three-dimensional network with distinctive porosity. ZIF-8 has lately been investigated in a number of applications, including gas storage, catalysis, electrochemical sensing, drug administration, etc., because of its distinctive design and physicochemical characteristics.

**Introduction:**

Porous materials have gotten a lot of scientific interest during the last five decades because of their inherent properties including large surface areas, massive pore volumes, and tuneable hole sizes, and the research will continue to develop in the future [1]. They are defined as any solid that has pores and voids and serves as the foundation for porous materials. Microporous, mesoporous, and macroporous materials are the three categories of porous materials. In microporous materials, micropores with widths or diameters of 2 nm can be discovered [2-3]. Mesoporous materials feature holes ranging in width from 2 to 50 nm, and macroporous materials have pores larger than 50 nm. The term "nanoporous" has lately become popular. Moreover their catalytic activity and absorption, porous materials have attracted the interest of many researchers to be developed for commercial application [4]. Zeolites, which are now widely employed in commercial water softening and purification as well as hydro-cracking catalysts in the petrochemical sector, are an example of a success story of this evolution and have grown into a giga-dollar international market. Assembled from metal ions and organic ligands, metal-organic frameworks (MOFs) are a type of nanoporous materials that show interesting characteristics, tuneable topologies, and a variety of functions [5]. Zeolitic imidazolate frameworks (ZIFs), a novel and distinct type of MOFs made up of metal ions and imidazolate linkers, have recently been discovered. ZIFs have a variety of structures that are similar to those of standard aluminosilicate zeolites. Typically, M2+ ions act as silicon while imidazolate anions form bridges that act as oxygen in zeolite frameworks, with the M-Im-M angle being approximately 145o [6-7]. Numerous ZIF materials offer a variety of possible uses due to their inherent porous properties, extensive functionalities, and remarkable thermal and chemical stabilities. Additionally, ZIFs have proven to be effective precursors or sacrificial templates for the creation of porous carbon-based nanocomposites due to their molecular-like organic-inorganic crystal structure [8].

**Development of Metal-Organic Framework (MOF):**

Due to their tremendous uses, metal-organic frameworks, or MOFs, are incredibly dynamic materials. When an inorganic component is joined to organic ligands by coordination bonds, MOFs organic-inorganic crystalline porous materials are developed. Two of the many intriguing aspects of these materials are their high and persistent porosity, as well as their flexibility in pore design and function. These characteristics make them suitable for a variety of applications, including encapsulation, drug delivery, gas detection, and catalysis. The surface area per gram of the MOFs developed by researchers is around 7800 square meters. For example, a full soccer field's worth of surface area may be filled with just a teaspoon-sized amount of this MOF compound [9].

MOFs' cage-like structure is being used in a variety of applications, including gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, and sensing. In addition to their direct applications, MOFs have been used as exceptional precursors for the production of inorganic functional materials with unrivaled design potentials, such as carbons, metal-based compounds, and their composites. Carbonaceous materials have a wide range of applications, including adsorption, catalysis, batteries, fuel cells, supercapacitors, medication administration, and imaging. Several sensors are important uses for carbonaceous materials because they are so closely related to human health [10-11].

Some of the essential ideas guiding the development of MOFs were derived from concepts found in the more venerable domains of coordination chemistry and zeolite chemistry [12].

Alfred Werner (1913 Nobel Laureate) is credited with developing coordination chemistry, which focuses on the interactions of organic and inorganic ligands with metal centers and investigates issues like isomerism and bonding in coordination compounds. Some of the earliest MOFs feature an inorganic component that contains lone polyhedral or tiny clusters similar to what is seen in coordination chemistry. Zeolite chemistry pioneered the idea of SBUs, leading to the creation of over 40 naturally occurring and 190 artificial zeolite frameworks with distinctive structural and topological characteristics. This refers to the geometry of the units specified by the point of extension in the context of MOFs, such as the carboxylate C atoms in the majority of carboxylate MOFs [13-14].

**Zeolite Imidazole Framework (ZIF):**

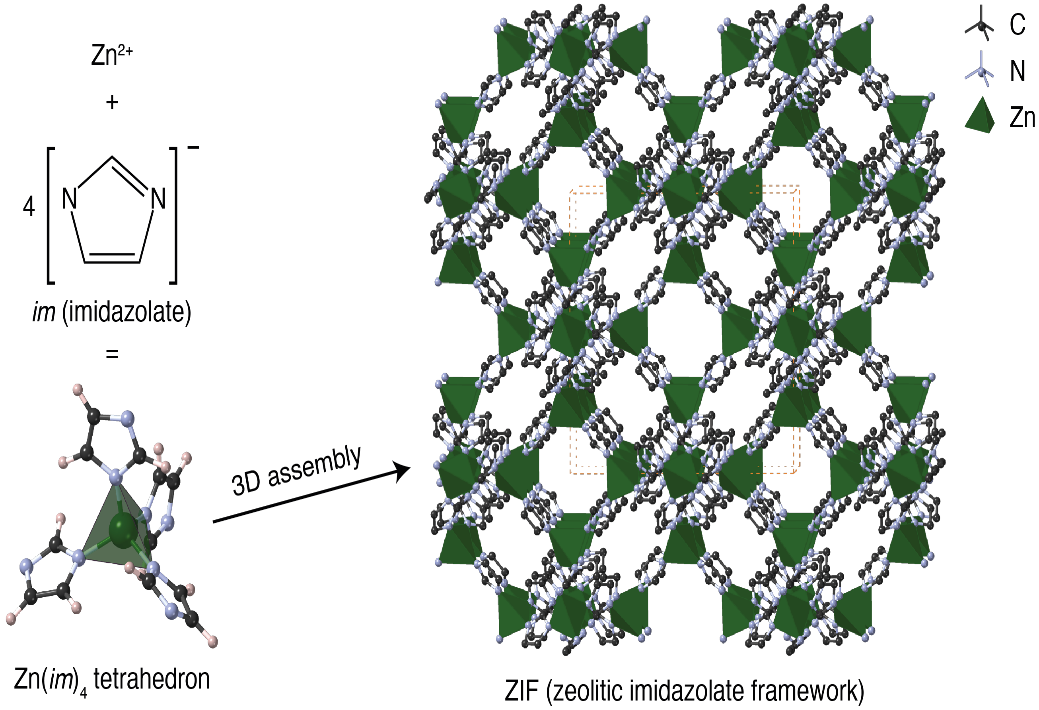
A specific class of MOFs named ZIF-8 was produced in my most recent work and subsequently used in other syntheses. The zeolitic imidazolate frameworks used as the foundation for the ZIF series MOFs were created by copolymerizing zinc and cobalt ions with imidazole-type linkers. The ZIF structures consist of nets of seven different aluminosilicate zeolites where the tetrahedral Si/Al clusters are replaced by Zn or Co and the bridging O by the bridging imidazolate [15].

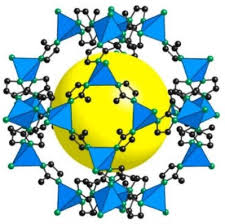
Since then, ZIF glass has received substantial interest from researchers as an unearthed form of well-known material. ZIF-4, ZIF-62, ZIF-76, and roughly 10 other members of the MOF family have all been successfully converted to their glassy states. Glass can be categorized into three main groups in conventional materials science: inorganic, organic, and metallic. The structure is composed of mixed ionic/covalent, covalent, or metallic bonds as chemical bonds. MOF glass, a relatively new organic-inorganic coordinated glass, has a vastly different structure from the three previously mentioned glasses. It's referred to as the fourth variety of glass [16].

Zeolites are extremely beneficial in catalysis. The constant tetrahedral coordination of the Si/Al connecting points and the two-coordinated oxide linkers limit the size of zeolites. There are only about 200 recognized zeolites. MOFs, on the other hand, have more diversified coordination geometries, polytopic linkers, and auxiliary ligands (F, OH, H2O, to name a few). It is also difficult to obtain zeolites with pore diameters larger than 1 nm, limiting zeolitic catalysis to relatively tiny organic molecules (typically no larger than xylenes) [17].

**Structure and Different Forms of ZIF:**

ZIFs have superior thermal and chemical stability when compared to other MOFs. For example, ZIF-8 was suspended in boiling water and several organic solvents for 7 days and retained its entire crystallinity. ZIF-8 can also survive temperatures of up to 550°C in N2, whereas MOF-5's permanently porous cubic structure decomposes at 450 °C in N2. ZIFs feature persistent porosity similar to zeolites and consistent pore size. For many years, the industry has relied on zeolites due to their durability in harsh environments. The similarities between zeolites and ZIFs have aided in understanding the fundamentals of ZIFs, as many of the concepts may overlap with those of zeolite chemistry, and will eventually aid in the implementation of ZIFs for industrial purposes [18].

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**Figure-1: Structure of Zeolitic Imidazolate Framework (ZIF)**

Additionally, ZIF materials would make excellent templates and precursors to generate porous carbon materials under the right synthesis circumstances because of the highly organized porous structures with rich organic species. Additionally, carbon composites containing nanostructured metal/metal oxide species are more likely to occur during the in situ carbonization process because of the regular arrangement of metal species in ZIF precursors. Under specific controlled synthesis conditions, the pure metal or metal oxide could likewise be produced from ZIF precursors. Future nanomaterial preparation and application will be made easier by these simple synthetic methods [19]. Due to structural variances, ZIF was categorized into numerous categories. ZIFs include ZIF-70, ZIF-69, ZIF-9, ZIF-14, ZIF-68, ZIF-90, ZIF-64, ZIF-11, ZIF-8, ZIF-L, ZIF-7, and ZIF-67. ZIF-8, ZIF-L, and ZIF-7 contain Zn2+, but ZIF-67 contains Co 2+. ZIF-7 was created in dimethyl formamide, while the others were created in the water. For ZIF-8, ZIF-L, and ZIF-67, the organic linker was 2-methyl imidazole, while for ZIF-7; it was benzimidazole [20].

**Synthesis Methods of ZIF – 8:**

This chapter investigates and presents the most recent breakthroughs in ZIF material synthesis, applications, and ZIF derivatives.

**ZIF Powder Synthesis:**

Most ZIF materials, particularly in the early stages of ZIF research, were created as powders that were isolated from reaction mixtures after solvents or other contaminants were removed. To date, both solvent-based and non-solvent-based synthesis techniques for powder-based ZIF materials have been developed [21].

**Solvent-Based Synthesis:**

**Solvothermal Method:**

Organic solvent systems such as N, N-dimethylformamide (DMF), N, N-diethyl formamide (DEF), and N-methyl pyrrolidine (NMP) were used to synthesize ZIF-1 to ZIF-12 crystals. 55 DMF/DEF/NMP were also utilized as solvents in the synthesis of various ZIF materials, including ZIF-60 to ZIF-77, 56 ZIF-78 to ZIF-82, 66 ZIF90, 25 ZIF-95, and ZIF-100. Later, several researchers synthesized ZIFs with DMF or DEF to examine the method of production and relative characteristics. Modified recipes based on Yaghi's approach have recently been created. To enhance material production, organic amines such as pyridine and triethylamine (TEA) were added as deprotonating agents to the DMF or DEF solvent. For example, TEA was used to create a micro-sized hexagonal rod-shaped ZIF-78 crystal, while ZIF-90 was created with the addition of pyridine in the DMF at room temperature [22].

**Hydrothermal Synthesis:**

Whereas the simple hydrothermal synthesis approach predominated in the early stages of ZIF research, organic solvents are unquestionably expensive, volatile, and unfriendly to the environment. Recently, great work has been given to the green and simple manufacture of ZIFs by utilizing fewer organic solvents or, finally, avoiding the usage of organic solvents altogether. Pan et al. were the first to demonstrate the production of ZIF-8 in an aqueous solution at ambient temperature using a simple procedure: after stirring for about 5 minutes, the zinc nitrate solution was combined with the 2-methylimidazole (MIm) solution, and the products were recovered by centrifugation. However, given that the stoichiometric molar ratio of zinc ions and MIm in ZIF-8 is Zn2+: MIm=1:2, it is clear that an excess of MIm (molar ratio of Zn2+: MIm=1:70) was squandered in this technique. As a result, much effort has been expended in the synthesis of ZIFs from stoichiometric molar ratios of metal ions and Im derivatives in alkaline solutions. Miyake et al., in particular, were successful in creating pure ZIF-8 crystals in an aqueous solution at ambient temperature, and the crystalline ZIF-8 could be formed from a molar ratio of Zn2+:MIm =1:20. Furthermore, Qian's group revealed that ZIF-67 nanocrystals could be produced in aqueous solutions at room temperature using the molar ratio of Co2+: MIm: H2O =1:58:1100 [23].

The addition of chemicals to water-based systems for ZIF manufacture also changed them. Both TEA 26 and ammonium hydroxide 83 were utilized as deprotonation agents to limit the utilization of the ligand MIm and start the production of ZIFs. Gross and colleagues were able to synthesize ZIF-8 and ZIF-67 in an aqueous solution with the addition of TEA at room temperature without the formation of by-products, allowing the metal ion: MIm molar ratio to be reduced to 1:4. Yao et al. also observed that in the presence of ammonium hydroxide, ZIF-8 could be synthesized in the following molar ratio: Zn2+: MIm: NH4+: H2O = 1:4:16:547. In an aqueous environment with additional additives such as triblock copolymers poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO)83 and polyvinyl pyro did one (PVP)84, ZIFs may be formed from stoichiometric metal ions and MIm ratio. For example, both ZIF-8 and ZIF-67 were synthesized from stoichiometric metal ions and MIm in aqueous ammonia systems in the presence of a triblock copolymer surfactant containing PEO groups, with the hope that the electrostatic attraction to the metal ions would promote the formation of porous ZIF-8 and ZIF-67. Shieh et al. discovered that in the presence of PVP, micro-sized ZIF-90 crystals may be formed in an aqueous solution (with a molecular weight of 4000). PVP was proposed to control crystal shape and prevent seed crystal aggregation [24,25].

We and other groups have recently effectively synthesized ZIFs from stoichiometric precursors using aqueous ammonia modulation. Wang's group revealed that ZIF-8 may be synthesized from stoichiometric precursors (Zn2+: MIm =1:2) in concentrated ammonium hydroxide aqueous solutions at room temperature. The addition of a suitable amount of ammonium hydroxide was discovered to be crucial for the production and development of ZIF-8 crystals via deprotonation and coordination processes. It was also discovered that ZIF-8 could be easily synthesized at ambient temperature from stoichiometric precursors in an aqueous ammonia solution without the use of any other additions. By adjusting the concentration of aqueous ammonia in the synthesis mixture, the structures, particle sizes, and textural qualities of the final ZIF-8 materials could be easily modified. Undoubtedly, these cost-effective synthesis strategies of ZIFs will greatly promote the large-scale production of ZIFs for practical applications [26].

**Ionothermal Synthesis:**

Ionothermal synthesis, which involves the use of green solvents such as ionic liquids and eutectic mixtures to make ZIFs, has recently been developed. Ionic liquids can not only act as both solvents and templates at the same time, avoiding the competitive interactions between the solvent framework and the template framework found in hydrothermal preparations, but they also have negligible vapor pressure and are non-flammable, allowing the synthesis to be performed in an open system. Furthermore, ionic liquids can be recycled for future usage. Morris and colleagues pioneered the use of ionic liquid in the production of ZIFs [27].

**Synthesis by Sonochemistry:**

Sonocrystallisation processes can also be used to create ZIFs. Sonochemical synthesis, as opposed to typical oven heating for ZIF preparations, can not only promote nucleation production but also help to disperse nucleation homogeneously. During the sonochemical synthesis, bubbles are generated and collapse in solutions, resulting in high local temperatures, pressures, and extraordinary heating and cooling rates. According to Seoane's study, pure ZIF-7, ZIF-8, ZIF-11, and ZIF-20 crystals were formed using ultrasound irradiation with a power of 110 W and a frequency of 47 kHz, at a lower temperature (45-60°C) and for a shorter duration (6–9 h) than traditional solvothermal synthesis [28].

**Solvent-Free Synthesis:**

**Solvent-Minimisation Method:**

Although the water-based system is more environmentally friendly and cost-effective than the organic solvent-based system, various issues, such as the usage of excessive imidazole sources and huge solvent washing, make the aqueous synthesis technique inefficient. As a result, solvent minimization techniques have recently been created. Shi et al., for example, used a steam-assisted conversion process to create porous ZIF-8 and ZIF-67 (or dry-gel conversion method). Unlike the traditional hydrothermal synthesis method, the solid phase containing metal salts and excess ligands was placed in a small Teflon cup surrounded by water vapor (or organic solvent DMF) for 24 hours at 120°C, and the small amount of water may have acted as a structure-directing agent in the synthesis. In addition, ZIF-8 samples were also generated by a vapor-assisted conversion method in nonpolar solvent n-heptane, where the transformation rate from the solid reagents to ZIF-8 was faster than that in methanol or DMF. The technique is straightforward: an evenly ground mixture of ZnO and MIm with a molar ratio of 1:2 was heated at 180°C for 12 hours, and ZIF-8 was recovered. Without further processing, the resultant ZIF-8 sample can be used for adsorptive applications. Beobide et al. also achieved the solvent-free synthesis of ZIFs, in which ZIFs were generated in a closed jar at temperatures ranging from 100 to 160°C via an acid-base reaction between ZnO/CoO/Co(OH)2 and imidazole ligands [29-30].



**Mechanochemical Synthesis:**

Mechanochemistry has shown tremendous promise as a green and efficient technique for material construction. As a result, a method for producing ZIFs by mechanochemical synthesis (via ball milling) has been established. In 2006, the first partial production of nonporous Zn(IM)2 was achieved through manual grinding of ZnO with a significant excess of imidazole. Adams et al. used the same nonporous Zn(IM)2 products via a two-step mechanochemical procedure that began with ZnCl2. Recognizing the limitations of oxide-based precursors for ZIF synthesis via neat grinding, Frii et al. used modified mechanochemical methods called liquid-assisted grinding (LAG) or ion-and liquid-assisted grinding (ILAG) to produce ZIFs at room temperature from a stoichiometric molar ratio (1:2) of ZnO and ligand such as imidazole, 2-methylimidazole, and 2-methyl imidazole [31-32].

**Secondary Growth Crystallisation:**

Secondary growth crystallization is typically used to make membranes in two phases. The crystal seeds are deposited on the bare or chemically modified support in the first step by using various strategies such as rubbing, dip-coating, thermal seeding, and reactive seeding by repeated growth; in the second step, a continuous polycrystalline layer grows under solvothermal or hydrothermal conditions. Internal spaces between seeds can be bridged by seed development, resulting in the formation of a continuous membrane. The seeded growth approach has the distinct advantage of allowing for systematic control of membrane orientation. This approach can also adjust other membrane parameters such as membrane thickness and grain boundary structure, which can lead to improved membrane performance [33].

**In-Situ Crystallisation:**

In situ crystallization methods can also be used to generate ZIF films or membranes in which the polycrystalline layer is formed on a plain or chemically modified support in a one-step or one-pot solvothermal or hydrothermal synthesis without any seeding growth procedure.Many researchers have investigated in situ crystallization methods for the creation of ZIF membranes. Bux et al. used an in situ crystallization approach to create a ZIF-8 membrane in a microwave-assisted solvothermal reaction. In summary, the solution mixture with porous titania support was charged into an autoclave and cooked in a microwave oven before forming a compact ZIF-8 layer on the porous titania support [34].

**Applications of ZIF Material:**

ZIF materials are finding new uses due to their high porosity, customizable compositions, and controllable topologies. Pure ZIFs and ZIF-based films/membranes have been developed as multifunctional materials with excellent performances that extend beyond their traditional uses as adsorbents and catalysts, and even contribute to advancements in fields ranging from sensing and electrical devices to drug delivery. The usual and new applications of ZIF materials are emphasized and discussed in this section [35].

**Photo Catalysis Behaviour:**

The following steps are typical of a photocatalytic reaction: The photocatalyst is changed into a charge-separated state, generating a mobile electron (e) and a hole (h+); lastly, pollutants can be eliminated by reacting with the transportable electron or hole. Photo-generated electron-hole pairs can be formed only when the energy of incident photons exceeds the band-gap energy of photocatalysts. Later, the electrons in the valence band will be transferred to the conduction band and become conduction e-, leaving an h+ in the valence band is a promising co-catalyst for heterogeneous photocatalysis, because it has a high conversion efficiency to light energy when degrading pollutants, ZIF-8 can quickly transfer the adsorbed light from the organic link to the metal-oxygen cluster, In essence, photocatalytic degradation of pollutants is the oxidation of pollutants by photo catalyst-produced active molecules [36-37].

**Antibacterial Responses:**

Antibacterial zinc metal oxide is generally implemented in biomedical applications. The metal is biocompatible and environmentally benign. Zn2+ derived from zinc metal oxide has been shown to enhance keratinocyte mobility and aid in wound healing. Metal-organic frameworks (MOFs) having a similar appearance to inorganic porous zeolites have recently been reported as zeolitic imidazolate frameworks (ZIF-8). The zeolite structure is made up of Zn2+ metal ions linked by an imidazolate linker. ZIF-8 is used in biomedical applications. However, a few ZIFs were microporous, causing pre-mature drug release. Various procedures have been used in recent years to prepare the composite incorporating ZIF-8 and mesostructured materials. Such composites were particularly effective because they combined the benefits of micropore ZIF-8 and mesoporous materials [38].

**Gas Sensing Performance:**

When the micro-reaction is turned into macro-signals, the change in energy band bending generated by the reaction of oxygen ions with CO would modify the total resistance/conductivity of the sensitive layer. When a polyhedral ZIF-8 nanomaterial gas sensor is tested for NO2 gas, the gas molecules trap free electrons from the adsorbed oxygen on the sensor's surface, resulting in the creation of a thick charge depletion layer on the ZIF materials' surface. The rapid adsorption of NO2 molecules generates a negative charge on the surface, resulting in a larger potential barrier. Due to the porosity of ZIF materials, it can easily sense the gas molecules released [39-40].

**Conclusion:**

ZIFs, which consist of imidazolate linkers and metal ions, are a new and distinct family of metal-organic frameworks with structures like those of traditional aluminosilicate zeolites. Numerous prospective uses for diverse ZIF materials have been made possible by their inherent porous characteristics, strong functions, and outstanding thermal and chemical stabilities. In the past several years, many research initiatives have appeared in this quickly developing field, spanning from synthetic methods to alluring ZIF applications.

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