

# METAL ORGANIC FRAME WORKS

## 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 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.

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

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## 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  $6,000 \text{ m}^2/\text{g}$  (Kent O K, 2020). 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.

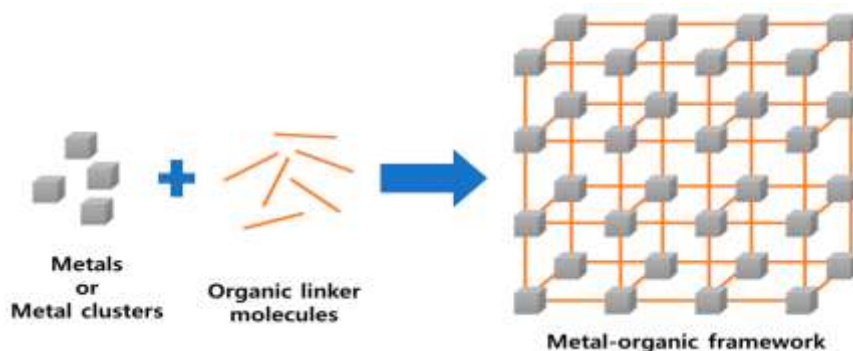
One of the defining characteristics of MOFs is their exceptional porosity. Their extensive surface area and porosity make them ideal for applications such as gas storage and separation, catalysis, drug delivery, and sensing. By adjusting the size, shape, and functionality of the pores, MOFs can selectively 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).



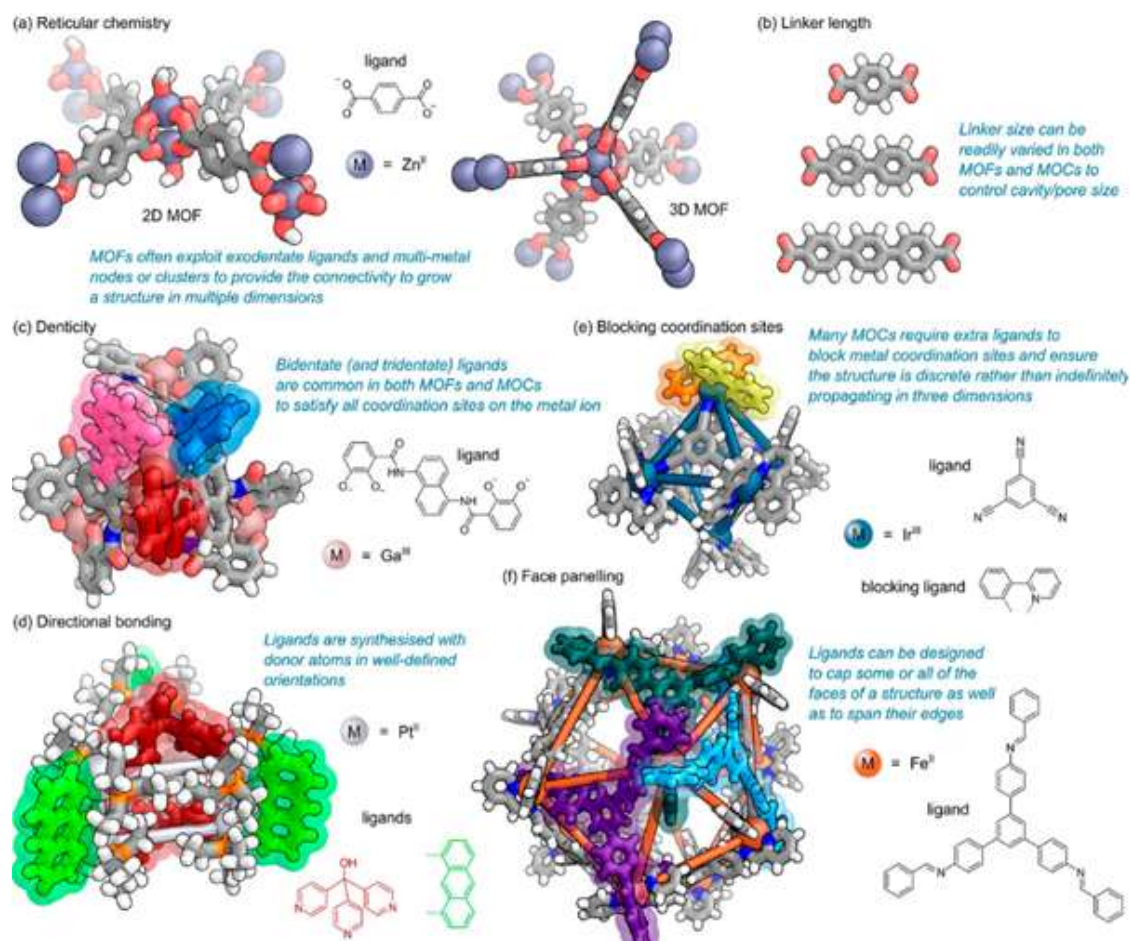
**Figure 1:** Structure of MOF

- **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).
1. **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.

## 2. 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 (-PO<sub>3</sub>H<sub>2</sub>) and phosphinate (-PO<sub>3</sub>H-) 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)<sub>4</sub>N-) 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 (C<sub>4</sub>H<sub>4</sub>O), thiophene (C<sub>4</sub>H<sub>4</sub>S), and pyrrole (C<sub>4</sub>H<sub>5</sub>N), can act as SBBs in MOFs. These linkers offer different electronic and chemical properties, contributing to the overall functionality of the MOFs.

**3. 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.

**1. 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:**

- **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.
- **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.
- **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.
- **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.
- **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.
- **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.

**2. 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:

- **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.
- **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.
- **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.
- **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.
- **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).

**3. 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, 2009).

4. **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.

- 5. 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).

- 6. 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:

- **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.
- **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.
- **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.

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 Vaitis,2020)

- 7. 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:**

- **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.
- **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.
- **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.
- **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.
- **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

1. **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:**

- **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.
- **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.
- **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.
- **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.
- **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.

**2. 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:

- **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.
- **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.
- **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.
- **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.
- **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:**

- **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.
- **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.
- **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.
- **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.
- **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.

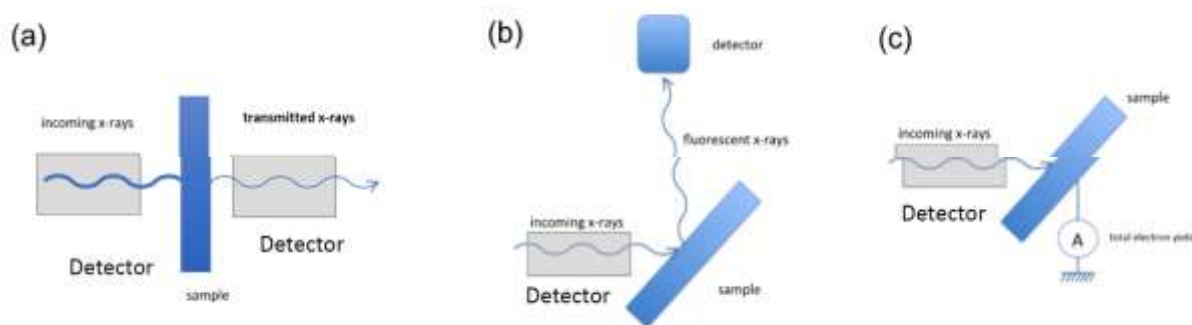
1. **Scanning Electron Microscopy (SEM):** SEM provides a high-resolution image of the MOF's surface morphology. It can reveal the shape, size, and distribution of MOF particles, as well as any surface defects or impurities.
2. **Gas Adsorption:** Gas adsorption experiments, such as nitrogen or carbon 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.
3. **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.

- 4. 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.
- 5. 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.
- 6. 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 investigate the fine structure of X-ray absorption (the international term is X-ray Absorption Fine Structure - XAFS spectroscopy or XAS – X-ray Absorption



**Figure 2:** 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 (Mikhail A Soldatov 2018). 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 ( Mikhail A Soldatov 2018).

## IX. APPLICATIONS OF MOFS

**1. 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:

- **Natural Gas Storage:** MOFs can absorb 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.
- **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.
- **Carbon Dioxide Capture:** MOFs can selectively adsorb carbon dioxide (CO<sub>2</sub>) 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).
- **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 CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, which are relevant to various industrial processes.
- **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.
- **Biogas Upgrading:** MOFs can be employed to upgrade biogas, a mixture of methane and carbon dioxide produced from organic waste. By selectively adsorbing CO<sub>2</sub>, MOFs can help increase the methane content in biogas, making it a more valuable energy source.
- **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.

- **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.
- **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.

**2. 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:

- **Gas Detection:** MOFs can be designed to selectively and sensitively detect specific gases, such as volatile organic compounds (VOCs), ammonia, nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), and hydrogen sulfide (H<sub>2</sub>S). These sensors are valuable in industrial settings, environmental monitoring, and safety applications (Tian Gao, 2023).
- **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)
- **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.
- **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.
- **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.

- **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.
- **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.
- **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 ).
- **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:

- **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)
- **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 ).
- **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.
- **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.

- **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.
- **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.
- **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.
- **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.
- **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.

**3. 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:

- **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.

In a recent review, the catalytic process of Metal-Organic Frameworks (MOFs) in biodiesel production was thoroughly examined. A key challenge in the synthesis of acid/base functionalized MOFs is preserving their stability, as it significantly impacts the integrity of their original structures. Consequently, various design strategies must be employed throughout the synthesis procedure to ensure the maintenance of the highly coordinated network (Shiva Prasad Gouda 2022). A MOF with enhanced stability could serve as an optimal candidate for the immobilization of

various enzymes, thereby facilitating environmentally friendly biodiesel production processes. (Hai-Long Jiang, 2013).

- **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, initial catalytic outcomes of aldehyde and ketone hydroboration with Ni-1@NU-1000 exhibits seven times increase in the TON (Turn Over Number) by grafting the organometallic precursor Ni-1 on the MOF material is reported. A similar trend was observed in Ni-2@NU-1000 by comparison with Ni-2. The supported materials can be operated under air and be recycled a few times without any noticeable drop in the catalytic properties. The inclusion of Ge in the ligand has the effect of reducing catalytic activity, although it does not impact the reaction's selectivity. In essence, grafting the organometallic complex onto the MOF material benefits not only the catalytic activity but also the overall durability of the catalyst. (Chunbai He, 2014).

- **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.

**Certainly, here's the paragraph with rearranged phrases while maintaining the same number of paragraphs:** A recent research article describes the design and construction of a colorimetric immunosensor for the analysis of proteins by utilizing 2D metal-organic framework (2D-MOF) nanomaterials as enzyme mimics. These nanomaterials exhibit a strong peroxidase mimetic activity and demonstrate good selectivity after specific aptamer modification. Using carcinoembryonic antigen (CEA) as an example, this immunosensor achieves an impressive detection performance, featuring a linear range from  $1 \text{ pg mL}^{-1}$  to  $1000 \text{ ng mL}^{-1}$  and an impressively low limit of detection (LOD) at  $0.742 \text{ pg mL}^{-1}$ . Moreover, the sensor successfully distinguishes the human serum of colorectal cancer patients from that of healthy individuals, suggesting the sensor's great potential in clinical applications. What's more important is the sensor's suitability for point-of-care (POC) testing in remote or resource-poor areas, thanks to the mass production, low cost, stability, ease of transport, and visual detection capability of the MOFs nanomaterials. (S.P Gauda 2022).

- **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.
- **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.

- **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.
- **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).
- **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), an intriguing class of synthetic photocatalysts, have demonstrated significant promise in the realm of solar energy conversion. This is primarily attributed to their extensively researched photoredox activity, which closely resembles that of titanium dioxide (TiO<sub>2</sub>), and their favorable optical responsiveness stemming from the linkers, effectively acting as antennae to harness visible light. (Ha Huu Do, 2022).

- **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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 substantial porosity inherent in the structures of both materials plays a pivotal role in enhancing their capacity for CO<sub>2</sub> adsorption. Furthermore, this porosity offers the opportunity to create efficient heterogeneous systems by encapsulating other nanomaterials, thereby forming composite materials. These resultant composites retain the inherent characteristics of the MOFs while acquiring additional distinctive properties, making them versatile and applicable in various domains. 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 highlights the effective operation of MOF-based catalysts when paired with co-catalysts. These co-catalysts play a pivotal role in facilitating the crucial activation of the epoxide ring-opening during the second step of the reaction sequence. Among the various co-catalyst materials examined, those with high electrophilic capabilities demonstrated



superior performance in catalyzing the reaction. Notably, tetrabutylammonium bromide (TBABr) emerged as the most effective co-catalyst for this process. Continuous modifications of porous MOFs yielded favorable outcomes in terms of enhancing their catalytic activity for the cycloaddition of CO<sub>2</sub> with epoxides. (Dr. Cheng-Xia Chen, 2022).

- **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 underscores the significance of Zr-containing MOFs, specifically UiO-66 and UiO-66-NH<sub>2</sub>, which have demonstrated remarkable activity, stability, and reusability as catalysts for the esterification of levulinic acid with various alcohols, including ethanol and n-butanol. This catalytic process yields biomass-derived alkyl levulinates, which hold substantial industrial importance. In comparison to previously reported solid acid catalysts, the catalytic efficacy of these Zr-MOFs generally surpasses that of most heterogeneous catalysts studied to date. Alkyl levulinates, a product of this process, have industrial relevance due to their applications as sustainable 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.

#### 4. **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:

- **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.
- **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).

- **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.
- **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.
- **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.
- **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.

**5. Future Scopes:** Metal-Organic Frameworks (MOFs) are a type of porous materials consisting of metal ions or clusters coordinated with organic ligands. They have ordered and crystalline structure, with a high surface area and tunable pore sizes. MOFs have gathered significant interest across various scientific and industrial fields. Considering ongoing research and developments, here are some potential future scopes and applications of MOFs:

- **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.
- **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 details the versatile applications of Metal–organic frameworks (MOFs) as heterogeneous catalysts in a wide range of organic reactions and polymerizations. MOFs, with their customizable morphology, pore sizes, and ligand functionalities, can be harnessed effectively in various catalytic processes. What sets MOFs apart from other porous materials like zeolites and activated carbons is their multifunctional organic linkers, modifiable metal sites, and the combination of high surface area and pore volume. These distinctive features enable MOFs to be functionalized through both pre-synthetic and post-synthetic modifications, resulting in a wide array of properties that cannot be readily achieved using traditional synthetic methods. High porosity in MOFs serves a dual purpose – it acts as a reaction channel and allows for the encapsulation of various compounds such as metal nanoparticles, metal oxides, polyoxometalates, and metalloporphyrins. These complexes housed within the MOF pores become easily accessible to reaction substrates, effectively sieved through the confined space provided by the MOF cages. Notably, steric hindrance impacts the yields of reactions, indicating that these reactions primarily occur within the pores. Furthermore, after suitable thermal activation, the metal nodes within MOFs can serve as catalytically active sites, exposing coordinatively unsaturated metal centers that facilitate biological recognition and catalytic reactions. These metal nodes are also amenable to exchange with other metal cations, offering an effective strategy for producing new materials, especially those that cannot be directly synthesized. The use of hetero-bimetallic MOFs has demonstrated enhanced catalytic performance compared to their monometallic counterparts, thanks to the synergistic effects of the two metals. Additionally, MOFs with external surface or structural defects, generated through various approaches, provide diverse catalytic active sites for effectively catalyzing different reactions. (Dan Zhao, 2022 ).

- **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.
- **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.

In a 2022 review, the latest research, discoveries, and difficulties related to the utilization of MOFs as drug delivery systems (DDSs) are introduced and evaluated. Special emphasis is placed on MOFs-based DDSs that respond to various stimuli, including multiple stimuli. Particularly noteworthy in the context of the COVID-19 pandemic is the application of MOFs in combined therapy and multifaceted systems. (Gao, 2022).

- **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 publication underscores the favorable characteristics of a meticulously crystalline porous metal-organic framework (MOFs), which boasts customizable chemistry and exceptional chemical resilience in the realm of eliminating diverse harmful contaminants. The paper primarily focuses on the contemporary advancements in MOFs and materials derived from MOFs, harnessing their potential in environmental applications. These applications are chiefly centered around water purification, gas retention, and the separation of gases. (Maranescu, 2022).

- **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 utilization of MOF composites in various battery types was summarized, encompassing metal-ion batteries, lithium-sulfur batteries, lithium-oxygen batteries, and zinc-air batteries, in addition to their application in supercapacitors. (Zhang, 2022 ).

- **Nanotechnology:** MOFs can be synthesized as nanoscale particles, leading to potential applications in nanotechnology, such as nanoscale drug delivery, nanocomposites, and nanosensors.
- **Smart Materials:** By integrating stimuli-responsive components into MOFs, scientists have the ability to fashion "smart" materials that alter their properties in reaction to external stimuli such as temperature, pressure, or humidity. Such materials have potential applications in areas like controlled drug release and adaptive membranes.

In a recent paper, the discussion revolves around the construction of "smart" metal-organic frameworks (MOFs) achieved by introducing responsive functional groups into MOF structures. These smart MOFs are integrated into membrane systems, enabling the modulation of gas transport under external fields, thus holding promise for applications in chemical engineering. A series of frameworks based on Mg-MOF-74-III and functionalized with arylazopyrazole groups were designed. Methylene amine chains of varying lengths are attached to the photosensitive azopyrazole segment. Molecular dynamics simulations reveal that the diffusion of CO<sub>2</sub> can be significantly altered by controlling the cis-to-trans isomerization of the functional unit, owing to the tunable interactions between adsorbate and adsorbent, as well as between adsorbate molecules in both states. By optimizing the length of the functional chain, a synergistic effect arises from spatial hindrance and adsorbate-adsorbent interactions, maximizing the stimuli-responsive kinetic separation of N<sub>2</sub> from CO<sub>2</sub>. This study presents a promising strategy for enhancing the potential of smart MOFs in gas separation applications. (Pingying, 2022).

- **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.

In a recent review, the focus is on the advancement of metal–organic frameworks (MOFs) as catalysts for two crucial processes: the conversion of carbon dioxide into short-chain hydrocarbons and the generation of clean energy from biomass. MOFs have primarily been employed either as catalyst support or in the preparation of catalysts derived from MOFs, often using them as a sacrificial template. These approaches have yielded promising outcomes, particularly in the hydrogenation and oxidation of biomass. Notably, MOFs have demonstrated remarkable performance in the hydrogenation of carbon dioxide, resulting in the production of light hydrocarbon fuels. Several critical factors influencing catalyst performance were identified, including the acidity of MOFs, the nature of metal nodes, surface area, and the dispersion of active sites. The review delves into a comprehensive discussion of these parameters, shedding light on their significance in achieving effective catalytic results. (Valdebenito, 2022).

Metal–organic frameworks (MOFs) have gained recognition as effective platforms for immobilizing enzymes. They serve as protective enclosures, sheltering enzymes from external environmental factors. A recent review places a spotlight on MOFs, detailing their synthesis techniques, properties, and wide-ranging applications. The review thoroughly examines various enzyme immobilization methods and elucidates potential chemical modifications. Furthermore, it explores the synergy of MOFs with other compounds, presenting a comprehensive approach to crafting optimal supports tailored to specific applications. (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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## REFERENCES

- [1] Kent O. Kirlikovali, Zhijie Chen, Timur Islamoglu, Joseph T. Hupp, Omar K. Farha."Zirconium-Based Metal–Organic Frameworks for the Catalytic Hydrolysis of Organophosphorus Nerve Agents", ACS Applied Materials & Interfaces, 2020
- [2] Zhou H C, Long JR, Yaghi OM. "Introduction to metal-organic frameworks" Chem Rev. 2012 112 (2 ) pp 673
- [3] V. V. Butova, M. A Soldatov, A A Guda, K A Lomachenko, C. Lamberti. "Metal Organic Frame works: Structure properties, methods of synthesis and characterization", Russian Chemical Reviews 85 (3) (2016) pp 280 -307
- [4] Baumann, A.E., Burns, D.A., Liu, B. et al. "Metal-organic framework functionalization and design strategies for advanced electrochemical energy storage devices". Commun. Chem 2, 86 (2019).
- [5] Islamoglu T, Chen Z, Wasson MC, et al. "Metal–Organic Frameworks against Toxic Chemicals". Chemical reviews. 2020;120(16):pp 8130-8160.
- [6] Yu-Ri Lee, Jun Kim, and Wha-Seung Ahn: "Synthesis of metal-organic frameworks A mini review" : Korean J. Chem. Eng., (2013) 30(9), pp1667-1680
- [7] Mikhail.A Soldatov, A. Martini, A.L. Bugaev, I. Pankin, Pavel.V. Medvedev, A.A. Guda, A.M. Aboraia, Y.S. Podkovyrina, A.P. Budnyk, A.A. Soldatov, C. Lamberti, "The Insights from X-ray Absorption Spectroscopy into the Local Atomic Structure and Chemical Bonding of Metal-organic Frameworks", Polyhedron 154, 1-486 (2018)

- [8] Seth M. Cohen, "Post synthetic Methods for the Functionalization of Metal–Organic Frameworks" : Chem. Rev. 112, 970 ( 2012)
- [9] Takashi Uemura, Nobuhiro Yanaia and Susumu Kitagawa: "Polymerization reactions in porous coordination polymers" : Chem. Soc. Rev., 2009,38, pp1228-1236
- [10] Zhenyu Zhao, Hong Li, Kai Zhao, Lyuting Wang, Xin Gao: "Microwave assisted synthesis of MOFs, Rational design via numerical simulation": vol 428 (2022) pp 131006.
- [11] Jacek Klinowsky, Filipe A Almeida Paz, Patricia SilvaandJoaoRocha: Microwave assisted synthesis of MOFs, Dalton transactions 2011 40 pp 322- 330
- [12] Varsha M V, GomathiNageswaran: "Review on Direct electrochemical synthesis of MOFs"; Journal of the Electrochemical Society 167 (2020) pp155527
- [13] Alberto Martinez Joaristi, Jana Juan- Alcaniz Pablo, Serra Crespo, FreekKapteijn and Jorge Gascon: "Electrochemical synthesis of some Archetypical Zn 2+, Cu2+ and Al3+" Cryst.Growth Des. 12 ( 2012) pp3489- 3498
- [14] Won-JinSon, Jun Kim Jaheon Kim, WhaSeungAhn; "Sonochemical synthesis of MOF-5" : Chemical Communication (2008) pp6336 – 6338
- [15] Christos Vaitsis, Georgia Sourkouni, Christos Argirusis: "Metal Organic Frame works for Biomedical applications" (2020) pp 223- 246
- [16] Meili Ding, Xuechao Cai and Hai long Jiang:" Improving MOF stability": approaches and applications Chem. Sci; (2019) 10 10209 -10230
- [17] D.C. Koningsberger, R. Prins, "X-ray absorption: principles, applications, techniques of EXAFS, SEXAFS, and XANES" John Wiley and Sons, New York, 1988.
- [18] Filipponi, A. Di Cicco, C.R. Natoli: "X- ray absorption spectroscopy and n-body distribution functions in condensed matter" ; Phys. Rev. B, 52 (1995) 15122-15134.
- [19] J.A. van Bokhoven, C. Lamberti, "X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications, Wiley, Chichester", 2016.
- [20] J.J. Kas, K. Jorissen, J.J. Rehr, "Real-Space Multiple-Scattering Theory of X-Ray Spectra",in: J.A. van Bokhoven, C. Lamberti (Eds.) X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications, John Wiley & Sons, Chichester (UK), 2016, pp. 51-72.
- [21] C. Lamberti, J.A. van Bokhoven, " Introduction: Historical Perspective on XAS". , Wiley, 2016.
- [22] E. Borfecchia, D. Gianolio, G. Agostini, S. Bordiga, C. Lamberti, "Characterization of MOFs". AFS for Everyone, Taylor & Francis, 2013.
- [23] Tian Gao, ShouwuYou, Haojao Wang, Xiang Zhao, ChangmengWang, Shujuan Xiao: "MOFs based photocatalytic self cleaning membranes for highly efficient waste water treatment" – A review Chemical Engineering Science 278 (2023) pp 118891
- [24] Chunbai He, Huangada Luandwenbin Lin: J. Am. "Nanoscale Metal Organic Frame works for Real time intra cellular pH sensing in live cells" Chem. Soc. (2014),136,35,pp12253-12256
- [25] Shiva Prasad Gouda, Amarajothi Dhakshinamoorthy, Samuel LalthazualaRokhum. "Metal-organic framework as a heterogeneous catalyst for biodiesel production: a review", Chemical Engineering Journal Advances, (2022) 100415.
- [26] Luz J. Barrios-Vargas, Niroshani S. Abeynayake, Carlee Secrist, Nghia Le et al. "Homogeneous MOF-supported catalysis: a direct comparison of catalytic hydroboration with Ni tripodal P E (E = Si, Ge) complexes ", Dalton Transactions, (2023) 52, 8883-8892.
- [27] Hai- Long, Jiang Dawei Feng, Kecheng Wang Zhi-Yuan Gu, Zhanwenwei, Ying pin Chen and Hong Cai Zhou : "An exceptionally stable, porphyrinic Zr metal Organic Frame work exhibiting pH dependent flourescence": JACS (2013) 135, pp13934 - 13938
- [28] Osama Shekhah: "Layer by layer method for the synthesis of and growth of surface mounted metal Organic Frame works": Materials (2010) 3 pp1302- 1315
- [29] Joshua G Hinman, Jacob G Turner, Daniel M. Hofmann, Catherine J Murphy: "Layer-by layer synthesis of conformal metal – organic frame work shell on gold nanorods". Chem. Mater. (2018) 30 20 pp 7255- 7261
- [30] Mahnaz Ahmadi, Seyed Mohammad, Ayyoubzadeh, Fatemeh Ghorbani- Bidkorpheh Soraya Shahhossoini, Simin Dadashzadeth, ElhamAsadian, Mona Mosayebnia and Saeed Siavashy: "Metal Organic Frame works- A universal material for biomedicine"; Heliyon 2021 e06914 Elsevier
- [31] Sebastian Henke, D. C. Florian Wieland, Mikhail Meilikhov, Michael Paulus, Christian Sternemann, Kirill Yusenko and Roland A. Fischer Multiple phase-transitions upon selective CO2 adsorption in an alkyl ether functionalized metal–organic framework—an in situ X-ray diffraction study Cryst. Eng. Comm, 2011,13 pp 6399-6404

- [32] N. K. Daud, N. H. I. M. Najib: CO<sub>2</sub> Adsorption on Zeolites and Fe-MOF for Carbon Capture and Storage (CCS) Vol. 8 No. 1 (2022) Journal of Chemical Engineering and Industrial
- [33] Hai-Long Jiang, Dawei Feng†, Kecheng Wang†, Zhi-Yuan Gu†, Zhangwen Wei†, Ying-Pin Chen† Hong-Cai Zhou An Exceptionally Stable, Porphyrinic Zr Metal–Organic Framework Exhibiting pH-Dependent Fluorescence Journal of American Chemical Society (2013) 135, 37, 13934
- [34] Shiva Prasad Gouda, Amarajothi Dhakshinamoorthy, Samuel Lalthazuala Rokhum : Metal-organic framework as a heterogeneous catalyst for biodiesel production: A review, Chemical Engineering Journal Advances; Volume 12, 2022, pp 100415,.
- [35] Luz J. Barrios-Vargas a, Niroshani S. Abeynayake a, Carlee Secrist a, Nghia Le a, Charles Edwin Webster a, Bruno Donnadiou a, David M. Kaphan b, Amitava D. Roy c, Ilich A. Ibarra d and Virginia Montiel-Palma Homogeneous versus MOF-supported catalysis: a direct comparison of catalytic hydroboration with Ni tripodal P3E (E = Si, Ge) complexes Dalton Trans., (2023) 52, 8883-8892
- [36] Ha Huu Do, Thi Hong Chuong Nguyen, Tuan Van Nguyen, Changlei Xia, Dang Le Tri Nguyen, Pankaj Raizada, Pardeep Singh, Van-Huy Nguyen, Sang Hyun Ahn, Soo Young Kim, Quyet Van Le,: Metal-organic-framework based catalyst for hydrogen production: Progress and perspectives, :International Journal of Hydrogen Energy, Volume 47, Issue 88,2022, pp 37552-37568
- [37] Dr. Cheng-Xia Chen, Yang-Yang Xiong, Xin Zhong, Pui Ching Lan, Dr. Zhang-Wen Wei, Dr. Hongjun Pan, Dr. Pei-Yang Su, Yujie Song, Dr. Yi-Fan Chen, Prof. Ayman Nafady, Dr. Sirajuddin, Prof. Shengqian Ma: Enhancing Photocatalytic Hydrogen Production via the Construction of Robust Multivariate Ti-MOF/COF Composites:Chem. Int. Ed. ( 2022) 61,
- [38] Musa, S. G., Aljunid Merican, Z. M., & Akbarzadeh, O. (2021). Study on Selected Metal-Organic Framework-Based Catalysts for Cycloaddition Reaction of CO<sub>2</sub> with Epoxides : A Highly Economic Solution for Carbon Capture and Utilization. Polymers, 13(22), pp 3905.
- [39] Cirujano, F. G., Corma, A., & Llabrés i Xamena, F. X.: Synthesis of biomass-derived levulinate esters over Zr-containing MOFs, Conversion of levulinic acid into chemicals: Synthesis of biomass-derived levulinate esters over Zr -containing MOFs. Chemical Engineering Science, (2015) 124, pp 52-60.
- [40] Dan Zhao, Wang Zhang, Si-Lei Xia & Guan-Jun Yang. Application of MOF-based nanotherapeutics in light-mediated cancer diagnosis and therapy. J.Nanobiotechnol 20, 421 (2022).
- [41] Gao F, Yan R, Shu Y, Cao Q, Zhang L. Strategies for the application of metal-organic frameworks in catalytic reactions. RSC Adv. (2022)12(16) pp10114-10125
- [42] Maranescu B, Visa A. Applications of Metal-Organic Frameworks as Drug Delivery Systems. Int. J. Mol. Sci. (2022) 23(8) pp 4458.
- [43] Zhang, Q., Yang, H., Zhou, T., Chen, X., Li, W., Pang, H., Metal–Organic Frameworks and Their Composites for Environmental Applications. Adv. Sci. 2022, 9, pp 2204-141
- [44] Yi Peng, Jia Xu, Jinming Xu, Jiao Ma, Yang Bai, Shuai Cao, Songtao Zhang, Huan Pang: Metal-organic framework (MOF) composites as promising materials for energy storage applications; Advances in Colloid and Interface Science; 307, (2022) pp102732,.
- [45] Pingying Liu, Ziqi Tian, and Liang Chen: Rational Design of Smart Metal–Organic Frameworks for Light-Modulated Gas Transport, ACS Applied Materials & Interfaces (2022) 14 (28), pp 32009-32017
- [46] Valdebenito, G., González-Carvajal, M., Santibañez, L., & Cancino, P. (2022). Metal–Organic Frameworks (MOFs) and Materials Derived from MOFs as Catalysts for the Development of Green Processes. Catalysts, 12(2), p 136.
- [47] Silva A R M, Alexandre J Y N H, Souza J E S, Neto J G L, de Sousa Júnior P G, Rocha M V P, Dos Santos JCS. The Chemistry and Applications of Metal-Organic Frameworks (MOFs) as Industrial Enzyme Immobilization Systems. Molecules. ; (2022) 27(14) p 4529.