International Journal of
Metallurgy and Alloys

ISSN: 2456-5113
Volume 10, Issue 1, 2024
January-June
DOI (Journal): 10.37628/IJMA

https://journalspub.com/journal/ijma/

Review IJMA

Synthesis and Characterization of Metal-Organic Frameworks for Gas Storage

Neha Sahu[1,*], Rizwan Arif[2]

Abstract

Metal-Organic Frameworks (MOFs) represent a class of highly porous materials formed by the coordination of metal ions with organic linkers, exhibiting exceptional potential for gas storage applications due to their high surface area, tunable pore sizes, and structural versatility. The synthesis and characterization of MOFs intended for the effective storage of gases like carbon dioxide, methane, and hydrogen are the main topics of this work. Solvothermal Hectic strategies, including solvothermal, hydrothermal, and microwave-assisted methods, were employed to optimize the formation of MOFs with desired properties. The synthesized MOFs were characterized using a suite of techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and nitrogen adsorption-desorption isotherms to evaluate their crystallinity, functional groups, morphology, and surface area, respectively. The gas adsorption capacities were assessed using volumetric and gravimetric methods under varying conditions of pressure and temperature. The results demonstrated that the MOFs exhibited significant adsorption capacities, highlighting their potential as materials for gas storage in applications ranging from clean energy storage to carbon capture and sequestration.

Keywords: Adsorption, gas storage, metal-organic frameworks (MOFs), porosity, surface area, synthesis

INTRODUCTION

A type of crystalline material known as Metal-Organic Frameworks (MOFs) is made up of metal ions or clusters arranged in relation to organic ligands to create one-, two-, or three-dimensional structures. Their unique porous nature and tunable properties make them highly attractive for various applications, particularly in gas storage [1].

Background and Importance

Due to the rising energy demand and the need to reduce environmental effects, effective gas storage systems are becoming more and more crucial. Traditional methods of gas storage, such as high-pressure tanks and cryogenic systems, often come with significant safety, economic, and efficiency challenges. MOFs offer a promising alternative due to their high surface area, adjustable pore sizes, and the ability to be functionalized with specific chemical groups to enhance gas adsorption capacities [2].

***Author for Correspondence**
Neha Sahu
E-mail: nehasahu082018@gmail.com

[1]Research Scholar, Department of Chemistry, School of Basic & Applied Sciences, Lingaya's Vidyapeeth, Faridabad, Haryana, India.
[2]Assistant Professor, Department of Chemistry, School of Basic & Applied Sciences, Lingaya's Vidyapeeth, Faridabad, Haryana, India.

Received Date: August 12, 2024
Accepted Date: September 15, 2024
Published Date: November 20, 2024

Citation: Neha Sahu, Rizwan Arif. Synthesis and Characterization of Metal-Organic Frameworks for Gas Storage. International Journal of Metallurgy and Alloys. 2024; 10(1): 25–30p.

Structure and Properties of MOFs

Composition

Metal nodes: Metal ions or clusters, such as zinc, copper, aluminum, or zirconium, serve as the nodes or vertices of the framework.

Organic linkers: Organic molecules, typically carboxylates, phosphonates, or sulfonates, link the metal nodes, forming a robust and highly porous structure [3].

Porosity

MOFs can exhibit extremely high surface areas (up to 7000 m^2/g) and large pore volumes, which are essential for gas storage. The pore size and distribution can be tailored by choosing appropriate metal nodes and organic linkers, allowing for the selective adsorption of specific gases [4].

Functionality

The chemical environment within the pores can be modified to enhance interactions with target gas molecules, improving storage capacity and selectivity. Figure 1 shows a general scheme of the three-dimensional metal-organic framework. Functional groups can be introduced to the organic linkers to create binding sites for specific gases [5].

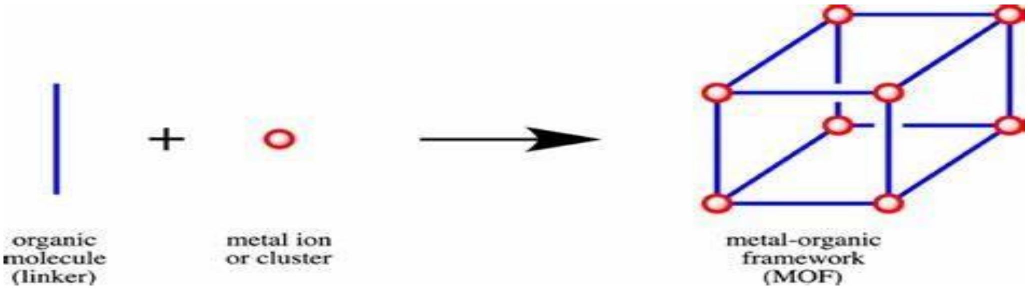

Figure 1. A general scheme of the three-dimensional metal-organic framework.

Advantages of MOFs for Gas Storage

High storage capacity: Compared to conventional storage techniques, MOFs can store a lot of gas at comparatively low pressures. For uses like methane storage for natural gas vehicles or hydrogen storage for fuel cells, this makes them more affordable and safer.

Selective adsorption: The tunable nature of MOFs allows for the selective adsorption of specific gases from mixtures. Applications involving the separation and purification of gases will find this very helpful.

Regenerability: MOFs can be regenerated through relatively simple processes, such as pressure or temperature swings, allowing for repeated use without significant loss of performance [6].

Research and Development

The synthesis and characterization of MOFs involve several key steps:

Synthesis: Various methods, including solvothermal, hydrothermal, microwave-assisted, and mechanochemical synthesis, are employed to create MOFs with desired properties.

Parameters: Parameters, such as temperature, pressure, solvent, and reaction time are carefully controlled to optimize the formation of the desired framework.

Techniques: Techniques, such as X-ray diffraction (XRD), gas adsorption isotherms, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) are used to analyze the structural, thermal, and morphological properties of MOFs.

Understanding these properties is crucial for tailoring MOFs for specific gas storage applications [7].

Applications and Future Prospects

MOFs have shown great potential in a variety of gas storage applications.

Hydrogen storage: MOFs can store hydrogen at densities approaching those required for practical use in fuel cell vehicles, offering a pathway to cleaner energy systems.

Methane storage: MOFs can store natural gas at lower pressures, making them suitable for use in natural gas-powered vehicles and reducing the need for high-pressure tanks [8].

Carbon Dioxide Capture

MOFs can selectively capture and store CO_2 from industrial emissions, contributing to efforts to reduce greenhouse gas emissions and combat climate change. The ongoing research in the synthesis and functionalization of MOFs aims to further enhance their gas storage capabilities and expand their practical applications. As understanding and technology advance, MOFs are poised to play a critical role in the development of sustainable and efficient energy storage solutions. For gas storage applications, MOFs are a highly promising and adaptable class of materials. Their unique properties, combined with the ability to tailor their structure and functionality, make them ideal candidates for addressing the challenges of modern gas storage needs [9].

LITERATURE

The synthesis and characterization of Metal-Organic Frameworks (MOFs) for gas storage is a significant area of research, with numerous studies highlighting their potential due to high surface areas, tunable porosity, and functionalization capabilities [10].

Synthesis of MOFs: Hydrothermal/Solvothermal Synthesis

MOFs are synthesized by dissolving metal salts and organic linkers in a solvent (water or organic solvent). The mixture is then heated in a sealed vessel (autoclave) at high temperature and pressure for a certain period [11].

Solvent-Free Synthesis

This involves grinding the metal salt and the organic linker together, leading to the formation of MOFs without the need for solvents. This method is more environmentally friendly [12].

Microwave-Assisted Synthesis

Microwave irradiation is used to heat the reaction mixture, resulting in faster and more energy-efficient synthesis [12].

Electrochemical Synthesis

An electrochemical cell is used where metal ions are generated from the anode and react with the organic linker in the solution to form MOFs [12].

Characterization of MOFs:

X-ray diffraction (XRD) is utilized to ascertain the MOFs’ phase purity and crystalline structure. It measure the surface area and pore size distribution of MOFs using the Brunauer-Emmett-Teller (BET) surface area analysis [13]. MOF crystal size and shape are examined using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). It is utilized to investigate the composition and thermal stability of MOFs, also known as thermogravimetric analysis (TGA).

Gas adsorption isotherms are used to calculate MOFs’ selectivity and gas storage capacity. The synthesis and characterization of MOFs for gas storage applications can be better understood by consulting these sources [14].

METHODOLOGY

Selection of metal ions and organic linkers: Choose metal ions (e.g., Zn, Cu, Fe) and organic linkers (e.g., carboxylates, imidazolates) based on desired properties and applications [14].

Solvothermal Synthesis

Mix metal salts and organic linkers in a solvent (e.g., DMF, water) in a Teflon-lined autoclave. For many hours to several days, heat the mixture to a certain temperature (usually between 100 and 200°C) to create MOF crystals, and then cool the mixture to room temperature [15].

Microwave-Assisted Synthesis

Mix metal salts and organic linkers in a solvent. Expose the mixture to microwave radiation for rapid heating. This method reduces reaction time and can produce high-quality crystals [15].

Sonochemical Synthesis

Use ultrasonic waves to promote the reaction between metal salts and organic linkers in a solvent. This method also reduces reaction time and can lead to high crystallinity [15].

Electrochemical Synthesis

Use an electrochemical cell with a metal electrode as the anode and an organic linker in the electrolyte. Apply potential to promote the formation of MOFs on the electrode surface [15].

Mechanochemical Synthesis

Grind salt and organic linkers together using a ball mill. This solvent-free method is environmentally friendly and efficient [16].

X-ray Diffraction (XRD)

Determine the crystal structure and phase purity. Powder XRD is commonly used to identify the crystalline phases and assess purity [16].

Scanning Electron Microscopy (SEM)

Analyze the morphology and particle size. Provides detailed images of the MOF surface structure.

Transmission Electron Microscopy (TEM)

Investigate the internal structure at a higher resolution than SEM. Useful for studying the nanoscale features. Using Fourier Transform Infrared Spectroscopy (FTIR), locate functional groups and verify if organic linkers are present. Examine the MOF's spectrum in comparison to the initial materials [17].

Thermogravimetric Analysis (TGA)

Examine the patterns of decomposition and thermal stability. Calculate how much weight varies with temperature. Surface area and pore size distribution are measured using the Brunauer-Emmett-Teller (BET) surface area analysis method. Gas adsorption techniques (e.g., nitrogen adsorption) are used to calculate BET surface area [18].

Gas Sorption Analysis

Evaluate gas storage capacity and selectivity. Measure adsorption isotherms for gases like CO_2, CH_4, and H_2 at various pressures and temperatures [18].

Nuclear Magnetic Resonance (NMR) Spectroscopy

Study the local chemical environment of atoms within the MOF. Solid-state NMR can provide information on the framework structure and dynamics [18].

X-ray Photoelectron Spectroscopy (XPS)

Examine the oxidation states and surface makeup of the metal ions. Provide details about the elements' chemical states inside the MOF. ICP-MS, or inductively coupled plasma mass spectrometry: Calculate the MOF's metal content. Accurate elemental analysis is provided.

- *Gas storage applications:* Hydrogen Storage: High surface area MOFs with suitable pore sizes can store significant amounts of hydrogen. Look for MOFs with strong metal-hydrogen interactions. Methane Storage: MOFs with large pore volumes and high surface areas are ideal for methane storage. Focus on frameworks that offer high volumetric and gravimetric storage capacities.

- *Carbon dioxide capture:* MOFs with functional groups that interact strongly with CO_2 (e.g., amines) are effective for CO_2 capture. Evaluate selectivity and capacity under different conditions (e.g., temperature, pressure). By carefully selecting synthesis methods and characterization techniques, it is possible to design and optimize MOFs for specific gas storage applications, enhancing their performance and practical utility.

CONCLUSIONS

The synthesis and characterization of Metal-Organic Frameworks (MOFs) for gas storage represents a significant advancement in materials science and engineering, providing promising solutions for energy and environmental challenges. The key points to consider in concluding the study on MOFs for gas storage are:

Solvothermal and hydrothermal synthesis: These methods remain the most widely used for producing high-quality MOFs with well-defined structures.

Mechanochemical synthesis: Offers a greener alternative, reducing the need for solvents and potentially lowering production costs.

Microfluidic and electrochemical methods: Emerging techniques that allow for precise control over the synthesis process and the potential for scalable production.

X-ray diffraction (XRD): A crucial technique for ascertaining the MOFs’ phase purity and crystalline structure.

Gas adsorption isotherms: Essential for determining MOF surface area, porosity, and gas storage capacity.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA): Provide details on phase transitions and thermal stability. FTIR, NMR, and UV-Vis spectroscopy methods are helpful in determining electronic characteristics, bonding environments, and functional groups.

Gas Storage Performance

High surface area and porosity: MOFs exhibit exceptional surface areas and porosity, crucial for high gas storage capacities.

Selectivity and uptake: MOFs can be tailored to enhance selectivity for specific gases, improving efficiency and performance for applications like CO_2 capture, H_2 storage, and CH_4 storage.

Stability and Regenerability: Long-term stability and ease of regeneration are vital for practical applications, with many MOFs demonstrating robust performance over multiple cycles.

REFERENCES

1. Babu S, Manoharan S, Ottappilakkil H, Perumal E. Role of oxidative stress-mediated cell death and signaling pathways in experimental fluorosis. Chem Biol Interact. 2022 Sep 25;365:110106.
2. Cai X, Xie Z, Li D, Kassymova M, Zang SQ, Jiang HL. Nano-sized metal-organic frameworks: Synthesis and applications. Coord Chem Rev. 2020 Aug 15;417:213366.
3. Chen H, You Z, Wang X, Qiu Q, Ying Y, Wang Y. An artificial olfactory sensor based on flexible metal–organic frameworks for sensing VOCs. Chem Eng J. 2022 Oct 15;446:137098.
4. Chen J, Wang G, Su X. Fabrication of red-emissive ZIF-8@ QDs nanoprobe with improved fluorescence based on assembly strategy for enhanced biosensing. Sens Actuators B Chem 2022 Oct 1;368:132188.
5. Cheng W, Tang X, Zhang Y, Wu D, Yang W. Applications of metal-organic framework (MOF)-based sensors for food safety: Enhancing mechanisms and recent advances. Trends Food Sci Technol. 2021 Jun 1;112:268-82.
6. Davey AK, Gao X, Xia Y, Li Z, Dods MN, Delacruz S, Pan A, Swamy S, Gardner D, Carraro C, Maboudian R. Amine-functionalized metal-organic framework ZIF-8 toward colorimetric CO2 sensing in indoor air environment. Sens Actuators B Chem. 2021 Oct 1;344:130313.

7. Ding M, Liu W, Gref R. Nanoscale MOFs: From synthesis to drug delivery and theranostics applications. Adv Drug Deliv Rev. 2022 Nov 1;190:114496.
8. Duan S, Dou B, Lin X, Zhao S, Emori W, Pan J, Hu H, Xiao H. Influence of active nanofiller ZIF-8 metal-organic framework (MOF) by microemulsion method on anticorrosion of epoxy coatings. Colloids Surf A Physicochem Eng Asp. 2021 Sep 5;624:126836.
9. Khan MF, Marwat MA, Shah SS, Karim MR, Aziz MA, Din ZU, Ali S, Adam KM. Novel MoS2-sputtered NiCoMg MOFs for high-performance hybrid supercapacitor applications. Sep Purif Technol. 2023 Apr 1;310:123101.
10. Feng Y, Wang Y, Ying Y. Structural design of metal–organic frameworks with tunable colorimetric responses for visual sensing applications. Coord Chem Rev. 2021 Nov 1;446:214102.
11. Geng P, Yu N, Macharia DK, Meng R, Qiu P, Tao C, Li M, Zhang H, Chen Z, Lian W. MOF-derived CuS@ Cu-MOF nanocomposites for synergistic photothermal-chemodynamic-chemo therapy. Chem Eng J. 2022 Aug 1;441:135964.
12. Gu C, Bai L, Pu L, Gai P, Li F. Highly sensitive and stable self-powered biosensing for exosomes based on dual metal-organic frameworks nanocarriers. Biosens Bioelectron.. 2021 Mar 15;176:112907.
13. Gu C, Liu J, Hu J, Wu D. Highly efficient separations of C2H2 from C2H2/CO and C2H2/H2 in metal–organic frameworks with ZnF2 chelation: A molecular simulation study. Fuel. 2020 Jul 1;271:117598.
14. Gupta NK, Kim S, Bae J, Kim KS. Fabrication of Cu (BDC) 0.5 (BDC-NH2) 0.5 metal-organic framework for superior H2S removal at room temperature. Chem Eng J. 2021 May 1;411:128536.
15. Hakimifar A, Morsali A. High-sensitivity detection of nitroaromatic compounds (NACs) by the pillared-layer metal-organic framework synthesized via ultrasonic method. Ultrason Sonochem. 2019 Apr 1;52:62-8.
16. Hao F, Yan XP. Nano-sized zeolite-like metal-organic frameworks induced hematological effects on red blood cell. J Hazard Mater. 2022 Feb 15;424:127353.
17. Hao F, Yan XP. Nano-sized zeolite-like metal-organic frameworks induced hematological effects on red blood cell. Sci Total Environ. 2022 Feb 15;424:127353.
18. Hao F, Yan ZY, Yan XP. Size-and shape-dependent cytotoxicity of nano-sized Zr-based porphyrinic metal-organic frameworks to macrophages. SciTtl Environ. 2022 Aug 10;833:155309.