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Journal of Composites and Compounds

The evolution and future potential of nanocatalysis: Metal-organic frameworks-derived

Mostafa Mabrouk *, Hanan H. Beherei

Refractories, Ceramics and Building Materials Department, National Research Centre, P.O. Box: 12622, Giza, Egypt

ABSTRACT

Metal-organic frameworks (MOFs) and their derivatives represent a groundbreaking category of materials characterized by their small pore sizes, lightweight nature, and adjustable physical and chemical properties. Renowned for their extensive surface areas and capacity for substantial adsorption, these materials hold significant promise in nanocatalysis applications. This review presents an in-depth analysis of various synthesis techniques for MOFs and explores their current roles as nanocatalysts, catalyst supports, and membranes in hydrogen production and environmental remediation. Additionally, the review discusses the potential benefits and challenges associated with the use of MOFs and similar materials as nanoscale catalysts. The objective is to encourage further development in this field and to provide critical insights for researchers focused on hydrogen generation and environmental cleanup.

ARTICLE INFORMATION

Article History:
Received 01 April 2025
Received in revised form 05 June 2025
Accepted 10 June 2025

Keywords:
Metal-organic frameworks (MOFs)
Synthesis methods
Hydrogen production
Environmental remediation
Catalyst supports
Nanostructured materials
Photocatalysis

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1. Introduction

Nanocatalysis is an emerging and significant field within chemistry that enhances the efficiency, accuracy, and eco-friendliness of chemical reactions [1]. By modifying nanocatalysts' size, shape, and surface properties, researchers can achieve distinctive advantages over conventional bulk catalysts. These modifications enable faster reaction rates and improved selectivity for specific chemical transformations [2]. Significant advancements in nanotechnology have created unique opportunities for research on catalysts. Well-defined metal nanocatalysts offer researchers the opportunity to investigate several fundamental aspects of catalysis. These include understanding active site mechanisms, exploring metal-support interactions, examining how surface atomic arrangements influence reaction pathways, and determining the relationships

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* Corresponding author: Mostafa Mabrouk, Email: mostafamabrouk.nrc@gmail.com

https://doi.org/10.61882/jcc.7.2.4

between catalyst structure, activity, and selectivity [3, 4]. Their surface area is large relative to their size, they respond swiftly, and they can alter their appearance and functionality in response to light and electricity. These attributes set them apart from bulk materials [5, 6]. Nanoparticles possess several distinctive properties that differentiate them from bulk materials. They exhibit exceptionally high surface-area-to-volume ratios, demonstrate rapid response times, and can modify their properties when exposed to light or electrical stimuli. These characteristics make nanoparticles particularly valuable in semiconductor applications, where they enhance thermal management, improve electrical conductivity, and integrate seamlessly with existing manufacturing processes. Their incorporation into semiconductor production not only improves current hardware performance but also enables entirely new technological applications [7-10]. The exceptionally high surface area of nanoparticles makes them ideal candidates for catalytic applications. Catalysts are essential components that accelerate chemical reactions across numerous industrial processes. They form the backbone of the global multi-billion-dollar chemical industry, enable sustainable chemical manufacturing practices, and play a critical role in environmental protection [11, 12]. Nanocatalysts are gaining more attention for use in renewable energy technologies including fuel cells, water electrolyzers, metal-air batteries, and CO_2 reduction methods [13, 14]. Recently, MOFs and their derivatives have attracted considerable interest due to their abundance of active sites and extensive surface area, which enhance their effectiveness in nanocatalysis [15]. MOFs consist of crystalline structures formed by metal components bonded together with unique organic molecules. These constructions exhibit a clear organization and cover a significant expanse [16].

MOFs, known as porous coordination polymers (PCPs), consist of small components that can be configured in linear arrangements or three-dimensional forms. These substances contain tiny holes and consist of metal atoms or clusters of atoms combined with specific organic molecules capable of creating various types of bonds [17-19]. The design of these structures offers flexibility, enabling adjustments by changing the type of metal and connectors, or by making additional modifications after manufacturing [20]. MOFs connect micro-sized areas to slightly larger meso-sized regions and possess remarkably high surface areas, reaching up to 10,000 square meters per gram based on Brunauer−Emmett−Teller (BET) analysis. This level is significantly greater than zeolites and activated carbons [21, 22]. In the 1990s, researchers like Robson [23], Moore [24], Yaghi [25], and Kitagawa [26] focused on creating and utilizing MOFs. More than 20,000 different types of MOFs have been documented. BASF produces several of these MOFs (MIL-53, HKUST-1, Fe-BTC, and ZIF-8, which are frequently utilized) in significant quantities, which can be purchased from suppliers such as MOF Technologies, Strem Chemical, and Sigma-Aldrich [27, 28]. Their capabilities comprise gas storage, energy conversion, chemical sensing, drug delivery, proton conduction, and aiding in chemical reactions. These materials find applications in diverse fields such as chemical and textile production, transportation, electric vehicles, food packaging, and respiratory systems [29]. This review aims to investigate the progress made in nanocatalysis, particularly focusing on materials sourced from MOFs, while also highlighting possible directions for future research and innovation. This paper offers an in-depth analysis of recent research concerning MOFs, which are considered promising candidates for nanocatalysts. It examines various methods for generating these materials and their potential roles as nanocatalysts in diverse applications. This review emphasizes the advantages and disadvantages of utilizing MOFs and similar materials as catalysts on a nanoscale. The objective is to facilitate their development and provide essential insights for researchers dedicated to hydrogen generation and environmental remediation.

2. Fundamental concepts in nanocatalysis

2.1. Definition and mechanisms of nanocatalysis

The idea of nanocatalysis surfaced in the early years of this century. At first, it referred to tiny metal particles loosely arranged and suspended in a liquid. These nanoparticles, synthesized using organometallic techniques, exhibited uniform and consistent sizes. Over time, the definition broadened to include various approaches for developing new catalysts. Presently, it provides model systems with nanoparticles placed on planar surfaces [30, 31]. Most nanocatalysts present unique advantages. These substances are chemically stable, economically favorable, possess low toxicity, are readily available, and demonstrate remarkable performance with light at a microscopic scale (ranging from 1 to 100 nm). Nanocatalysts provide various benefits, including durability, affordability, and a decreased environmental impact [32]. In the last ten years, nanocatalysis has become a key area in chemistry, leveraging meticulously designed tiny metal particles to speed up chemical reactions. As a branch of green chemistry, nanocatalysis provides environmentally friendly alternatives for carrying out significant chemical processes without causing ecological harm. Its importance is growing rapidly. The form of the nanocatalyst plays a vital role in the early phases of the electron transfer reaction. The ability to enhance reaction rates is linked to the number of surface atoms located at the corners and edges of nanoparticles (NPs). Throughout the reaction, the corners and edges of the NPs can undergo distortion, causing the shape of the altered nanoparticles to evolve more rapidly. It is clear that a modification in shape affects the energy required for activation [33]. Nanocatalysts exhibit distinctive properties, including the effects of their small size on their electronic features and their increased reactivity on the surface. These characteristics play a crucial role in determining their performance in chemical reactions. This section explores how these factors improve the efficiency and selectivity of catalysts while enabling particular reactions that are difficult to accomplish with larger materials [34]. By altering nanocatalysts' chemical and physical characteristics—such as their size, shape, material composition, and structure—we can regulate their effectiveness. As a result, the use of nanocatalysts in chemical processes has skyrocketed in areas like making chemicals, collecting and storing energy, and protecting the environment [35, 36].

As illustrated in Fig. 1, the fundamental procedure of nanocatalysis typically follows the traditional stages of heterogeneous catalysis: initially, reactants adsorb onto the surface of the catalyst; then, the reactants are activated and converted at their active sites; and ultimately, the products desorb. However, at the nanoscale, these steps are affected by several distinct factors [6].

Historically, scientists have frequently employed polyhedrons as representations for nanoparticles (NPs). In these studies, it is often assumed that the reactive parts of nanoparticles are mainly located at the corners and edges, where there are fewer bonds. Using quantum dots improves the ability of materials to conduct electricity, convert energy, and provide more sites for chemical reactions. This dramatically boosts the effectiveness of the materials for electrocatalysis [37-39]. In systems involving photocatalysis and electrocatalysis, further mechanisms such as charge transfer, plasmonic enhancement, and local field effects become relevant, broadening the capability and adaptability of nanocatalysts [40].

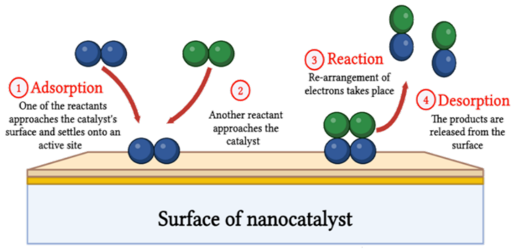

Fig. 1. Four-step mechanism of heterogeneous catalysis on a nanocatalyst surface: (1) reactant adsorption onto active sites, (2) surface migration and reactant orientation, (3) catalytic reaction with electron rearrangement and bond formation, and (4) product desorption with catalyst regeneration. The high surface-area-to-volume ratio of nanocatalysts provides numerous active sites for enhanced catalytic efficiency, particularly relevant for MOF-derived nanocatalytic systems.

2.2. Role of MOFs in catalysis

Nanostructures obtained from MOFs are highly valued because of their numerous tiny pores, large surface area, and unique properties. Generally, these structures necessitate careful modification or breakdown of MOFs. This procedure results in metal oxides, metal carbides, metal sulfides, metal phosphides, and carbon-based composites [41]. These attributes make them excellent candidates for hosting, arranging, and modifying catalytic sites at the molecular scale. In contrast to traditional porous materials, MOFs offer a flexible design. This flexibility enables us to systematically arrange organic and inorganic components to fulfill the specific needs for catalytic purposes [42, 43]. In catalysis, MOFs can serve multiple roles, including acting as catalysts to speed up reactions, providing support for other catalytic agents, or being engineered to create compact, structured catalysts [44]. MOFs can host active metal components within their frameworks or incorporate reactive groups into their organic linkages when used directly. These materials have proven effective in various reactions, such as oxidation, hydrogenation, and carbon coupling (Fig. 2) [45]. Nonetheless, their ability to improve reactions is frequently limited by their inefficiency under challenging situations. To address this limitation, composite materials have been created by integrating MOFs with other materials to enhance their durability and functionality [46].

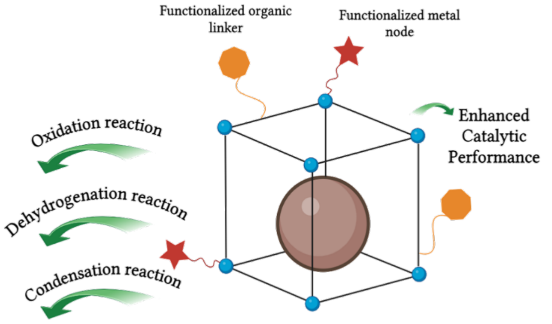

Fig. 2. Functionalization strategies and catalytic applications of hierarchically porous MOFs in nanocatalysis. The framework structure features metal nodes (blue) and organic linkers forming interconnected pores, with functionalization achieved through modified organic linkers (orange) and metal nodes (red stars). This design enables diverse catalytic applications including oxidation, dehydrogenation, and condensation reactions, leading to enhanced catalytic performance through synergistic effects of high surface area, controlled porosity, and strategically positioned functional groups.

MOFs speed up chemical reactions by keeping vital components apart, thereby reducing the chance of them clustering. Their shape versatility facilitates molecular movement, enabling accurate functionality. Changing elements like ligands or adding metal ions post-synthesis can improve their effectiveness in intricate reactions [47, 48]. MOFs are being developed into more compact and stable catalysts that improve efficiency while maintaining their porous structures and evenly distributed metals. This research suggests the possibilities for eco-friendly chemical processes, renewable energy projects, and approaches for environmental cleanup [47, 49, 50].

3. Synthesis of MOF-derived nanocatalysts

In recent decades, the creation of MOFs has garnered significant interest. Their varied and fascinating structures render them useful in multiple areas related to porous materials. This includes methods that employ microwaves, ultrasound, electrochemical, mechanochemical, hydrothermal, and solvothermal methods, among other techniques (Fig. 3). Furthermore, particular solvents and agents are used to aid in developing the intended types of MOFs.

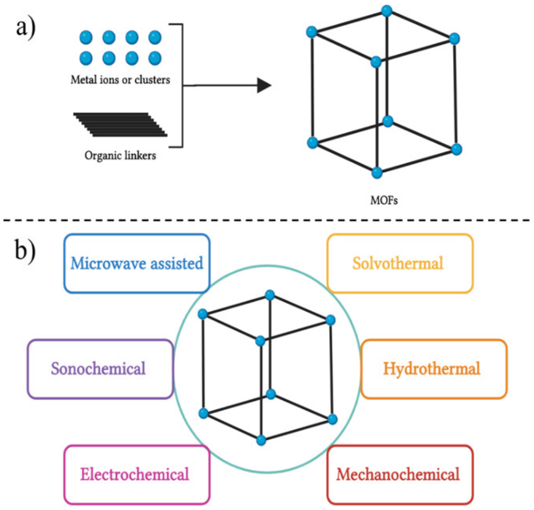

Fig. 3. a) Illustration of MOFs' building blocks and structure. b) Methods commonly used for as-prepared MOF synthesis.

3.1. Microwave assisted method

Microwave methods have gained popularity for the swift synthesis of MOFs using high-temperature water [51]. The microwave method is utilized to create small-sized metal and oxide particles. This approach offers an effective way to produce heat by having electromagnetic waves interact with the charged particles in dynamic solvents. Microwave heating accelerates reactions, enhances control over various phases, and enables the precise shaping of crystals [52].

To create metal nanocrystals, the solution was heated in a microwave for 24 hours or more (Fig. 4). This technique places a combination of the appropriate solvents inside a Teflon container. The container is securely sealed and placed in the microwave for the required temperature and duration. The role of the microwave is to convert electromagnetic energy into heat. When exposed to an electric field, the molecules in the liquid mixture speed up, leading to a rise in temperature [53].

In a composite material, polar molecules usually orient themselves in response to an electric and magnetic field, leading to a constant repositioning. Within a solid, electromagnetic waves induce an electric current, producing heat due to the material's resistance to electrical flow. The process of generating heat varies somewhat when it occurs within a solution. In the presence of an electromagnetic field and variable field conditions, polar substances like water and ethanol often orient themselves accordingly. As a result, the molecules permanently shift their positions. Utilizing the correct frequency causes the molecules in motion to strike each other, leading to significant energy production and a temperature rise. In microwave-assisted heating, energy consumption is reduced because radiation interacts directly with the solution or heated materials.

Quick crystal formation, clear choice of different crystal types, careful control over the shape and size of crystals, and purity are the primary goals of the microwave-assisted MOF synthesis method [54].

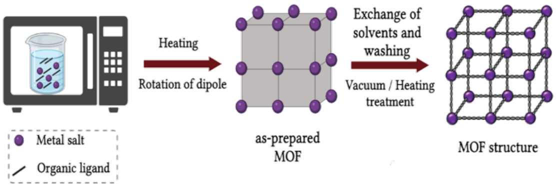

Fig. 4. Microwave-Assisted synthesis of MOF structures.

3.2. Sonochemical method

Sonochemistry studies the changes molecules experience when exposed to high-frequency sound waves, usually between 20 kHz and 10 MHz. The interaction between ultrasound waves and a reaction solution results in bubble formation. These bubbles create small regions that are extremely hot and under high pressure for a short duration.

This promotes rapid chemical reactions and facilitates the quick formation of tiny crystals [55-57]. High-quality crystals of MOF-5 and MOF-177, measuring 5–25 µm and 5–20 µm, respectively, were synthesized using the sonochemical approach with 1-methyl-2-pyrrolidone as a solvent, resulting in significantly shorter reaction times [58, 59].

3.3. Electrochemical method

Different types of MOFs are carefully produced using the electrochemical technique. HKUST-1 was initially synthesized by BASF in 2005 using an electrochemical method [60]. Their main goal was to separate specific negatively charged ions, like chloride, perchlorate, or nitrate, during the synthesis process. This was intended to avoid the formation of harmful ions (like nitrate and chloride), making the electrochemical approach a more environmentally friendly means of producing MOFs without complex procedures. The method eschews the use of metal salts, which helps eliminate the generation of hazardous substances, including nitrate and other undesirable by-products. This renders the process safe for the environment. A key aspect of this method for producing MOFs involves introducing metal ions through electrical means rather than by dissolving a metal salt in a liquid or by reacting metal with acid to generate the ions [54]. The electrochemical technique for fabricating MOFs utilizes electrons to release metal ions into a solution containing dissolved organic compounds and an electrolyte; instead of relying on metal salts, it acquires metal through anodic dissolution. The electrode is immersed in a solution containing PBU, typically along with a material that facilitates electrical conduction. When an appropriate voltage is applied, the metal dissolves, and the required metal particles for MOF formation are found on the exterior surface of the electrode. The metal ions rapidly interact with the organic linker in the solution, forming the MOF adjacent to the electrode surface (Fig. 5). In the presence of a protic solvent, metal deposits on the cathode, while hydrogen gas is produced. The electrochemical method proves to be an effective way to consistently achieve a greater quantity of solid material compared to the traditional batch process [61].

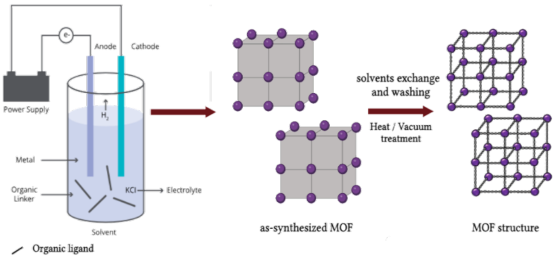

Fig. 5. Electrochemical synthesis of MOF structures.

3.4. Mechanochemical method

The approach relies on physical forces rather than a liquid at room temperature to form coordination bonds, achieved by either manually grinding the materials or, more frequently, utilizing automatic ball mills. Occasionally, a small amount of liquid may be incorporated into the solid mixture, which aids in the formation of one-dimensional, two-dimensional, and three-dimensional coordination polymers [62].

The mechanochemical technique facilitates the movement of materials, reduces particle size, increases temperatures, and can cause some ingredients to melt, accelerating the reaction rate. This safe and environmentally friendly method allows for rapid production of highly pure and effective materials. Employing mechanical chemistry to synthesize MOFs is noteworthy as it provides an alternative method to traditional high-temperature and high-pressure techniques.

However, a significant challenge with this approach is that it results in solid materials that are not amenable to structural analysis using single-crystal X-ray methodologies [63].

3.5. Hydrothermal and solvothermal method

This section examines the creation of MOFs through hydrothermal synthesis. The creation and breaking of bonds necessitate energy, which also occurs during the assembly of MOFs, due to the interactions between organic linkers and metal ions. MOFs can be produced using any apparatus that provides a steady heat source [64].

Heat can originate from various sources, such as a hydrothermal oven, microwave, electromagnetic waves, sound waves, and electric power. Although the methods for producing MOFs in different forms are generally straightforward, they remain relatively underexplored.

Hydrothermal synthesis occurs in water at temperatures exceeding its boiling point, while solvothermal processes involve water and other compatible liquids. Both types of synthesis typically take place in sealed containers like autoclaves or pressure vessels.

They often utilize polar solvents, which are heated above their boiling points and can include dimethyl formamide, acetone, dimethyl sulfoxide, acetonitrile, water, and alcohol [65-67].

Furthermore, since the solubility of the starting materials varies, a mixture of these solvents is often used. In hydrothermal synthesis, the behavior of the solvent is also influenced, which can accelerate crystal growth. The primary advantage of hydrothermal synthesis over solvothermal synthesis is that it allows for the more environmentally friendly and cost-effective production of MOFs [68, 69].

For example, Gao and his team discovered that combining a specific chemical known as asymmetric bis(bidentate)-2-

pyrimidinecarboxylate with CdII produced a MOF featuring a RHO structure. Conversely, applying 5-(20-pyrimidyl)tetra-zolate with CdII led to forming square grid-like architectures [70]. Xu and his colleagues synthesized two varieties of microporous yttrium compounds that exhibit distinct arrangements of connecting elements surrounding the Y^{3+} centers. Both varieties possess comparable one-dimensional channels and were created using a yttrium salt and trimethyl 1,3,5-benzenetricarboxylate through a reaction in a DMF and water mixture, as well as DEF and water [71]. Compared to the hydrothermal method, the solvothermal approach allows for enhanced control over the shape, size, and quality of crystals. In this scenario, the initial substances and chemicals are subjected to heating along with a solvent that has a high boiling point. This process takes place in specialized metal containers designed to endure high pressure and temperature, with specific dimensions [72]. During this procedure, metal ions and organic compounds are combined with organic liquids containing formamide, which can be either protic or aprotic (aprotic solvents refer to liquids that lack hydrogen atoms bonded to oxygen). Combining various solvents can address issues arising from the distinct solubility behaviors of ingredients [73]. Glass containers are suitable for lower temperatures, while a specialized stainless-steel vessel lined with Teflon is necessary for high temperatures (above 400 K) during the reaction (Fig. 6).

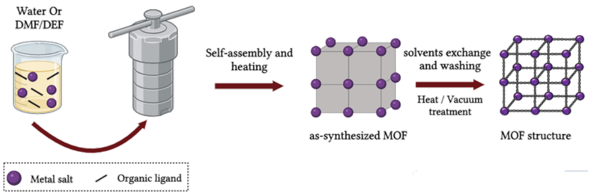

Fig. 6. Conventional Solvothermal Synthesis of MOF Structures.

Regardless of whether you choose an aprotic solvent without hydrogen or a protic one that contains it, it’s essential to heat the sealed vessel beyond the solvent's boiling point to elevate the internal pressure. Solvothermal and nonsolvothermal reactions are mainly influenced by temperature. Solvothermal reactions happen in a closed container at high temperatures, above the boiling point of the liquid used, and these reactions occur under pressure created by the heat.

On the other hand, nonsolvothermal reactions occur at temperatures equal to or lower than the boiling point of the liquid, and they happen at standard pressure. Under these extreme conditions, the solvent is heated above its boiling point, facilitating salt dissolution and streamlining the process. Additionally, a lengthy procedure is required to form crystals from a solution, to develop crystals with a significant internal surface area [74, 75]. Table 1 displays examples of MOFs synthesized using various techniques, including microwave, sonochemical, electrochemical, mechanochemical, solvothermal, and hydrothermal methods.

4. Applications of MOF-derived nanocatalysts

4.1. Hydrogen production

4.1.1. MOF-derived metal nanoparticles

Nickel-based catalysts were utilized to generate hydrogen via an electrochemical approach [87]. However, their limited activity restricted their application in catalysis. Various methods have been explored to improve the efficiency of hydrogen production (HER). For instance, Wang and his team synthesized nickel nanoparticles on a carbon scaffold using a thermal process derived from a nickel-based metal-organic framework for hydrogen extraction. Ammonia (NH_3) gas was employed to modify the nickel metal surface.

The results demonstrated that nickel nanoparticles produced at a pressure of 0.4 bar (Ni-0.4NH_3) exhibited a slight additional voltage of 88 mV when evaluated at a 20 mA/cm2 current. These impressive outcomes were attributed to the synergistic effects of nitridation and the carbon layers [88].

Cao and his group conducted another investigation into the Ni metal-based MOF nanocatalyst. The researchers discovered that Ni@NC-rGO produced a significant amount of hydrogen and showcased remarkable performance over a prolonged duration. This was attributed to the synergy between the graphene layers and carbon, including nitrogen [89]. Kuang et al, [90] conducted another study to generate metal nanoparticles from MOFs. They synthesized bimetallic copper and cobalt nanoparticles supported on a carbon substrate (CuCo@NC) by heating ZIF-67 and copper hydroxide.

The findings indicate that CuCo@NC exhibited excellent performance as a hydrogen evolution reaction (HER) catalyst, achieving a 145 mV overpotential at a 10 mA/cm^2 current density. This enhanced performance can be attributed to the synergistic effects of the small metal particles and nitrogen incorporation. The group led by Stylianou created MIL-125-NH_2 as a nanocatalyst, alongside Ni_2P nanoparticles that enhance the process. They mixed these components in a solution of CH_3CN, NEt_3 (which provides extra electrons), and water, and subsequently exposed it to a 300 W Xe lamp with visible light.

The Ni_2P/MIL-125-NH_2 catalyst exhibited high efficiency due to Ni_2P's intense activity, which facilitates effective electron transfer from the MOF [91]. A hydrogen production rate of 894 $\mu molh^{-1}g^{-1}$ was achieved, with efficiencies of 27% at 400 nm and 6.6% at 450 nm. The photocatalyst was recycled through 7 cycles, each lasting 12 hours.

Table 1

Overview of various synthetic routes (microwave, electrochemical, solvothermal, hydrothermal, mechanochemical, and sonochemical) for the preparation of MOFs.

Synthetic routes	Metal salt	Organic ligand	MOFs	Preparation conditions	Ref.
Electrochemical method	$Al(NO_3)_3·9H_2O$	H_3BTC	Al-MIL-100	electrolyte: KCl, 50 mA, 333.15 K	[76]
	Cu electrode	H_3BTC	MOF-199	electrolyte: TBATFB, 12 V for 1.5 h	[77]
Hydrothermal method	$ZrCl_4$	2-amino terephthalic acid	NH_2-UiO-66	24 h at 120 °C	[78]
	$Cr(NO_3)_3·9H_2O$	H_2BDC	Cr-MIL-101	8 h at 220 °C	[79]
Mechanochemical method	$Mg(NO_3)_2·6H_2O$	H_4dobdc	MOF-74	5 min	[80]
Microwave-assisted method	$HfCl_4$ and $ZrCl_4$	H_2BDC	Hf-UiO-66 and Zr-UiO-66	90 W, 3 min	[81]
	$FeCl_3·6H_2O$	H_2BDC	Fe-MIL-53	80 W, 5 min at 50 °C	[82]
	$FeCl_3·6H_2O$	H_3BTC	MIL-100(Fe)	-	[83]
Solvothermal method	$Zn(NO_3)_2·6H_2O$	H2BDC	MOF-5	4 h at 120 °C	[84]
	Eu $(NO_3)_3$ ·$6H_2O$	H_3TATAB	Eu–MOF	72 h at 120 °C	[85]
Sonochemical method	$ZrOCl_2·8H_2O$	Fumaric acid	MOF Zr–fum	30 min	[86]

4.1.2. MOFs-derived metal/metal oxide nanoparticles

The importance of producing hydrogen in alkaline solutions has been shown to have advantages for industrial uses. However, finding efficient non-noble catalysts that can match the performance of platinum catalysts in alkaline conditions is difficult.

Developing effective electrode materials for hydrogen generation from water-alkali remains a complicated issue [92-94]. Research has shown that creating a metal oxide layer on a metal surface can improve its effectiveness in facilitating the HER in a basic solution [95]. The presence of nickel (Ni) at the interface of nickel and nickel oxide (NiO) has been recognized as an essential factor in the efficacy of the NiOx@baoo-like carbon nanotube catalyst [96].

A separate research study by Bai and colleagues concentrated on producing metal or metal oxide utilizing an MOF precursor. By converting ZIF-67 into cobalt metal and subjecting it to heated oxygen, they created a structure with cobalt at its center, surrounded by cobalt oxide, all embedded within a carbon matrix. This catalyst outperformed other catalyst types (Co and Co_3O_4) for hydrogen production and exhibited a low energy requirement of 0.221 V in a 1.0 M potassium hydroxide solution.

The researchers showed that Co_3O_4 layers can effectively separate charges, and the Co centers are vital for promoting electron transfer to the carbon framework. Neppolian and his team developed a NH_2-MIL-125(Ti) material incorporating Cu_2O by encapsulating Cu_2O nanoparticles after the primary material was synthesized (Fig. 7) [97].

In Cu_2O/NH_2-MIL-125(Ti), the Cu_2O nanoparticles present within the material facilitated electron movement, while the Ti^{3+} sites aided in charge separation, significantly lowering the likelihood of electron-hole recombination. A H_2 production rate of 11055.5 $\mu mol h^{-1} g^{-1}$ was attained under solar illumination, 28 times greater than that of the unmodified MOF, and the catalytic performance was maintained over five recycling cycles.

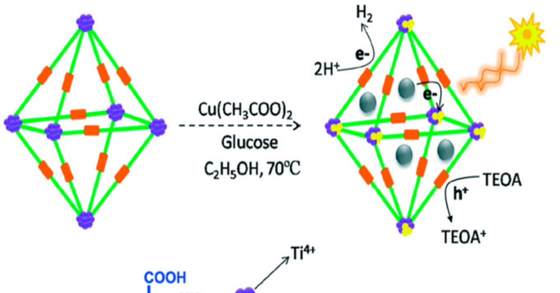

Fig.7. Fabrication of Cu_2O cocatalyst in the NH_2-MIL-125(Ti) by post-synthetic encapsulation. Reprinted from [97] with permission of Karthik et al. (2018).

Several recent investigations have integrated the semiconductor TiO_2 with a MOF to create an effective photocatalyst [98]. This configuration efficiently utilizes visible light and prevents the recombination of electron-hole pairs [99-101]. The Cheng team synthesized hollow titanium dioxide nanoparticles coated with ZIF-8 using sonochemistry. The concluding analysis revealed that ZIF-8 was distributed across the TiO_2 HNP surface. The measured quantum efficiency reached an impressive 50.89%, with the photocatalyst producing hydrogen at a rate 3.5 times greater than conventional TiO_2 nanoparticles, thanks to its unique double-layer structure functioning in unison [99].

4.2. Environmental remediation

The use of MOFs in wastewater treatment poses various technical challenges, but it also creates promising opportunities and ideas for future research [102]. Due to their large surface area and adjustable pore sizes, MOFs can be designed using various chemical materials. This approach offers efficient alternatives for adsorbing and removing different pollutants from wastewater [103-106]. In a 2016 proposal by Shooto and colleagues, it was suggested that electrospinning could be a viable method for generating nanofibers from MOFs to address these issues. In their attempt to enhance the removal of heavy metals and modify the strength of the materials, they created composite nanofibers using polyvinyl alcohol (PVA) combined with Sr-TBC, La-TBC, and Sb-TBC; however, the outcomes did not meet their expectations [107]. Scientists have recently discovered a method to bond ZIF-8 or ZIF-67 to bacterial cellulose (BC) aerogels, facilitating their easy retrieval from water (Fig. 8a) [108, 109]. The newly created large macro-MOFs preserved the structural characteristics of ZIF-8, ZIF-67, and BC, which are characterized by notable porosity, versatility, and an expansive surface area. The BC@ZIF-8 composite aerogel exhibited exceptional effectiveness in capturing lead (Pb(II)) at a rate of 390 mg/g and cadmium (Cd(II)) at 220 mg/g. At the same time, the ZIF-67/BC/CH aerogels showed efficacy in eliminating copper ions (Cu(II)) and chromium ions (Cr(VI)), achieving capacities of 200.6 mg/g and 152.1 mg/g, respectively. The MOF was evenly distributed throughout the composite aerogel and remained intact throughout the pollutant removal process. Furthermore, the composite aerogel can swiftly revert to its original shape after being compressed and dried (Fig. 8b).

One practical approach to improve MOFs' adsorption properties is to alter their surface features. This action, known as functionalization, involves adding specific groups that attract and retain particular pollutants. For example, Valverde and his team explored the alteration of MOF nanoparticles by incorporating cysteine, which significantly boosted their capacity to adsorb mercury ions (Hg^{2+}) from water. Their findings revealed that the adsorption capacity increased from 8 mg/g to 30 mg/g. This demonstrates that modifying the surface can enhance the performance of MOFs in real water scenarios [110].

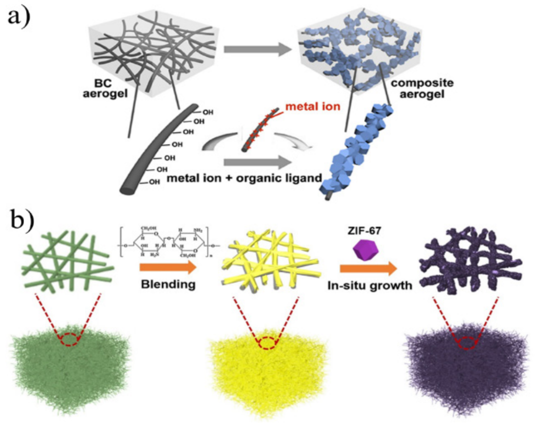

Fig. 8. a) The fabrication process of BC@MOFs composite aerogels, b) Schematic fabrication process of ZIF-67/BC/CH aerogels. Reprinted from [108] and [109] with permission of Ma et al. (2019) and Li et al. (2020).

One additional effective method involves creating MOF composites that merge the advantageous qualities of MOFs with other materials to improve their capacity to absorb various substances. Chowdhury et al. [111] found that a blend of aluminum-based compounds and graphene oxide (GO) effectively attracts and captures lead ions (Pb^{2+}) from water. The inclusion of GO, known for its large surface area and numerous active sites, significantly boosted the absorption efficiency compared to using only the MOF.

Recently, Pen and colleagues developed hybrid membranes utilizing MIL-based MOFs constructed on electrospun PAN nanofibers (NH_2-MIL-53Al/PAN). They could hold up to approximately 59 mg/g of Co (II). These achievements could enhance the performance of the MOF membrane in applications that separate substances, such as nanofiltration and reverse osmosis [112]. Jian and Wang [113] described a case of MOF mixtures that can rapidly oxidize and adsorb As(III) simultaneously. They incorporated ZIF-8 nanocrystals into β-MnO_2 wire structures to form a one-dimensional composite known as β-MnO_2@ZIF-8. The capacity β-MnO_2@ZIF-8 to adsorb As(III) was 1.6 times greater than that of pure ZIF-8 (reaching 140 mg/g). This enhancement is attributed to the high surface area of ZIF-8 (883 m^2/g) and the potent oxidizing capability of β-MnO_2 (Fig. 9). After 30 minutes, the composite could be effortlessly removed from the water, while the ZIF-8 remained suspended.

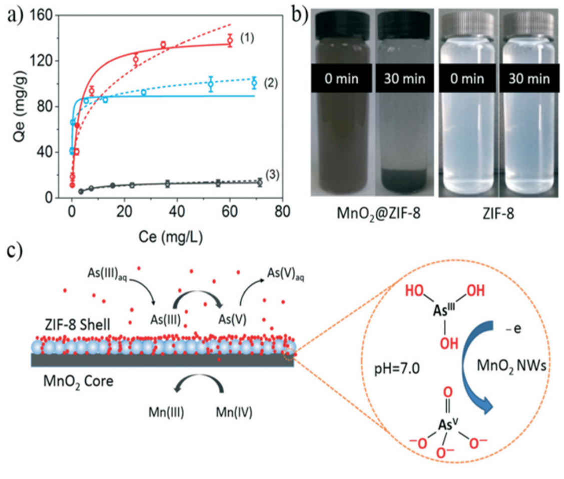

Fig. 9. (a) The fitted adsorption isotherms of As(III) on (1) MnO_2@ZIF-8 nanowires, (2) ZIF-8, and (3) β-MnO_2 nanowires are shown, with the solid line depicting the Langmuir model and the dashed line representing the Freundlich model. (b) Images of two vials containing MnO_2@ZIF-8 nanowires and ZIF-8 nanoparticles after allowing them to settle for 0.5 hours in water are presented. (c) A schematic representation of the As(III) removal process using MnO_2@ZIF-8 nanowires is illustrated, where the blue section indicates ZIF-8 particles and the red section signifies As(III) ions. (Reprinted from [113] with permission of Jian et al. (2016).)

5. Challenges in MOF-derived nanocatalysis

MOF-derived nanocatalysis faces challenges in achieving stability and longevity under extreme reaction conditions, such as high temperatures, moisture, acidic or basic environments, or oxidative conditions. The pyrolysis process can lead to structural wear, metal leaching, or aggregation of active sites, affecting catalytic efficiency. MOF-derived nanocatalysts are increasingly being explored for renewable energy applications, such as fuel cells, water electrolyzers, metal-air batteries, and CO_2 emission reduction technologies. Their large surface area, adjustable active sites, and structural flexibility make them attractive for reactions like OER, HER, and CO_2 [114-116].

The effectiveness of MOFs as catalysts heavily depends on controlling their metal nanoparticles' dimensions, form, and organization. These characteristics influence their surface energy, interactions with other atoms, and electronic configuration [117, 118]. Failure to regulate the generation of new particles in MOF thermal decomposition can produce a range of particle sizes and lead to aggregation, ultimately impacting their catalytic performance. Achieving uniformity remains challenging despite using stabilizing agents, modifying heating rates, and providing templates as part of the process [119].

Low electrical conductivity of MOF-derived catalysts, particularly in electrocatalysis and energy conversion, is a significant challenge due to their insulating properties, resulting from organic linkers and non-conjugated frameworks [120]. Pyrolysis enhances conductivity in electron-rich reactions, but a scalable method has yet to be established, despite potential strategies like heteroatom doping, conductive substrates, and hybrid structures with metal components[121-123].

The challenges associated with mass transport hinder the efficient utilization of nanocatalysts derived from MOFs. Despite being naturally porous, their small pores may become obstructed, they can experience partial collapse or carbonize inconsistently [124-126].

This can hinder the movement of reactants and products to and from active sites, potentially reducing the reaction rate. Additionally, when ions struggle to navigate through confined or inadequately connected areas, it can negatively impact the performance of electrochemical systems. In order to tackle these issues, we require improved engineering techniques. This process involves developing layered pore architectures, employing temporary molds, or utilizing specific linkers to enhance aeration and electrical conductivity [127, 128].

6. Future directions and innovations

Material design innovations are enhancing nanocatalysis's future using MOFs. These techniques emphasize the production of limited quantities of materials essential for MOFs. This allows us to determine the metal components' arrangement, materials, and environment. This process involves making MOFs that include different metals or other materials.

These frameworks generate nanostructures that enhance the efficiency of chemical reactions. Single-atom catalysts (SACs) made from MOFs are interesting because they use atoms efficiently, and their electronic properties can be changed easily. Computational modeling and machine learning are used in material design to find the best MOF structures for specific chemical reactions. Scientists are looking into using nanocatalysts made from MOFs for renewable energy. This encompasses technologies such as fuel cells, devices for water splitting, metal-air batteries, and methods for decreasing CO_2 emissions.

7. Conclusion

This article explores recent findings regarding the application of two kinds of materials known as MOFs specifically MOF composites and MOF derivatives as miniature catalysts. MOF-based materials combine the beneficial properties of their parent materials, resulting in enhanced advantages. This combination can enhance strength, magnetic properties, and the mobility of electrons. MOF composite materials and their various forms demonstrate significantly enhanced properties when compared to the original MOFs. They are effective at bonding with different materials, enhancing the rate of chemical reactions, exhibiting specific preferences, and can be utilized repeatedly. They play a crucial part in spreading, taking in, and breaking down water pollution. Nevertheless, certain issues remain to be addressed before these materials can be applied in daily life. Overall, we've achieved significant advancements, but improvements are still necessary in the design and manufacturing processes of MOFs. By tackling current issues and investigating innovative mixed materials, MOFs can significantly improve water management and protect public health. By utilizing these new materials, wastewater treatment could become more straightforward, highly effective, and environmentally beneficial.

Author contributions

Mostafa Mabrouk: Writing – original draft, Writing – review & editing; **Hanan H. Beherei:** Writing – original draft, Writing – review & editing, Conceptualization**.**

Funding

No funding was received for this study.

Conflict of interest

The authors declare no conflict of interest.

Data availability

No data is available.

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