Metal Organic Frame works

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**ABSTRACT**

Metal-organic frameworks (MOFs) are a class of materials that consist of metal ions or clusters coordinated with organic ligands to form ultra high porosity materials with enormous internal surface areas and highly structured frameworks. The extraordinary degree of variability for both the organic and inorganic components of their structures make MOFs of tunable for potential applications in various fields. In the present review article a detailed discussion about primary and secondary building blocks of MOFs, classification of MOFs and methods of synthesis are included. The methods of Characterisation and factors which decide the stability, properties are also described. The applications of MOFs in various fields such as gas storage and separation, sensors, catalysis and biomedical field are also discussed.

**Key words:** Metal Organic Frame works, organic linkers, gas storage, catalysis, drug delivery

**I. INTRODUCTION**

Metal-organic frameworks (MOFs) are a class of materials that consist of metal ions or clusters coordinated with organic ligands to form porous and highly structured frameworks. Metal−organic frameworks, or MOFs, have emerged as an extensive class of crystalline materials with ultrahigh porosity (up to 90% free volume) and enormous internal surface areas, extending beyond 6,000 m2 /g. These properties, together with the extraordinary degree of variability for both the organic and inorganic components of their structures, make MOFs of interest for potential applications in clean energy, most significantly as storage media for gases such as hydrogen and methane, and as high-capacity adsorbents to meet various separation needs. (Zhou H C, 2012)

MOFs feature a unique crystalline structure composed of metal nodes connected by organic linkers, resulting in a high surface area and a vast network of pores. These structures can be fine-tuned by selecting different metals, ligands, and architectures, allowing for exceptional control over the material's properties.

One of the defining characteristics of MOFs is their exceptional porosity. Their extensive surface area and porosity make them ideal for applications such as gas storage and separation, catalysis, drug delivery,and sensing. By adjusting the size, shape, and functionality of the pores, MOFs can selectively adsorb or capture specific molecules, making them highly customizable for various applications.

The discovery and development of MOFs have revolutionized materials science and have opened up new possibilities for solving challenges in energy, environmental sustainability, and healthcare. Researchers continue to explore and engineer new MOFs with enhanced properties, making them an exciting and rapidly growing field of study.

MOFs are a unique class of materials with ordered structures, high porosity, and a wide range of applications. Their versatility, tunability, and potential for solving various challenges have positioned them as promising candidates for future advancements in research, technology, and industry (V. V. Butova, 2016).

**II. STRUCTURAL ASPECTS**

The structural aspects of MOFs play a crucial role in their properties and applications. Here are some key points about the structural aspects of MOFs (Baumann, 2019).

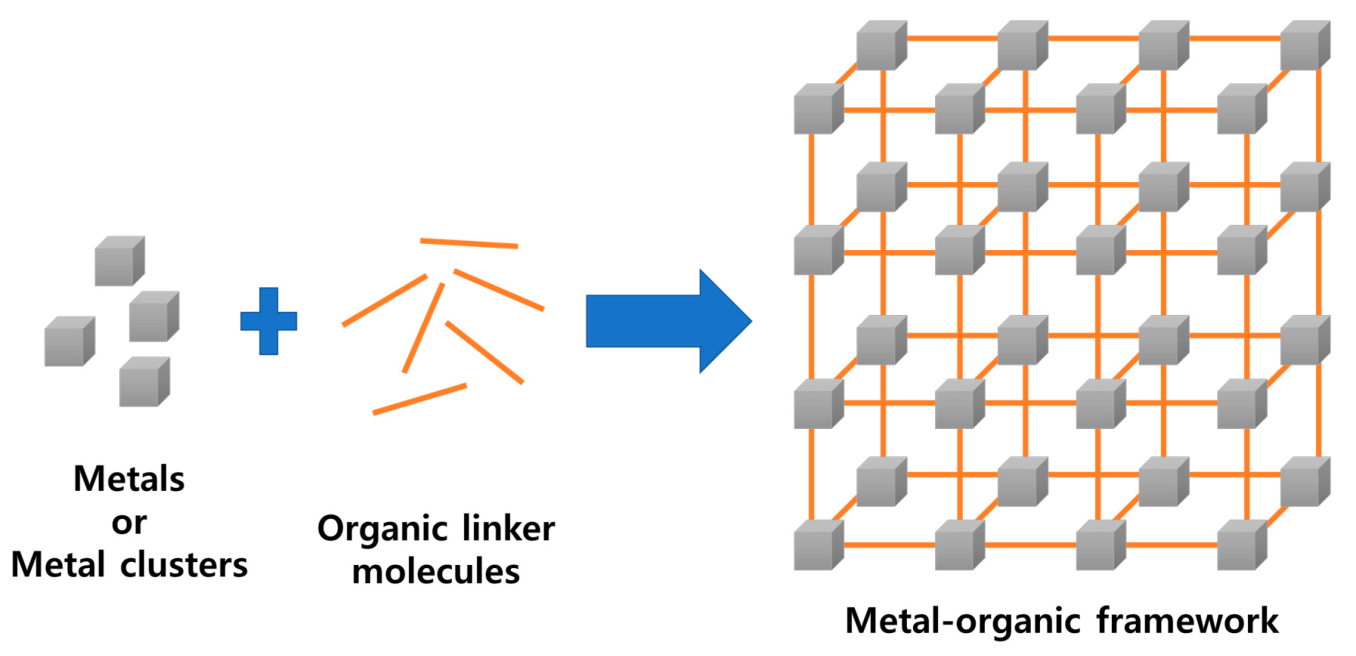


Figure 1. Structure of MOF

* Basic Unit: The basic unit of MOFs consists of metal nodes connected by organic linkers. These metal nodes can be transition metals, lanthanides, or other metal species. The organic linkers are typically organic molecules containing functional groups such as carboxylates, pyridines, or imidazoles.
* Topology: MOFs can have diverse topologies, which refer to the network connectivity between metal nodes and organic linkers. There are numerous known MOF topologies, such as cubic, hexagonal, and various open frameworks. Topology influences the porosity and stability of MOFs.
* Dimensionality: MOF structures can be one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D). In 1D and 2D MOFs, the metal nodes and organic linkers form chains or layers, respectively. 3D MOFs have a fully connected network of metal nodes and organic linkers. 3D structures are generally preferred for higher porosity and increased surface area.
* Porosity: One of the defining features of MOFs is their high porosity. The arrangement of metal nodes and organic linkers creates pores and cavities within the MOF structure. These pores can have different sizes and shapes, allowing for the adsorption and storage of gases, liquids, and other molecules. The porosity of MOFs is often quantified in terms of surface area and pore volume.
* Flexibility: Some MOFs exhibit structural flexibility or dynamic behavior, which means that their framework can undergo reversible structural changes in response to external stimuli such as temperature, pressure, or guest molecule sorption. This flexibility can be advantageous for applications like gas separation or drug delivery.
* Modularity: The structure of MOFs is highly modular, meaning that the choice of metal nodes and organic linkers can be varied to design MOFs with specific properties. Modularity offers great flexibility in tuning the pore size, functionality, and stability of MOFs for targeted applications (Baumann, 2020).

**A. PRIMARY BUILDING UNITS**

The primary building blocks of MOFs are metal nodes (also known as metal clusters) and organic linkers. These building blocks come together to form the framework of the MOF structure. Here is a closer look at each:

Metal nodes: Metal nodes are typically metal ions or clusters that serve as the coordination centers in MOFs. These metal nodes can be transition metals such as copper, nickel, or zinc, as well as lanthanide ions like cerium or yttrium. The metal nodes provide coordination sites for interaction with the organic linkers.

Organic linkers: Organic linkers are organic molecules that contain functional groups capable of coordinating with the metal nodes. The coordination between the metal nodes and organic linkers is typically through coordination bonds, such as coordination of carboxylates, pyridines, imidazoles, or other functional groups to metal centers. The organic linkers play a significant role in defining the connectivity, shape, and functionality of the MOF framework.

The combination of metal nodes and organic linkers results in the formation of coordination bonds, creating a 3D network structure. The coordination bonds can be strong enough to maintain the structural integrity of the MOF while being reversible, which enables dynamic properties such as structural flexibility and guest molecule sorption.

The choice of metal nodes and organic linkers allows for a wide range of MOF compositions and properties. By selecting different metal nodes and functional groups in the organic linkers, researchers can tailor the properties of MOFs for specific applications, such as gas storage, catalysis, separations, and sensing. The modularity of MOFs allows for the design and synthesis of MOFs with desired structural features and characteristics.

**B. SECONDARY BUILDING UNITS**

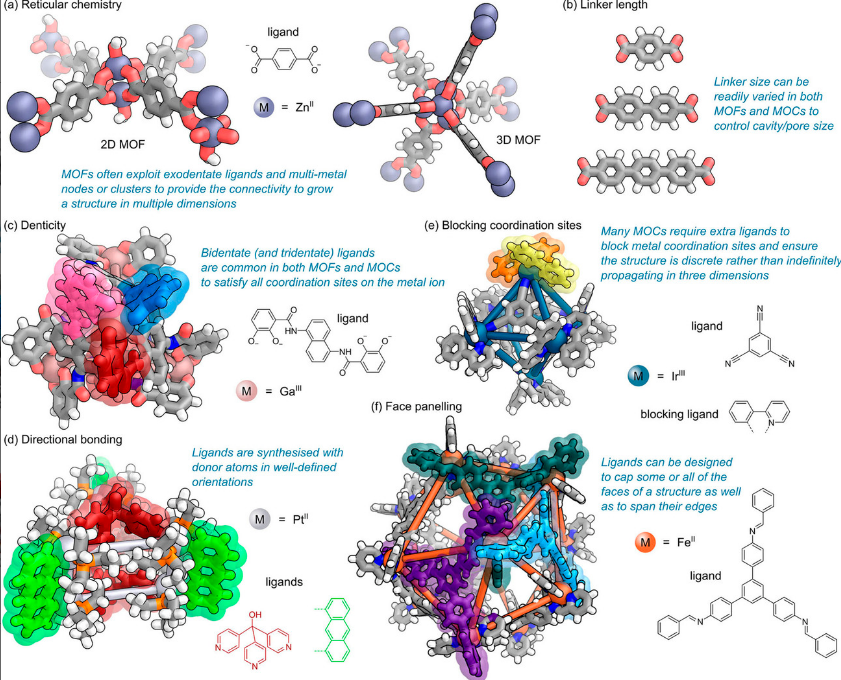


Figure 2. Different secondary building blocks

Secondary building blocks (SBBs) in metal-organic frameworks (MOFs) refer to the organic ligands or linkers that connect the metal nodes and form the three-dimensional framework structure. These SBBs play a crucial role in determining the properties, porosity, and functionality of the MOFs.

Here are some common types of SBBs used in MOFs:

* Carboxylate linkers: Carboxylate groups (-COO-) are widely used as SBBs in MOFs due to their ability to coordinate with metal ions. Examples include terephthalate (benzene-1,4-dicarboxylate), isophthalate (benzene-1,3-dicarboxylate), and adipate (hexanedioate). These linkers allow for the formation of robust MOF structures.
* Nitrogen-based linkers: Nitrogen-containing ligands such as pyrazine (1,4-diazine), pyridine (azabenzene), and triazole (-N=CH-) can also act as SBBs in MOFs. These linkers can provide additional functionality and contribute to the stability and electronic properties of the MOFs.
* Phosphonate and phosphinate linkers: Phosphonate (-PO3H2) and phosphinate (-PO3H-) groups are commonly used as SBBs in MOFs. These linkers offer the advantage of incorporating phosphorus into the framework structure, leading to enhanced chemical stability and diverse functionalities.
* Imidazole-based linkers: Imidazole and its derivatives are frequently used as SBBs in MOFs. The presence of nitrogen and the aromatic nature of imidazole rings allow for strong coordination with metal ions, leading to the formation of stable frameworks.
* Bipyridyl and terpyridyl linkers: Bipyridyl (-N(CH)4N-) and terpyridyl (2,2’:6’,2”-terpyridine) ligands are widely used as SBBs in MOFs. Their rigid structure and ability to coordinate with multiple metal ions make them suitable for constructing highly ordered and porous frameworks.
* Aliphatic or aromatic diamine linkers: Diamine-based linkers, such as ethylenediamine, piperazine, or biphenyldiamine, can be used as SBBs to introduce additional functionality and increase the complexity of MOF structures.
* Heterocyclic linkers: Various heterocycles, including furan (C4H4O), thiophene (C4H4S), and pyrrole (C4H5N), can act as SBBs in MOFs. These linkers offer different electronic and chemical properties, contributing to the overall functionality of the MOFs .

**C. CLASSIFICATION OF METAL ORGANIC FRAME WORKS**

Metal-organic frameworks (MOFs) can be classified based on various criteria, including their composition, structure, and properties. Here are a few common classification approaches for MOFs:

**Composition-based classification:**

* Organic-inorganic MOFs: These MOFs consist of metal ions connected by organic ligands.
* Inorganic MOFs: These MOFs are composed of metal ions linked by inorganic ligands, such as cyanide or carbonate groups.
* Heterometallic MOFs: These MOFs contain two or more types of metal ions connected by organic or inorganic ligands .

**Topology-based classification:**

MOFs can be classified based on their underlying topological network, which refers to the arrangement of metal nodes and organic ligands within the framework. This classification identifies different MOF structures and their connectivity patterns, often named after their discoverers or specific characteristics (e.g., zeolite-like, pillared-layer, or diamondoid).

**Porosity-based classification:**

MOFs are often categorized based on their porosity, which refers to the presence of empty spaces or cavities within the framework. These porous MOFs are commonly classified as:

* Microporous MOFs: These have small pores (typically less than 2 nm in diameter), suitable for adsorption and separation applications.
* Mesoporous MOFs: These have larger pores (between 2 nm and 50 nm), often used for catalysis, drug delivery, and sensing.
* Hierarchical MOFs: These have a combination of micropores and mesopores, providing enhanced porosity and improved mass transport properties.

**Application-based classification:**

MOFs can be classified based on their intended applications, such as gas storage and separation, catalysis, drug delivery, sensing, or optoelectronics. Some MOFs are specifically designed for certain applications, while others may have diverse functionalities.

**Metal-based classification:**

MOFs can be categorized based on the type of metal ions present in their structure. For example, one can classify MOFs as zinc-based, copper-based, or lanthanide-based MOFs, depending on the predominant metal ion used.

It is important to note that these classification schemes are not mutually exclusive, and MOFs can often fit into multiple categories based on their specific characteristics. The classification of MOFs continues to evolve as new structures and applications are discovered, leading to a more comprehensive understanding of these materials.

These are just a few examples of the many possible SBBs that can be used to construct MOF frameworks. The choice of SBBs depends on factors such as the desired structure, properties, and intended applications of the MOF. By selecting appropriate SBBs, researchers can tailor the properties and functionality of MOFs for specific purposes. Understanding and controlling the structural aspects of MOFs is crucial for tailoring their properties and optimizing their performance in various applications

**III. SYNTHESIS METHODS**

Understanding and controlling the structural aspects of MOFs is crucial for tailoring their properties and optimizing their performance in various applications such as gas storage, catalysis, sensing, drug delivery, and more.

**A. THE BOTTOM-UP APPROACH**

The Bottom up approach for MOF (Metal-Organic Framework) synthesis involves the self-assembly of metal ions or clusters with organic linkers to form a three-dimensional porous framework. This process starts at the atomic or molecular level and gradually builds up the MOF structure.

Here are the main steps involved in the bottom-up synthesis of MOFs:

1. Selection of metal ions: The first step is to choose the appropriate metal ions or clusters that will serve as the inorganic nodes in the MOF structure. The selection is based on the desired properties and applications of the MOF.

2. Selection of organic linkers: Organic linkers play a crucial role in MOF synthesis as they connect the metal ions to form the framework. The choice of organic linkers depends on factors such as their coordination ability, size, shape, and functionality. These linkers are typically organic molecules containing functional groups like carboxylic acids, amines, or pyridines.

3. Coordination assembly: In this step, the metal ions and organic linkers are mixed together in a suitable solvent, often in a specific molar ratio, and allowed to self-assemble via coordination bonding. The coordination bonds form between the metal ions and the functional groups of the organic linkers, resulting in the formation of a precursor structure.

4. Crystallization: The precursor structure undergoes a crystallization process, where the formation of strong covalent bonds stabilizes the framework and leads to the formation of well-defined MOF crystals. The choice of solvent, reaction temperature, and reaction time plays a critical role in controlling the crystallization process.

5. Washing and drying: After the crystallization step, the resulting MOF crystals are typically washed with solvents to remove any unreacted or residual materials. The washed MOF crystals are then dried under controlled conditions to obtain the final solid MOF material.

6. Post-synthetic modifications (optional): Depending on the specific requirements, post-synthetic modifications can be performed to further modify the properties of the MOF. These modifications may involve introducing guest molecules into the MOF pores, functionalizing the organic linkers, or metal ion exchange, among other techniques.

The bottom-up approach allows for precise control over the structure, porosity, and functionality of MOFs by carefully selecting the building blocks and tuning the synthesis conditions. This approach has led to the development of a wide range of MOF materials with diverse properties and applications in areas such as gas storage, catalysis, sensor technology, and drug delivery.

**B. TOP DOWN APPROACH**

Top down methods for Metal-Organic Frameworks (MOFs) synthesis involve starting from a predefined metal precursor or linker and building the framework layer by layer. Here are a few commonly used **top down synthesis** methods for MOFs:

1. LIGS (Layer-by-Layer Inorganic Growth on Surfaces): This method involves growing MOF layers on a substrate, such as a metal oxide or metal surface, by sequentially adding metal ions and organic linker molecules in a controlled manner.

2. Direct Synthesis: This method involves the direct reaction of metal precursors and organic linkers under suitable conditions to form the desired MOF. This can be done in solution or through other techniques like solvothermal or hydrothermal methods.

3. Solvent-Assisted Ligand Incorporation (SALI): This approach involves the use of a solvent to assist in the formation of the MOF structure. The solvent can help in the initial coordination of metal ions and linker molecules, allowing for controlled growth of the MOF.

4. Deposition on Substrates: In this method, a pre-formed MOF is deposited onto a substrate through techniques like spin coating, drop-casting, or vapor-assisted deposition. This allows for the precise control of MOF thickness and orientation.

5. Stepwise Linker/Cation Exchange: This technique involves the exchange of ligands or metal cations in a pre-existing MOF framework to create new MOF structures with different properties. It allows for the modification or functionalization of existing MOFs.

These are just a few examples of top-down methods used for MOF synthesis. The choice of method depends on the desired properties, scalability, and specific requirements of the application (Yu-Ri Lee, 2013).

**C. ALTERNATIVE SYNTHESIS ROUTES**

There are several top-up methods that can be used for MOF preparation. These methods involve adding metal ions or linker molecules to an existing MOF structure to modify its composition or properties. Here are a few commonly used top-up methods (Mikhail.A Soldatov, 2018).

**Solvothermal Top-up:** In this method, a pre-existing MOF is immersed in a solvent containing additional metal ions or linker molecules. By subjecting the mixture to solvothermal conditions, the new components diffuse into the existing MOF structure, leading to the formation of a modified MOF.

**Liquid-phase Exfoliation and Reconstruction**: This method involves the exfoliation of a pre-existing MOF structure followed by the addition of new metal ions or linker molecules. The exfoliated MOF layers are dispersed in a solvent, and the new components are added, allowing for the reconstruction of the modified MOF structure.

**Solid-state Top-up:** In this method, a pre-existing MOF is mechanically grounded or milled with new metal ions or linker molecules. The resulting mixture is then subjected to suitable synthetic conditions, such as heat or pressure, to facilitate the formation of a modified MOF structure.

**Ion-exchange Top-up**: This method involves the exchange of metal ions within a pre-existing MOF structure with new metal ions. The MOF is immersed in a solution containing the desired metal ions, and through diffusion and ion exchange processes, the new metal ions replace the existing ones, leading to the formation of a modified MOF.

**Ligand Replacement Top-up**: In this method, the linker molecules in a pre-existing MOF are replaced with new linker molecules. This can be achieved by dispersing the MOF in a solvent containing the new linker molecules and allowing for the exchange to occur. The solvent is then removed, resulting in the formation of a modified MOF with different linker compositions (Seth M. Cohen, 2012).

These top-up methods provide a versatile approach to modify the properties and composition of existing MOFs. They allow for the incorporation of different metals or linker molecules, leading to the creation of MOFs with tailored properties for specific purposes. The bottom-up approach for MOF (Metal-Organic Framework) synthesis involves the self-assembly of metal ions or clusters with organic linkers to form a three-dimensional porous framework. Depending on the specific requirements, post-synthetic modifications can be performed to further modify the properties of the MOF. These modifications may involve introducing guest molecules into the MOF pores, functionalizing the organic linkers, or metal ion exchange, among other techniques ([Takashi Uemura](https://pubs.rsc.org/en/results?searchtext=Author%3ATakashi%20Uemura), 2009).

**D. MICROWAVE ASSISTED SYNTHESIS**

Microwave-assisted synthesis of metal-organic frameworks (MOFs) is a technique that uses microwaves to accelerate the synthesis process. The microwave-assisted synthesis of MOFs offers several advantages over traditional synthesis methods. The main advantage is the significantly reduced reaction time. Microwave heating allows for rapid and uniform heating of the reaction mixture, promoting faster reactions and reducing the overall synthesis time.

Furthermore, microwave-assisted synthesis can result in improved product yields and increased crystallinity of the MOFs. The rapid heating and efficient energy transfer in microwaves can help overcome kinetic barriers and promote the formation of well-defined crystalline structures (Zhenyu Zhao, 2022) .

To perform a microwave-assisted synthesis of MOFs, the reaction mixture, typically containing the metal ions and organic ligands, is placed in a microwave reactor. The reactor is then subjected to microwave irradiation, which rapidly heats the mixture to the desired reaction temperature. The reaction progress can be monitored using various characterization techniques, such as X-ray diffraction or spectroscopy (Jacek Klinowsky, 2011).

It is worth noting that microwave-assisted synthesis of MOFs requires careful optimization of reaction parameters, including microwave power, reaction time, and solvent choice. Additionally, precautions should be taken to ensure the safe handling of microwaves and avoid any potential hazards.

Overall, microwave-assisted synthesis has emerged as an efficient and versatile method for the rapid preparation of MOFs, offering advantages such as reduced reaction time, improved product yields, and enhanced crystallinity.

**E. ELECTROCHEMICAL SYNTHESIS**

Electrochemical synthesis of metal-organic frameworks (MOFs) involves the use of an electrochemical cell to synthesize these porous materials. Electrochemistry offers a unique approach to control and manipulate the assembly of MOF structures, allowing for precise tuning of their properties.

The electrochemical synthesis of MOFs involves the electrochemical reduction or oxidation of metal ions and the coordination of organic ligands to form the framework structure. The process typically takes place in a three-electrode cell setup, consisting of a working electrode (usually a conductive substrate), a counter electrode, and a reference electrode. The working electrode serves as the site for the electrochemical reactions, while the counter electrode and reference electrode complete the circuit.

During the electrochemical synthesis, the metal ions are reduced or oxidized at the working electrode, providing reactive intermediates for the coordination with the organic ligands. The ligands, either pre-dissolved or provided in situ, coordinate with the metal ions to form the MOF structure. The applied potential and the reaction conditions control the growth of the MOF, allowing for the precise control of its morphology, size, and crystallinity.

There are several advantages to electrochemical synthesis of MOFs. Firstly, it offers better control over the reaction kinetics and the growth of the MOF structure. The potential applied can be adjusted to control the rate of metal reduction or oxidation, leading to the controlled growth of MOFs with desired properties.

Secondly, electrochemical synthesis can be performed under mild conditions, which minimizes the need for harsh solvents or high temperatures. This makes the technique more environmental friendly and allows for the synthesis of MOFs with delicate or sensitive ligands.

Lastly, electrochemical synthesis can be performed on various substrates, including conductive materials, such as metals or conductive polymers. This allows for the direct growth of MOFs on the substrate, creating composite materials with unique functionalities and applications.

However, electrochemical synthesis of MOFs also has certain challenges. The selection of appropriate metal ions and ligands, as well as optimization of the electrochemical conditions, can be complex. Careful consideration of the electrochemical parameters, such as applied potential, current density, and electrolyte composition, is necessary to achieve the desired MOF structure.

In conclusion, electrochemical synthesis provides a promising approach for the controlled synthesis of MOFs, offering advantages such as precise control over MOF growth, mild reaction conditions, and the ability to create composite materials. Further research and development in this field can lead to the discovery of new MOFs with tailored properties for various applications (Varsha M V, 2020), (Alberto Martinez Joaristi,, 2012).

**F. SONOCHEMICAL SYNTHESIS**

Sonochemical synthesis, also known as ultrasound-assisted synthesis, is a technique that utilizes high-intensity ultrasound waves to facilitate chemical reactions. This approach has been applied to the synthesis of metal-organic frameworks (MOFs) to improve reaction kinetics, enhance product yield, and control the morphology and properties of the resulting MOFs.

In sonochemical synthesis of MOFs, the high-frequency sound waves create cavitation bubbles in the reaction mixture. These bubbles rapidly expand and collapse, generating localized hotspots and high energy microenvironments. The collapse of these bubbles creates high pressures and temperatures, leading to enhanced mass and heat transfer, as well as intense shear forces. These conditions can promote mixing, accelerate reactions, and favor the formation of MOF structures.

The advantages of sonochemical synthesis in MOF formation include:

1. Faster reaction kinetics: The cavitation bubbles created by ultrasound provide localized high energy conditions, which can accelerate chemical reactions, including the solvothermal synthesis of MOFs. The enhanced mass and heat transfer within these bubbles can facilitate the diffusion of reactants and improve the mixing of reactants, leading to faster reactions and shorter synthesis times.

2. Improved product yield and purity: Sonochemical synthesis can improve the yield and purity of MOFs by enhancing the reaction efficiency. The localized hotspots and intense shear forces created during cavitation can break down agglomerates, enhance nucleation, and reduce defects in the MOF structures, resulting in higher yields and improved product quality.

3. Control over MOF morphology and properties: The application of ultrasound waves during MOF synthesis can influence the particle size, crystallinity, and morphology of the resulting MOFs. By controlling the ultrasound parameters such as intensity, frequency, and duration, it is possible to tailor the properties of the MOFs for specific applications.

Despite the advantages, sonochemical synthesis of MOFs also has limitations. The high-energy conditions generated by ultrasound can lead to excessive heating and degradation of sensitive organic ligands. Therefore, careful optimization of the synthesis parameters is required to prevent undesirable side reactions or the formation of non-targeted products.

1. In conclusion, sonochemical synthesis has emerged as a promising technique for the rapid and controlled synthesis of MOFs. It offers advantages such as faster reaction kinetics, improved yield and purity, and control over MOF morphology and properties. Further research and optimization of the sonochemical synthesis parameters can contribute to the development of new MOFs with tailored properties for various applications (Won-JinSon, 2008) (Christos Vaitsis,2020)

**G. LAYER BY LAYER SYNTHESIS**

Layer-by-layer (LbL) synthesis is a versatile technique used to fabricate materials with precise control over their structure, layer thickness, and composition. This approach has also been applied to the synthesis of metal-organic frameworks (MOFs), offering a way to create thin films or coatings of MOFs with tailored properties.

In LbL synthesis of MOFs, the MOF material is deposited onto a substrate in a sequential and alternating manner. This is typically achieved by immersing the substrate in solutions containing the MOF precursors or ligands. Each immersion step leads to the formation of a new MOF layer on the substrate. The process can be repeated multiple times to build up the desired thickness and tailor the composition or properties of the resulting MOF film.

The key steps involved in layer-by-layer synthesis of MOFs are as follows:

1. Substrate preparation: The substrate is cleaned and functionalized to promote adhesion and provide a suitable surface for the MOF layers. This may involve treatments such as surface activation, self-assembled monolayers, or template deposition.

2. Immersion in precursor solutions: The substrate is immersed in a solution containing the desired MOF precursor or metal ions. The substrate is then rinsed to remove excess solution and non-adhered precursors.

3. Ligand exchange: The substrate is subsequently immersed in a solution containing the desired organic ligand for the MOF. The ligand exchange process allows the growth of the MOF layer on the substrate by coordinating with the metal ions.

4. Layer repetition: Steps 2 and 3 are repeated alternately to build up multiple layers of the MOF material. The number of cycles can be controlled to achieve the desired thickness and tailor the properties of the resulting MOF film.

5. Post-treatment: After the layering process, the MOF film may undergo additional treatments such as thermal annealing or solvent exchange to enhance the crystallinity or remove any residual solvents or impurities.

The advantages of layer-by-layer synthesis of MOFs include precise control over film thickness, composition, and properties. This technique allows for the formation of uniform and conformal MOF films on different substrates, making it suitable for applications such as sensors, membranes, catalysis, and energy storage devices.

However, it is important to note that LbL synthesis of MOFs also has limitations. The slower growth rate of MOF layers compared to other materials can result in longer synthesis times. Additionally, the choice of substrate and ligand must be compatible with the layering process to ensure good adhesion and homogeneous growth of the MOF layers (Christos Vaitsis, 2020)

In conclusion, layer-by-layer synthesis offers a versatile and controllable approach for fabricating thin films or coatings of MOFs. It enables the precise tailoring of MOF film properties, making it suitable for various applications. Continued research and optimization of the layering process will further expand the possibilities for MOF film synthesis and their integration into functional devices.

**IV. FACTORS INFLUENCING THE SYNTHESIS OF MOFS**

**A. SOLVENT**

Solvent selection in the synthesis of metal-organic frameworks (MOFs) plays a crucial role in determining the final properties and characteristics of the MOF material. The choice of solvent can impact various aspects of MOF synthesis, including:

1. Solubility of reactants: MOF precursors, such as metal ions and organic ligands, typically need to dissolve in the solvent before forming the MOF structure. The solvent choice should ensure good solubility of the reactants to facilitate their interaction and subsequent MOF formation. Different solvents have different solvation abilities, which can affect the extent of reaction and the resulting yield of the MOF.

2. Reaction kinetics: Solvents can influence the rate of MOF formation by affecting the reaction kinetics. Different solvents have different viscosities and diffusion coefficients, which can alter the transport of reactants, intermediates, and byproducts. Solvents with higher diffusion coefficients and lower viscosities generally promote faster reaction rates and shorter synthesis times. Additionally, solvents with good solvating abilities can enhance mass transport and reaction kinetics.

3. Morphology and crystallinity: The choice of solvent can influence the morphology and crystallinity of the synthesized MOF. Some solvents can lead to the formation of larger crystals with well-defined shapes, while others may result in smaller, more uniform particles. The solvent properties, such as polarity, boiling point, and evaporation rate, affect the nucleation and growth of MOF crystals, thereby impacting their size, shape, and overall crystallinity.

4. Framework flexibility: Certain solvents can interact differently with the MOF structure, affecting its flexibility or rigidity. Solvents that form strong interactions with the MOF ligands can induce changes in the framework, altering its conformation and resulting in different pore sizes and structures. This solvent-induced flexibility can be exploited to create flexible MOFs or to control guest molecule uptake/release in the MOF material.

5. Selectivity and guest inclusion: In some cases, the choice of solvent can influence the guest inclusion properties of the MOF. Certain solvents can selectively interact with specific guest molecules, enabling their preferential inclusion/exclusion from the MOF structure. This selectivity can be advantageous in applications such as gas separations or sensing

It is important to carefully consider the solvent choice in MOF synthesis to achieve the desired properties and characteristics of the material. Researchers often experiment with different solvents or solvent mixtures to optimize the synthesis conditions and tailor the MOF material for specific applications.

**B. TEMPERATURE AND pH**

Temperature plays a crucial role in the synthesis of metal-organic frameworks (MOFs) and can have several effects on the final product. Here are some of the effects of temperature on MOF synthesis:

1. Reaction kinetics: The rate at which the MOF forms is strongly influenced by temperature. Higher temperatures generally accelerate reaction kinetics, resulting in faster crystal growth and shorter synthesis times. However, very high temperatures can also lead to uncontrollable nucleation and rapid crystal growth, potentially affecting the size, morphology, and crystallinity of the MOF.

2. Solubility: Temperature can impact the solubility of MOF precursors and intermediates in the reaction solution. Increasing the temperature can enhance solubility and improve the reactivity of the reactants. Conversely, lowering the temperature may lead to reduced solubility and slower reaction rates. It is important to find a balance between temperature and solubility to achieve proper nucleation and controlled crystal growth.

3. Structural stability: MOFs can be temperature-sensitive, and different temperatures can affect their stability. Some MOFs may undergo structural transformations or even decomposition at elevated temperatures, leading to the loss of crystallinity or changes in their properties. Therefore, it is crucial to determine the appropriate temperature range that maintains the stability and integrity of the MOF during synthesis.

4. Crystal size and morphology: Temperature can influence the size and morphology of MOF crystals. Higher temperatures generally result in larger crystal sizes, while lower temperatures can lead to smaller, more well-defined crystals. The growth mechanism and kinetics of the MOF can be altered by temperature, affecting the crystal shape and surface characteristics.

5. Impurities and defects: Temperature can also affect the formation of impurities or defects in the MOF structure. Higher temperatures can promote the incorporation of impurities or result in the formation of defects in the crystal lattice. It is important to control the synthesis temperature to minimize impurities and defects and ensure the desired structure and properties of the MOF material.

Optimizing the temperature during MOF synthesis is crucial for achieving the desired product. It requires balancing reactivity, crystal growth kinetics, and stability. By carefully adjusting the temperature, researchers can control the size, shape, porosity, and other properties of the resulting MOF material to meet specific application requirements.

The pH of the reaction environment plays a significant role in the synthesis of metal-organic frameworks (MOFs). It can influence the formation, structure, and properties of the resulting MOF material.

Here are some effects of pH on MOF synthesis:

1. Crystal growth: The pH can affect the crystal growth rate and morphology of the MOF. Different pH conditions can influence the nucleation and growth kinetics, leading to variations in crystal size, shape, and crystallinity. Higher pH values often result in faster crystal growth, while lower pH values can result in slower or inhibited growth.

2. Ligand protonation and deprotonation: MOFs are typically formed by the coordination of metal ions with organic ligands. The pH of the reaction solution can influence the protonation or deprotonation of ligands. For example, at lower pH values, acidic functional groups on the ligands may become protonated, affecting their coordination ability and the resulting MOF structure.

3. Stability and solubility: The pH can also affect the stability and solubility of MOF precursors and intermediates. Certain metal ions or ligands may have different solubilities or reactivity under different pH conditions, which can affect the yield and purity of the final MOF product.

4. MOF topology and structure: The pH can influence the formation of different MOF topologies and structures. Certain pH conditions may favor the formation of certain types of linkages or coordination geometries, leading to variations in the resulting MOF structure. Controlling the pH during synthesis can allow for the targeted synthesis of specific MOF structures.

5. Hydrolysis and metal ion speciation: Depending on the pH, metal ions used in MOF synthesis can undergo hydrolysis reactions, which can impact the formation of metal-oxide clusters or species. These species can subsequently influence the formation and properties of the resulting MOF material.

To optimize the synthesis of MOFs, it is important to carefully consider and control the pH of the reaction environment. This can be achieved by adjusting the pH of the precursor solutions or using pH buffer solutions. By controlling the pH, researchers can tune the properties and characteristics of the MOF material, such as porosity, surface charge, and stability, to meet specific application requirements.

**V. FACTORS AFFECTING STABILITY OF MOFS**

The stability of metal-organic frameworks (MOFs) is influenced by several factors, including:

1. Metal Ion Coordination: The type and coordination of the metal ion used in the MOF can affect its stability. Some metal ions form stronger bonds with organic linkers, enhancing MOF stability.

2. Organic Linker Selection: The choice of organic linkers impacts MOF stability. Rigid and robust linkers usually lead to more stable frameworks.

3. Pore Size and Structure: The size and arrangement of pores within the MOF can influence its stability. Well-defined pores may help in accommodating guest molecules and prevent framework collapse.

4. Solvent and Environmental Conditions: The choice of solvent during MOF synthesis, as well as exposure to various environmental conditions (such as humidity and temperature), can affect stability.

5. Thermal Stability: The MOF's ability to withstand high temperatures without structural degradation is essential for practical applications.

6. Water Stability: MOFs with good water stability are more suitable for applications in moist environments or for storage of water-sensitive materials.

7. Interactions with Guest Molecules: The presence of guest molecules within the MOF may influence its stability, depending on the strength of interactions and the ability to exchange guest molecules.

8. Defects and Imperfections: The presence of defects or imperfections in the MOF structure can impact its stability, affecting mechanical and chemical robustness.

9. Ligand Functionalization: The functional groups attached to the organic ligands can enhance MOF stability by introducing additional interactions.

10. Ligand/Metal Ratios: The stoichiometric ratio of metal ions to organic linkers can affect the overall stability and properties of the MOF.

Understanding these factors is crucial for designing and synthesizing MOFs with improved stability and tailored properties for various applications.

**VI. PROPERTIES OF MOF**

**Optical Properties**

MOFs can exhibit various optical properties due to their unique structure and composition. Here are some important optical properties of MOFs:

1. Luminescence: Many MOFs possess luminescent properties, meaning they can emit light when excited by an external energy source. The luminescence can arise from different mechanisms, such as ligand-to-metal charge transfer, metal-centered emission, or energy transfer between metal ions. Tuning the ligands and metal ions in the MOF structure can enable control over the color and intensity of the emitted light.

2. Photoluminescence Quantum Yield: Photoluminescence quantum yield (PLQY) is a measure of how efficiently a material can convert absorbed photons into emitted photons. MOFs can exhibit high PLQYs, making them suitable for various applications such as sensing, lighting, or optoelectronic devices.

3. Near-Infrared (NIR) Absorption: Some MOFs can absorb light in the near-infrared region, which is of interest for applications like photothermal therapy, imaging, or light harvesting in solar cells. The choice of metal ions and ligands in the MOF structure can be tailored to achieve NIR absorption properties.

4. Nonlinear Optical (NLO) Effects: Certain MOFs can exhibit nonlinear optical phenomena such as second-harmonic generation (SHG) or third-order nonlinear optical effects. These properties are useful for applications in optics, telecommunications, and photonic devices.

5. Photochromism: Photochromic materials can change their color or optical properties upon exposure to light, typically by undergoing reversible structural changes. Some MOFs exhibit photochromic behavior, where their absorption or luminescence properties can be switched between different states by light irradiation.

6. Optical Waveguiding: MOFs with specific pore structures can act as optical waveguides, confining and guiding light within their channels. This property can be utilized for light transportation and waveguide-based optical sensing applications.

It's important to note that the optical properties of MOFs can be highly dependent on factors such as the choice of metal ions, ligands, and structural features. By carefully designing the MOF structure and composition, it is possible to tailor their optical properties for various applications in optics and photonics.

**VII. CHARACTERISATION TECHNIQUES FOR EVALUATING MOF**

The characterization of MOFs involves studying their physical, chemical, and structural properties, which are crucial for understanding their potential applications. Some common techniques used for the characterization of MOFs include:

X-ray Diffraction (XRD): XRD is used to determine the crystal structure and phase purity of MOFs. It provides information about the unit cell dimensions, bond lengths, and angles, which are important for understanding the framework topology.

* Scanning Electron Microscopy (SEM): SEM provides a high-resolution image of the MOF's surface morphology. It can reveal the shape, size, and distribution of MOF particles, as well as any surface defects or impurities.
* Gas Adsorption: Gas adsorption experiments, such as nitrogen or carbon dioxide adsorption, are commonly performed to determine MOF's surface area, pore size distribution, and porosity. This information is important for evaluating their potential for gas storage, separation, and catalysis.
* Thermogravimetric Analysis (TGA): TGA measures the weight loss of a MOF as a function of temperature. It helps determine the thermal stability and decomposition behavior of MOFs by monitoring the release of gas, solvent, or ligand molecules.
* Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectroscopy is used to identify and characterize chemical functional groups present in MOFs. It provides information about the stretching and bending vibrations of these groups, which can help in understanding bonding and coordination in MOF structures.
* Nuclear Magnetic Resonance (NMR) Spectroscopy: NMR spectroscopy is used to study the local environment of metal ions and ligands in MOFs. It provides valuable information about the coordination geometry and connectivity of the metal centers.
* Powder X-ray Photoelectron Spectroscopy (PXPS): PXPS is utilized to determine the oxidation states and electronic structure of metal ions in MOFs. It provides information about the metal-ligand interactions and can help in understanding the reactivity and catalytic properties of MOFs.

These characterization techniques collectively provide valuable insights into the composition, structure, surface area, porosity, thermal stability, and spectroscopic properties of MOFs, which are vital for tailoring their properties for specific applications.

**VIII. ANALYSIS OF MOF ACTIVE SITES BY X RAY ABSORPTION SPECTROSCOPY**

X-ray absorption spectroscopy is of special importance in the study of MOFs, since it serves to study the local environment of metal clusters surrounded by guest molecules, which is essential for the understanding of the MOF activity. X-ray absorption spectroscopy (D.C. Koningsberger, 1988) (A. Filipponi, 1995)( J.A. van Bokhoven, 2016) (J.J. Kas, 2016) (C. Lamberti,2016 is the ideal technique to investigate the structural and electronic configuration of metal centers hosted inside nanostructured materials such as MOFs (J.J. Das, 2016). Such methods investigates the fine structure of X-ray absorption (the international term is X-ray Absorption Fine Structure - XAFS spectroscopy or XAS – X-ray Absorption 



Figure 3 Interaction of X-rays

Spectroscopy) that is present across a specific edge (K, L, M) of a selected element. Unlike X-ray scattering techniques, XAS is consequently an element selective technique. XAS experiments are mainly performed at large scale research facilities (synchrotron radiation sources) able to provide a brilliant X-ray source in a very large energy interval from soft to hard X-rays (although also IR, visible and UV regions are covered)]. The high flux and the high brilliance of the X-ray beams generated at synchrotron sources makes time and space resolved experiments possible. The high flux allows also highly diluted samples to be measured, while focused beams allows the measurements on samples where only a small amount of a substance is available, provides a response that is proportional to the primary process. The scheme of the experiment for detection by several methods: true absorption –“transmission” (a), fluorescence yield (b), total electron yield (c).

Although experimentally acquired in the same data collection, the XAFS spectrum is traditionally divided into two main parts: the region of the near(XANES) and far away (EXAFS) from the adsorption edge .

**IX. APPLICATIONS OF MOFS**

**A. GAS STORAGE AND SEPARATION**

Metal-Organic Frameworks (MOFs) have shown great promise in gas storage and separation applications due to their high surface area, tunable pore sizes, and unique adsorption properties. Here are some specific applications of MOFs in this field:

1. Natural Gas Storage: MOFs can adsorb large amounts of natural gas, including methane, at relatively low pressures. This makes them attractive materials for efficient and compact storage of natural gas, which is essential for energy storage and transportation.

2. Hydrogen Storage: MOFs have been investigated as potential materials for safe and efficient hydrogen storage. Hydrogen is a clean and renewable energy carrier, but its low density presents challenges for storage. MOFs with tailored pore sizes and high adsorption capacities could help address this issue and contribute to the advancement of hydrogen-based technologies.

3. Carbon Dioxide Capture: MOFs can selectively adsorb carbon dioxide (CO2) from gas mixtures, making them suitable for carbon capture and storage (CCS) applications. CCS is crucial for reducing greenhouse gas emissions from industrial processes and power plants (C. Lamberti, 2016).

4. Separation of Gas Mixtures: MOFs can be engineered to selectively adsorb specific gases from gas mixtures. This property is valuable for separating gases with similar properties, such as CO2/CH4, CO2/N2, and C2H2/C2H4, which are relevant to various industrial processes.

5. Air Purification: Some MOFs have demonstrated the ability to adsorb harmful gases and pollutants from the air, including volatile organic compounds (VOCs) and toxic gases. These MOFs could be used in air purification systems to improve indoor air quality and mitigate environmental pollution.

6. Biogas Upgrading: MOFs can be employed to upgrade biogas, a mixture of methane and carbon dioxide produced from organic waste. By selectively adsorbing CO2, MOFs can help increase the methane content in biogas, making it a more valuable energy source.

7. Natural Gas Sweetening: Natural gas often contains impurities like sulfur compounds, which need to be removed before use. MOFs can serve as adsorbents for sulfur removal, a process known as "sweetening," ensuring the natural gas meets the required purity standards.

8. Breathing MOFs: Some MOFs exhibit "breathing" behavior, where their structures expand or contract in response to changes in gas pressure or temperature. This property can be harnessed for pressure-swing adsorption processes, enhancing the efficiency of gas separation.

9. Gas Sensing: MOFs with specific interactions for certain gas molecules can be utilized as gas sensors for leak detection, environmental monitoring, and safety applications (E. Borfecchia, 2013 )

The wide range of pore sizes, metal centers, and organic ligands in MOFs allows for precise tuning of their adsorption properties, making them versatile candidates for various gas storage and separation challenges. As research in this field continues, we can expect to see even more tailored MOFs designed for specific gas adsorption applications, contributing to a more sustainable and efficient energy and environmental landscape.

**B. SENSORS**

Metal-Organic Frameworks (MOFs) have garnered significant interest as promising materials in the field of gas sensing due to their unique properties and tunable structures. Here are some applications of MOFs in gas sensing:

1. Gas Detection: MOFs can be designed to selectively and sensitively detect specific gases, such as volatile organic compounds (VOCs), ammonia, nitrogen oxides (NOx), carbon monoxide (CO), and hydrogen sulfide (H2S). These sensors are valuable in industrial settings, environmental monitoring, and safety applications (Tian Gao, 2023 ).

2. Environmental Monitoring: MOF-based gas sensors can be deployed for real-time monitoring of air quality in urban areas, industrial sites, and confined spaces. They help identify pollutant levels and enable timely interventions to mitigate harmful effects on human health and the environment (Chunbai He, 2014)

3. Breath Analysis: MOF sensors have been explored for diagnosing medical conditions by analyzing the composition of exhaled breath. The unique adsorption properties of MOFs allow them to capture specific breath biomarkers associated with certain diseases, potentially leading to early detection and personalized medical treatments.

4. Indoor Air Quality: MOF gas sensors can be integrated into smart buildings and ventilation systems to monitor indoor air quality. They can detect harmful gases and trigger ventilation systems or alert building occupants to take corrective actions.

5. Industrial Process Monitoring: In industrial settings, MOF gas sensors can monitor gas emissions, leaks, or process changes. By providing real-time data on gas concentrations, they help maintain process efficiency, safety, and compliance with environmental regulations.

6. Food Quality and Safety: MOF-based gas sensors can detect trace amounts of volatile compounds indicative of food spoilage or contamination. They are useful in the food industry to ensure the quality and safety of perishable products.

7. Explosive Detection: Some MOFs possess high selectivity and sensitivity to certain explosive compounds. Integrating MOF sensors into security systems can aid in detecting trace amounts of explosives in airports, public venues, and critical infrastructure.

8. Environmental Remediation: MOFs can be used in gas sensors to monitor and control emissions during environmental remediation processes. For example, in soil or groundwater remediation projects, MOF sensors can help track the presence of volatile organic contaminants (Hai- Long, 2013 ) .

9. Gas Leak Detection: MOF sensors can be applied to detect gas leaks in various contexts, such as natural gas pipelines, storage facilities, and industrial equipment. Early detection of gas leaks is crucial to prevent potential hazards and reduce losses. One of the significant advantages of MOFs in gas sensing is their high surface area and ability to be functionalized with various organic ligands. This allows for the tailored design of MOFs for specific gas sensing applications, resulting in improved sensitivity, selectivity, and response times. As research in MOFs continues, we can expect further advancements in gas sensor technology, enabling a wide range of practical applications in diverse fields (Osama Shekhah, 2010 ) (Joshua G Hinman, 2018 ) .

Metal-Organic Frameworks (MOFs) have also found applications in optical sensing due to their unique properties and tunable structures. Here are some of the applications of MOFs in optical sensing:

1. Luminescent Sensors: Certain MOFs exhibit luminescence properties, meaning they can emit light when exposed to specific analytes or environmental conditions. By incorporating luminescent MOFs into sensor platforms, they can be used to detect and quantify target molecules or changes in their surroundings (Mahnaz Ahmadi, 2021) (Sebastian Henke,2011)

2. pH Sensing: MOFs with pH-responsive properties can act as indicators of acidity or alkalinity. When exposed to a solution with a different pH, the MOF's luminescence can change, allowing for accurate pH measurements in various applications, including environmental monitoring and biomedical research (N. K. Daud, 2022 ) .

3. Ion Sensing: MOFs can be tailored to selectively capture specific ions from a solution. The change in the MOF's luminescence upon interaction with ions enables their detection and quantification in analytical chemistry and environmental monitoring.

4. Gas Sensing with Luminescence: In addition to gas adsorption, some MOFs exhibit changes in their luminescence properties upon gas exposure. By integrating luminescent MOFs into gas sensing platforms, they can provide optical readouts for gas detection with enhanced sensitivity.

5. Temperature Sensing: Temperature-responsive MOFs can be utilized as optical thermometers. Changes in the MOF's luminescence intensity or emission wavelength correlate with variations in temperature, making them suitable for temperature monitoring in diverse applications.

6. Humidity Sensing: MOFs can be engineered to respond to changes in humidity levels. The MOF's luminescence properties can vary with humidity, enabling the development of optical humidity sensors.

7. Metal Ion Sensing: Some MOFs can selectively capture and detect specific metal ions. By employing luminescent MOFs, the presence and concentration of metal ions in samples can be determined.

8. Biological and Medical Sensing: MOFs can be functionalized with specific ligands to detect biomolecules, such as proteins, nucleic acids, and other biological analytes. These MOF-based optical sensors hold promise in medical diagnostics and research.

9. Environmental Monitoring: Optical sensors based on MOFs can be used to monitor changes in environmental parameters, including pollutant levels, water quality, and soil conditions.

The ability to tailor the structure and composition of MOFs allows researchers to create optical sensors with high sensitivity, selectivity, and stability. Integrating MOFs into optical sensing platforms opens up exciting possibilities for a wide range of applications in research, industry, environmental monitoring, and healthcare. As research in MOFs and their optical properties progresses, we can expect further advancements and novel applications in optical sensing technologies.

**C. CATALYSIS**

Metal-Organic Frameworks (MOFs) have shown promising applications in catalysis due to their unique properties, such as high surface area, tunable structures, and versatile coordination environments. Here are some of the ways MOFs are being used in catalysis:

1. Heterogeneous Catalysis: MOFs can serve as heterogeneous catalysts, where reactions occur on the surface of the MOF material. Their large surface area provides ample active sites for catalytic reactions, and their tunable structures allow for precise control of catalytic properties.

A recent review discussed catalytic activity of MOF in biodiesel production. The stability of MOFs is one of the major issues in the synthesis of acid/base functionalized MOFs as it affects the pristine structures. Therefore, different design strategies need to be adopted during the synthesis process to keep the highly coordinated network intact. More stable MOF could be an ideal candidate to immobilize types of enzymes to promote eco-friendly production of biodiesel (Hai-Long Jiang, 2013).

2. Homogeneous Catalysis: MOFs can also be employed as homogeneous catalysts when they act as the source of catalytically active species in solution. By incorporating metal ions or metal clusters into the MOF structure, they can serve as highly efficient and recyclable homogeneous catalysts for various chemical transformations.

In a recent research article, preliminary catalytic results on the hydroboration of aldehydes and ketones with Ni-1@NU-1000 show a seven-fold increase in the TON(Turn Over Number) by grafting the organometallic precursor Ni-1 onto the MOF material is reported. The same trend was observed in Ni-2@NU-1000 by comparison with Ni-2. The supported materials can be handled under air and be recycled a few times with no apparent decrease in the catalytic properties. The presence of Ge in the ligand decreases the catalytic activity but does not affect the selectivity of the reaction. In sum, not only the catalytic activity but also the robustness of the catalyst is benefited by grafting of the organometallic complex onto the MOF material (Chunbai He, 2014) .

3. Enzyme Mimics: MOFs with tailored structures can mimic the functions of enzymes, catalyzing specific reactions with high selectivity and efficiency. These "artificial enzymes" hold potential for industrial applications and biomimetic catalysis.

 A recent research article describes how a colorimetric immunosensor was designed and constructed for the analysis of protein by taking advantage of 2D metal–organic framework (2D-MOF) nanomaterials as enzyme mimics. The nanomaterial shows a strong peroxidase mimetic activity, and good selectivity after it is modified with a specific aptamer. Therefore, taking carcinoembryonic antigen (CEA) as an example, this immunosensor achieves a good detection performance with a linear range from 1 pg mL−1 to 1000 ng mL−1 and a limit of detection (LOD) of 0.742 pg mL−1. Moreover, the sensor can successfully distinguish the human serum of colorectal cancer patients from healthy people, which suggests that this sensor has great potential in clinical applications. More importantly, the mass production, low cost, stability and ease of transport of the MOFs nanomaterials, as well as the ability for visual detection will make this sensor suitable for point-of-care (POC) testing in remote or resource-poor areas [35].

4. Green Chemistry: MOFs can promote green and sustainable catalytic processes. They can facilitate solvent-free reactions or use environmentally friendly solvents, leading to more sustainable and eco-friendly synthesis routes.

5. Selective Catalysis: MOFs can be engineered to exhibit selective catalytic properties, allowing for the efficient conversion of specific reactants while minimizing undesired side reactions. This selectivity is crucial in fine chemical synthesis and pharmaceutical manufacturing.

6. Gas Separation and Conversion: Some MOFs can act as catalysts for gas separation and conversion processes. They can facilitate the separation of specific gas mixtures or promote chemical reactions, such as the conversion of carbon dioxide to useful products.

7. Water Splitting: MOFs have been explored for water splitting reactions, which generate hydrogen gas for potential use as a clean and renewable energy source (Luz J. 2023).

8. Photocatalysis: MOFs with light-absorbing properties can act as photocatalysts, using solar energy to drive chemical reactions. They have applications in water splitting, pollutant degradation, and organic synthesis under mild conditions.

According to a recent research article, titanium metal–organic frameworks (Ti-MOFs), as an appealing type of artificial photocatalyst, have shown great potential in the field of solar energy conversion due to their well-studied photoredox activity (similar to TiO2) and good optical responsiveness of linkers, which serve as the antenna to absorb visible-light (Ha Huu Do, 2022).

9. Carbon Capture and Utilization: MOFs can be used as catalysts in carbon capture and utilization processes, helping to convert captured carbon dioxide into valuable products, such as chemicals or fuels.

The application of metal-organic framework-based catalytic materials for the CO2 cycloaddition with epoxides in some recent studies was summarized and reported in a recent review. MIL-101(Cr) and HKUST-1 based MOFs were identified as a high potential MOF catalysts for the conversion of CO2 into cyclic organic carbonates. The two forms of MOF materials, MIL-101(Cr) and HKUST-1, were both identified to possess special features that gave the advantage in catalyzing the reaction of CO2 with epoxides. Both MIL-101(Cr) and HKUST-1 frame works were characterized with Lewis-acid property due to the presence of metal (II) ions at their metal centers and their structural flexibilities. Thus, allowing their modifications by replacing different functional groups in the organic ligand of MIL-101 and substituting the metal centers in HKUST-1 respectively, while maintaining their backbone structures. The large porosity in the structures of the two materials contributed to their adsorption ability in CO2 and can also be utilized in making effective heterogeneous system by encapsulation of other nanomaterials to form composites. The resultant composites would preserve the original properties of the MOFs, while gaining additional unique properties that can be applied in different applications. There is currently on-going research to improve the catalytic properties of the two MOFs (MIL-101(Cr) and HKUST-1) for better performance. The review also shows that MOF-based catalysts operate effectively when coupled with a co-catalyst. The presence of a co-catalyst helps in performing the crucial role of the activation of the epoxide ring-opening in the second step of the reaction chain. Among the several co-catalyst materials, the one with high electrophilic ability served the best in catalyzing the reaction and for this process, tetrabutylammonium bromide (TBABr) was proven to show the highest performance. The continuous modification of the porous MOFs revealed positive results towards increasing their catalytic activity for CO2 cycloaddition with epoxides (Dr. Cheng-Xia Chen,  2022).

10. Biomass Conversion: MOFs have shown potential in catalyzing biomass conversion processes, facilitating the transformation of renewable feedstocks into useful chemicals and biofuels.

A recent research article emphasises how Zr-containing MOFs, UiO-66 and UiO-66–NH2, have been found to be active, stable and reusable catalysts for the esterification of levulinic acid with various alcohols, viz., ethanol and n-butanol, leading to biomass-derived alkyl levulinates of industrial relevance. As compared to other solid acid catalysts previously reported, the catalytic activity of the Zr-MOFs is in general higher than most of the heterogeneous catalysts studied so far. Alkyl levunates hold industrial relevance due to their applications as renewable solvents, potential biofuel additives, and as intermediates for the synthesis of pharmaceuticals and fine chemicals (Musa, 2021).

The ability to design and synthesize MOFs with specific properties for targeted catalytic applications makes them highly attractive for various industrial and environmental catalytic processes. As research in MOFs and catalysis continues, we can expect further advancements and expanded applications in this field.

**D. BIOMEDICAL APPLICATIONS**

MOFs (metal-organic frameworks) have gained significant attention in biomedical research due to their unique properties and potential applications in various areas. Here are some of the biomedical applications of MOFs:

1. Drug Delivery: MOFs can serve as carriers for controlled drug delivery. The porous structure of MOFs allows for the encapsulation of drugs within their cavities or channels. MOFs can be functionalized with specific targeting ligands or stimuli-responsive components to achieve targeted and controlled drug release at specific sites or in response to external stimuli, such as pH, temperature, or light.

2. Imaging Agents: MOFs can be designed or modified to exhibit excellent imaging capabilities. By incorporating fluorescent or luminescent dyes or metal ions within their structure, MOFs can be utilized as contrast agents for various imaging modalities, such as fluorescence imaging, magnetic resonance imaging (MRI), or positron emission tomography (PET). MOFs can enhance imaging contrast, improve signal-to-noise ratios, and enable multimodal imaging.

A recent review provides up-to-date developments of NMOF-based therapeutic platforms for cancer treatment with emphasis on light-triggered therapeutic strategies and introduces their advances in cancer diagnosis and therapy in recent years (Cirujano, 2015).

3. Biosensors and Diagnostics: MOFs can be used to develop biosensors for detecting specific biomarkers or analytes of interest. The large surface area and tailored pore structures of MOFs allow for the immobilization of biomolecules, such as enzymes or antibodies, enabling sensitive detection and quantification. MOFs can also be functionalized to respond to specific signals or generate measurable signals upon target binding, making them valuable tools for diagnostics and point-of-care testing.

4. Photodynamic Therapy (PDT): MOFs can be functionalized to act as photosensitizers in photodynamic therapy. By incorporating photosensitizing molecules into the MOF structure, they can generate reactive oxygen species upon light irradiation, selectively killing cancer cells. The controlled release capabilities of MOFs can further enhance the efficacy of photodynamic therapy by delivering the photosensitizers specifically to tumor sites.

5. Tissue Engineering: MOFs can be used in tissue engineering applications by providing a scaffold for cell growth and tissue regeneration. MOFs can be designed with suitable pore sizes, surface functionalization, and biocompatible materials to support cellular adhesion, proliferation, and differentiation. They can also be used to deliver bioactive molecules or growth factors for controlled tissue regeneration.

6. Antimicrobial Applications: Some MOFs possess inherent antimicrobial properties, exhibiting the ability to inhibit the growth of bacteria, fungi, or viruses. The porous structure of MOFs can help in controlled and sustained release of antimicrobial agents, providing a platform for antimicrobial coatings, wound dressings, or drug delivery systems to combat infections.

These are just a few examples of the potential biomedical applications of MOFs. Ongoing research continues to explore and expand the applications of MOFs in various areas of biomedicine, aiming to improve drug delivery systems, diagnostics, imaging, and therapy.

**E. FUTURE SCOPES**

Metal-Organic Frameworks (MOFs) are a class of porous materials composed of metal ions or clusters coordinated with organic ligands. They possess an ordered and crystalline structure, with a high surface area and tunable pore sizes. Due to their unique properties, MOFs have garnered significant interest across various scientific and industrial fields. considering ongoing research and developments, here are some potential future scopes and applications of MOFs:

1. Gas Storage and Separation: MOFs can adsorb gases like hydrogen, methane, and carbon dioxide at high densities, making them promising materials for gas storage and separation applications. The development of MOFs with enhanced selectivity and capacity for specific gases could lead to efficient storage and separation technologies.

2. Catalysis: MOFs show excellent potential as catalysts due to their tunable and accessible active sites. Researchers are exploring MOFs as catalysts for a wide range of chemical reactions, including organic transformations and industrial processes, which could lead to more sustainable and efficient chemical manufacturing.

A recently published review explains how Metal–organic frameworks can be employed as heterogeneous catalysts and applied in a wide range of organic reactions and polymerizations. The designable morphology, pore size and ligand functionality of MOFs make it possible for them to be used in diverse catalytic reactions. MOFs stand out from a variety of porous materials like zeolites and activated carbons with their multifunctional organic linkers, modifiable metal sites and high surface area and pore volume, which also can be functionalized *via* their metal nodes and organic ligands by means of pre-synthetic and post-synthetic modifications to generate versatile properties that could not be directly synthesized under traditional synthetic methods. High porosity has been utilized not only as a reaction channel but also for the encapsulation of metal nanoparticles, metal oxides, polyoxometalates and metalloporphyrins. Loading these complexes into the pores of MOFs make them accessible to the reaction substrate, which can be sieved *via* a confined space environment provided by the cages of the MOFs. Sterically hindered substrates also show diminished yields as compared to small substrates, proving that the reactions mainly take place inside the pores. In addition, the metal nodes can be utilized as catalytically active sites after adequate thermal activation, which exposes coordinatively unsaturated metal centers that promote biological recognition and catalytic reactions. These metal nodes can also be exchanged by other metal cations, which is an effective strategy for generating new materials, especially these unavailable by direct synthesis. Hetero-bimetallic MOFs have exhibited enhanced catalytic performance as compared to their monometallic analogues because of the bimetallic synergy. Moreover, the external surface or structural defects of MOFs generated by different approaches also have diverse catalytic active sites for effectively catalyzing different reactions (Dan Zhao, 2022 ).

3. Sensing and Detection: MOFs' structure can be tailored to exhibit selective and sensitive interactions with specific molecules or ions, making them suitable for use in sensors and detectors. MOFs have the potential to revolutionize gas sensing, environmental monitoring, and medical diagnostics.

4. Drug Delivery Systems(DDS): MOFs offer an ideal platform for controlled drug delivery systems. Their porous structure allows for the encapsulation and controlled release of pharmaceutical compounds, leading to improved drug efficacy and reduced side effects.

A review published in 2022 presents and assesses the most recent research, findings, and challenges associated with the use of MOFs as DDSs. Specific attention is given to the stimuli- and multistimuli-responsive MOFs-based DDSs. Of great interest in the COVID-19 pandemic is the use of MOFs for combination therapy and multimodal systems (Gao, 2022).

5. Environmental Applications: MOFs could play a crucial role in environmental protection and remediation. They can be designed to capture and store pollutants or hazardous substances from air and water, aiding in environmental cleanup efforts.

A recent paper highlights the promising properties of a highly crystalline porous metal–organic frameworks (MOFs), with tailorable chemistry and excellent chemical stability in the field of removing various hazardous pollutants. The review concentrates on the recent progress of MOFs and MOF-based materials and exploit their environmental applications, mainly including water treatment, gas storage and separation (Maranescu, 2022).

6. Energy Storage and Conversion: MOFs hold promise for energy storage applications, including batteries and super capacitors. Additionally, they may find use in photovoltaics and other energy conversion devices due to their tunable electronic properties.

In a recent review, the applications of MOF composites in batteries, covering metal-ion batteries, lithium-sulfur batteries, lithium-oxygen batteries and zinc-air batteries, as well as [super capacitors](https://www.sciencedirect.com/topics/physics-and-astronomy/electrochemical-capacitor) were summarised (Zhang, 2022 ).

7. Nanotechnology: MOFs can be synthesized as nanoscale particles, leading to potential applications in nanotechnology, such as nanoscale drug delivery, nanocomposites, and nanosensors.

8. Smart Materials: By incorporating stimuli-responsive components into MOFs, researchers can create "smart" materials that change their properties in response to external stimuli like temperature, pressure, or humidity. Such materials have potential applications in areas like controlled drug release and adaptive membranes.

A recent paper discusses how smart metal–organic frameworks (MOFs) are constructed by introducing stimuli-responsive functional groups into MOF platforms. Through membrane systems containing smart MOFs, external field-modulated gas transport can be achieved, which finds potential applications in chemical engineering. A series of Mg-MOF-74-III-based frameworks functionalized by arylazopyrazole groups were designed. Methylene amine chains with various lengths are attached to the photoresponsive azopyrazole moiety. Molecular dynamics simulations show that CO2 diffusion can be remarkably changed by controlling the cis-to-trans isomerization of the functional unit due to the tunable adsorbate–adsorbent and adsorbate–adsorbate interactions of the two states. With the optimal length of the functional chain, the spatial hindrance and adsorbate–adsorbent interaction exhibit a synergetic effect to maximize the stimuli-responsive kinetic separation of N2 over CO2. This work provides a promising strategy for elevating smart MOFs’ potential in gas separation (Pingying, 2022).

9. Industrial Applications: MOFs could find uses in the petrochemical and chemical industries for gas purification, separations, and catalysis, leading to more energy-efficient and environmentally friendly processes.

A recent review about the development of metal–organic frameworks (MOFs) serving as catalysts for the conversion of carbon dioxide into short-chain hydrocarbons and the generation of clean energies starting from biomass. MOFs have mainly been used as support for catalysts or to prepare catalysts derived from MOFs (as sacrifice template), obtaining interesting results in the hydrogenation or oxidation of biomass. A good performance in the hydrogenation of CO2 into light hydrocarbon fuels was observed. The common patterns to be considered in the performance of the catalysts are the acidity of MOFs, metal nodes, surface area and the dispersion of the active sites, and these parameters were discussed (Valdebenito, 2022).

Metal–organic frameworks (MOFs) are highlighted as efficient supports for enzyme immobilization. They can be used to ‘house’ a specific enzyme, providing it with protection from environmental influences. A recent review emphasizes their synthesis strategies, properties, and applications; explores the existing methods of using immobilization processes of various enzymes; and lists their possible chemical modifications and combinations with other compounds to formulate the ideal supports for a given application (Silva, 2022).

**X. CONCLUSIONS**

It is important to note that MOF research is an ongoing and rapidly evolving field. As scientists continue to explore and understand the properties of MOFs, new applications and innovative uses may emerge, expanding their potential in various industries and addressing current societal challenges.

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