Green Synthesis of Robust Metal-Organic Frameworks: A Sustainable Approach for Advanced Applications

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DOI: https://doi.org/10.51584/IJRIAS.2025.100900023

Received: 08 September 2025; Accepted: 14 September 2025; Published: 11 October 2025

ABSTRACT

Metal-organic frameworks (MOFs) have emerged as versatile materials with applications in gas separation, catalysis, and energy storage due to their high porosity and tunable structures. However, traditional synthesis methods often involve toxic solvents and high energy inputs, limiting scalability and environmental sustainability. This review explores green synthesis strategies for robust MOFs, focusing on water-based hydrothermal and ambient temperature approaches that enhance stability and performance. Key examples include aluminum-based MOFs for water adsorption and zirconium-based frameworks for gas purification, demonstrating high yields, stability in harsh conditions, and efficient applications in heat allocation and ethylene separation. These methods align with the principles of sustainable chemistry, paving the way for their industrial adoption.

Keywords: Metal-organic frameworks, Sustainability, Green synthesis, Robust MOFs, Hydrothermal synthesis

INTRODUCTION

Metal-organic frameworks are crystalline materials composed of metal ions or clusters that are coordinated to organic linkers, forming porous structures with vast surface areas. Robust MOFs, particularly those with tetravalent metals like zirconium or aluminum, exhibit enhanced chemical and thermal stability, making them suitable for real-world applications. Green synthesis emphasizes the use of eco-friendly solvents, such as water, and mild conditions to minimize environmental impact. This approach addresses challenges in scalability and toxicity associated with conventional methods using organic solvents or high temperatures. Recent advances in ambient and hydrothermal green syntheses have enabled the production of MOFs with tailored properties for energy-efficient processes.

Synthesis Methods

Hydrothermal Green Synthesis

Hydrothermal methods utilize water as the solvent under elevated temperatures and pressures, facilitating the assembly of metal nodes and organic linkers. For instance, the synthesis of CAU-10pydc, an aluminum-based MOF, involves mixing aluminum salts with pyridine dicarboxylate in water, followed by heating to form helical aluminum chains linked into a three-dimensional channel structure. This process achieves high scalability with minimal waste, avoiding toxic modulators.

Ambient Temperature Synthesis

Ambient synthesis occurs at room temperature, reducing energy consumption. Approaches include stepwise assembly or direct mixing of precursors. For robust tetravalent MOFs, such as those based on zirconium, water or minimal solvents are used to form stable frameworks. A notable example is the “bottle-around-ship” strategy for incorporating metal nanoparticles into MOFs, creating composites at ambient conditions.

Aqueous-Phase Scalable Synthesis

Aqueous synthesis at mild conditions yields robust MOFs like ZU-901, a zirconium-based framework, with

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume X Issue IX September 2025

99% yield. This method involves pore engineering to optimize adsorption properties, using water as the sole solvent for eco-friendly production. Other strategies incorporate waste materials, such as polyethylene terephthalate (PET) for linkers, further enhancing sustainability.

RESULTS AND DISCUSSION

Structural and Stability Properties

Green-synthesized robust MOFs demonstrate exceptional structural integrity, characterized by high crystallinity and porosity, as evidenced by powder X-ray diffraction (PXRD) and gas adsorption isotherms. These properties are critical for their performance in demanding applications. For instance, CAU-10pydc, an aluminum-based MOF synthesized via hydrothermal methods, exhibits a unique S-shaped water adsorption isotherm with a working capacity of 0.31 mL H_2O mL^{-1}. This behavior is attributed to strong hydrogen bonding interactions between water molecules and hydroxyl groups within the framework's helical aluminum chains, enhancing its suitability for water adsorption applications. The material maintains structural stability under repeated adsorption-desorption cycles, with no significant loss of crystallinity after exposure to humid conditions.

ZU-901, a zirconium-based MOF produced through aqueous-phase synthesis, showcases ultra-microporous channels and remarkable stability across a wide range of chemical environments, including acidic (pH 2), basic (pH 12), and aqueous conditions. Its high yield (99%) and robust framework are achieved through pore engineering, optimizing the pore size distribution for selective gas adsorption. The stability of ZU-901 is further confirmed by its consistent performance over multiple regeneration cycles, making it a promising candidate for industrial separations.

Composites such as metal nanoparticle-incorporated MOFs (MNPs@MOFs), synthesized via the ambient "bottle-around-ship" method, combine the chemical stability of robust MOFs with the catalytic properties of metal nanoparticles. These composites exhibit reproducible core-shell structures, with PXRD confirming the retention of the MOF's crystallinity post-nanoparticle integration. Their enhanced stability under reductive conditions positions them as effective catalysts for reactions such as CO_2 reduction, where the MOF protects the nanoparticles from aggregation while facilitating substrate access.

Applications

Water Adsorption and Heat Allocation

CAU-10pydc demonstrates exceptional performance in water adsorption-driven heat allocation, achieving coefficients of performance (COP) of 0.79 for cooling and 1.72 for heating, with a heat storage capacity of 273.5 kWh m^{-3}. These metrics highlight its potential for solar-driven cooling and heating systems, particularly in low-temperature environments. The S-shaped isotherm enables efficient water uptake and release at moderate relative pressures, reducing energy requirements for regeneration compared to traditional adsorbents like silica gels. This makes CAU-10pydc a sustainable alternative for energy-efficient thermal management systems, with scalability enhanced by its water-based synthesis.

Gas Separation and Purification

ZU-901 excels in gas separation, particularly in ethylene/ethane separation via pressure swing adsorption (PSA). Its ultra-microporous structure selectively adsorbs ethylene, producing polymer-grade ethylene (99.9% purity) with an energy consumption approximately one-tenth that of conventional cryogenic distillation methods. The S-shaped adsorption isotherm allows mild regeneration conditions, further reducing operational costs. This efficiency, combined with the MOF's stability in harsh chemical environments, positions ZU-901 as a transformative material for industrial gas purification processes.

Catalysis and Beyond

MNPs@MOF composites, synthesized under ambient conditions, exhibit synergistic effects between the

MOF's porous structure and the catalytic activity of embedded nanoparticles. For example, these composites demonstrate enhanced efficiency in peptide hydrolysis and CO_2 reduction, with turnover frequencies significantly higher than those of standalone nanoparticles. The MOF matrix stabilizes the nanoparticles, preventing leaching and enabling recyclability. Beyond catalysis, green-synthesized MOFs show promise in environmental applications, such as wastewater remediation, where their high surface area and tunable pore chemistry enable efficient removal of organic pollutants. Additionally, their integration into biosensors leverages their structural precision for selective detection of biomolecules, opening avenues for medical diagnostics.

Sr. No	MOF Example	Synthesis Method	Key Properties	Applications
1	CAU-10pydc	Hydrothermal (water-based)	S-shaped isotherm, high stability, 0.31 mL/g water uptake	Heat allocation, cooling/heating
2	ZU-901	Aqueous ambient	Ultra-microporous, acid/base stable, 99% yield	Ethylene purification, PSA
3	MNPs@MOFs	Ambient "bottle-around-ship"	Catalytic synergy, reproducible core-shell	CO_2 reduction, peptide hydrolysis

Analysis and Implications

The success of green synthesis methods lies in their ability to produce MOFs with tailored structural and functional properties while minimizing environmental impact. The high yields and stability of frameworks like ZU-901 underscore the scalability of aqueous-phase synthesis, addressing a key barrier to industrial adoption. The use of water as a solvent eliminates the need for toxic organic solvents, aligning with green chemistry principles. Moreover, the versatility of these MOFs across applications—from energy storage to catalysis—demonstrates their potential to address global challenges such as energy efficiency and environmental remediation. However, challenges remain, including optimizing synthesis conditions for even lower energy inputs and exploring the integration of renewable feedstocks for linker production.

CONCLUSION

Green synthesis of robust MOFs represents a paradigm shift toward sustainable materials science, enabling scalable production with minimal environmental footprint. By integrating water-based and ambient methods, these frameworks achieve superior stability and performance in energy, environmental, and catalytic applications. Future research should focus on further optimization and commercialization to address global challenges in energy efficiency and pollution control.

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