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# Synthesis and application of Al trimesate-based metal-organic framework: a critical review

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This review comprehensively explores the synthesis and diverse applications of the Al trimesate-based metal-organic framework, MIL-96 (Al). It begins with an introduction to the structure and properties of MIL-96 (Al), followed by an in-depth discussion of various synthesis strategies, including hydrothermal, microwave irradiation, electrochemical, mechanochemical, and sonochemical methods. The paper then delves into environmental remediation applications, highlighting MIL-96 (Al)'s effectiveness in fluoride and heavy metal removal, as well as in the elimination of volatile organic compounds (VOCs) and CO<sub>2</sub>. The review further examines the role of MIL-96 (Al) in catalysis and its emerging significance in battery technology, showcasing its versatility and potential in sustainable energy solutions. Finally, the paper concludes with perspectives on future research directions, emphasizing the ongoing development and optimization of MIL-96 (Al) for environmental and energy-related applications.

## KEYWORDS

metal organic framework, synthetic strategies, environmental remediation, catalysis, battery

## 1 Introduction

As technology has advanced, the production of novel materials, including Metal-Organic Frameworks (MOFs), has escalated (Ebrahimi Farshchi et al., 2023). Developed initially in the 1990s (Liao et al., 2013), early MOF research primarily focused on experimenting with various metal salt and linker combinations. This exploration aimed to create MOFs with distinct crystalline structures, high surface areas, and large pore volumes (Qian et al., 2023). Over time, the focus expanded to include diverse synthesis routes and a broad spectrum of applications (Chen et al., 2023; Guo et al., 2023). MOFs are synthesized using several methods, with the traditional solvothermal method being one of the earliest (Liao et al., 2013; Ahmad et al., 2018; Fiaz et al., 2020). While effective, solvothermal synthesis is time-consuming, prompting researchers to investigate alternative, more efficient methods. These include electrochemical synthesis, mech microwave-assisted synthesis, mechanochemical and sonochemical approaches (Varsha and Nageswaran, 2020; Głowniak et al., 2021a; Głowniak et al., 2021b). These innovative techniques have proved advantageous in synthesizing MOFs more rapidly while maintaining or even enhancing their performance. The versatility of MOFs is evident in the extensive research into their potential applications. MOFs have been found capable of drug delivery, gas separation and storage, catalysis, sensing, and energy storage. Each application utilizes the unique properties of MOFs, such as their customizable pore structures and surface areas, to achieve

specific functional goals. The continued exploration and development of MOFs and their synthesis methods promise further advancements in various fields, from medicine to environmental science and energy technology (Mahmoodi et al., 2017; Mahmoodi et al., 2018; Zhang et al., 2022).

MIL-96(Al) boasts remarkable porosity, high thermal stability, and selective absorption capabilities for various pollutants. These exceptional traits render it a robust and versatile material for the removal of a variety of pollutants, from fluoride ions in drinking water to harmful greenhouse gases in the atmosphere. Its potential in mitigating heavy metals and VOCs further underlines its comprehensive applications in the field of environmental cleanup (Qiu et al., 2015; Mehdinia et al., 2018; Wang et al., 2019; Zhou et al., 2019; Mahmoodi et al., 2020). MIL-96 (Al)'s potential in catalysis and battery technology is rooted in its unique structural and chemical characteristics. For catalysis, the high surface area of MIL-96 (Al), combined with its porous framework, offers numerous active sites for chemical reactions. This structure facilitates the absorption and interaction of reactants, thereby enhancing the efficiency and selectivity of various catalytic processes. Additionally, the stability of MIL-96 (Al) under different chemical environments makes it suitable for a wide range of catalytic applications. In battery technology, MIL-96 (Al)'s high porosity and large surface area are key assets. These properties enable better electrode material utilization and improved ion transport, which are crucial for battery performance. The structural stability of MIL-96 (Al) is also beneficial, contributing to the longevity and cycle stability of batteries. These features make MIL-96 (Al) a promising candidate for developing advanced battery materials, particularly for applications requiring high capacity and durability. However, to the best of our knowledge, there has been no exploration of reviews related to the synthesis and application of MIL-96 (Al).

The objective of this review paper is to provide a comprehensive overview of the synthesis, applications, and potential advancements of MIL-96 (Al). The review aims to critically examine various synthesis strategies, including hydrothermal, microwave irradiation, electrochemical, mechanochemical, and sonochemical methods, and their impact on the properties of MIL-96 (Al). Additionally, the paper seeks to explore the significant roles of MIL-96 (Al) in environmental remediation, catalysis, and battery technology, highlighting its versatility and potential for innovation in these fields. The ultimate goal is to offer insights into the future directions and challenges in the development and application of MIL-96 (Al), underscoring its importance in both environmental and technological domains.

## 2 Synthetic strategies

The synthesis of MIL-96 (Al) typically adheres to the foundational procedures, although it often undergoes modifications in various synthetic parameters, including adjustments in reaction time, temperature, pH, the incorporation of additives, and the utilization of support materials, among others (García Márquez et al., 2012; Wang et al., 2019). Among the diverse synthetic techniques available, hydrothermal methods are particularly favoured due to their inherent advantages and

procedural simplicity (Fang et al., 2020; Mahmoudi et al., 2020; Zhang et al., 2022). Nevertheless, as time has progressed, several advanced synthetic methodologies to produce MIL-96 (Al) have also emerged. Each of these approaches possesses its distinct advantages and limitations. However, the development of a synthesis protocol that combines ease of execution, environmental friendliness, maintenance of crystallinity, and scalability is of paramount importance (Mahmoudi et al., 2020; Tomar and Singh, 2021; Keshta et al., 2023). Within the scope of this comprehensive review, the fabrication of MIL-96 (Al) is meticulously examined through two primary methods: the hydrothermal process and microwave synthesis. Each of these methods is presented alongside its respective morphology, as briefly outlined in Table 1.

### 2.1 Hydrothermal reactions

Hydrothermal synthesis is a frequently employed method to produce MIL-96 (Al) and typically occurs within a Teflon-lined autoclave, precisely controlled at a specific temperature. This approach is favoured over alternative synthetic techniques for several compelling reasons, including its feasibility, simplicity, ability to yield high crystallinity, and cost-effectiveness in comparison to other methods (Ndlwana et al., 2021; Steenhaut et al., 2021; Zheng et al., 2022). The synthesis of MIL-96 relies on two primary precursors: the aluminium source ( $\text{Al}^{3+}$ ), which acts as the metal cluster, and 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ), serving as the organic linker within the secondary building unit of MIL-96 (Al). When water and organic solvents are used as media, the reactions are classified into hydrothermal reactions and solvent hydrothermal reactions, respectively.

Hydrothermal synthesis of MIL-96 (Al) takes place at elevated temperature ( $>140^\circ\text{C}$ ) and pressure ( $>1\text{ atm}$ ). This specific condition accelerates the growth of MIL-96 (Al) crystals from initially water-insoluble components (Nadimpalli et al., 2018). Consequently, most studies have reported synthesis temperatures ranging from  $140^\circ\text{C}$  to  $220^\circ\text{C}$ , using a Teflon-lined autoclave, with synthesis times spanning from 24 h to 48 h. The molar ratio of  $\text{Al}^{3+}$ :  $\text{H}_3\text{BTC}$  can be adjusted within a range of 1–12, allowing precise control of MIL-96 (Al)'s morphology. Furthermore, changes in the morphology of MIL-96 (Al) can also be achieved by substituting some of the  $\text{Al}(\text{NO}_3)_3$  with alternative aluminium sources like red mud and aluminium isopropoxide. For instance, an increase in aluminium isopropoxide content led to a gradual decline in crystallinity and particle size of the products. As the amount of aluminium isopropoxide continued to rise, it began to influence the morphology, impacting the growth of different crystal facets (Liu et al., 2015). Moreover, the partial replacement of  $\text{H}_3\text{BTC}$  with trimethyl 1,3,5-benzenetricarboxylate ( $\text{Me}_3\text{BTC}$ ) can also be employed to modulate crystal growth. With an increasing percentage of  $\text{Me}_3\text{BTC}$ , there is a corresponding rise in the relative ratio of the (102) crystal face, coupled with a decrease in the relative ratios of the (200) and (100) planes, as compared to bulk MIL-96 (Al). The addition ratio of  $\text{Me}_3\text{BTC}$  in the dual ligand does not alter the fundamental structure of MIL-96 (Al) products but does influence the orientation of crystal growth in MIL-96 (Al). The underlying mechanism for controlling MIL-96 (Al) morphology using dual metal and dual organic sources lies in the competitive

TABLE 1 The synthetic ways to generate some typical examples of MIL-96 (Al) crystals.

Sample	Metal source	Organic source	Mole ratio	Conditions	Morphology	Ref
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	2.75:1	30 mL DI water, 200 °C, 24 h	Pencil	Zhang et al. (2014)
Ce-MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	2.75:1	30 mL DI water, 200 °C, 24 h	Pencil	Yang et al. (2017)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	7:1	10 mL DI water, 210 °C, 24 h	Rice grain	Wang et al. (2019a)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	6.8:1	25 mL DI water, 210 °C, 24 h	Hexagonal spindle-shaped	Liu et al. (2015)
MIL-96 (Al) (RM)	Red mud	H <sub>3</sub> BTC	7:1	210 °C, 24 h	Dodecahedron-shaped	Wang et al. (2020)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	1:1	10 mL of DI-DMF mixture (4:1), 140 °C, 24 h	Spindle shaped	Mehdinia et al. (2018)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	7:1	15 mL DI water, 210 °C, 24 h	Regular-shaped	Zhou et al. (2019)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	12:1	7 mL DI water, 190 °C, 30 min, microwave irradiation	Octadecahedral	Qiu et al. (2015)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	3.17:1	26.93 mL DI water, 220 °C 48 h	Hexagonal rod	Abid et al. (2020)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	7:1	5 mL DI water, 210 °C 24 h	Parallelepiped-shaped crystals	Loiseau et al. (2006)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	4.74:1	26.8 mL DI water, 220 °C 48 h	Hexagonal	Azhar et al. (2018)
MIL-96 (Al)-methanol	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	4.74:1	26.8 mL DI water, 0.1 mL methanol, 220 °C 48 h	Hexagonal	Azhar et al. (2018)
MIL-96 (Al)-ethanol	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	4.74:1	26.8 mL DI water, 0.1 mL ethanol, 220 °C 48 h	Hexagonal	Azhar et al. (2018)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	1:1	150 mL DI water, 150 mL DMF, Reflux 16 h	-	Andrés et al. (2018)
MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	2:1	8 mL DI water, 2 mL DMF, 190 °C 8 h	Hexagonal bifrustum shaped	González-Santiago et al. (2023)
NiPt-MIL-96 (Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	1:5	5 mL DI water, 0.08 g NaOH, 210 °C 12 h; DMF, 150 °C 5 h for further purification	-	Wen et al. (2015)
Pt/MIL-96(Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	5.22:1	5 mL DI water, 210 °C 24 h; DMF, 150 °C 5 h for further purification	Hexagonal prism and fusiform	Xue et al. (2018)
RuCo/MIL-96(Al)	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>3</sub> BTC	12:1	7 mL DI water, 210 °C 12 h; DMF, 150 °C 5 h for further purification	Nanofibrous	Lu et al. (2017)

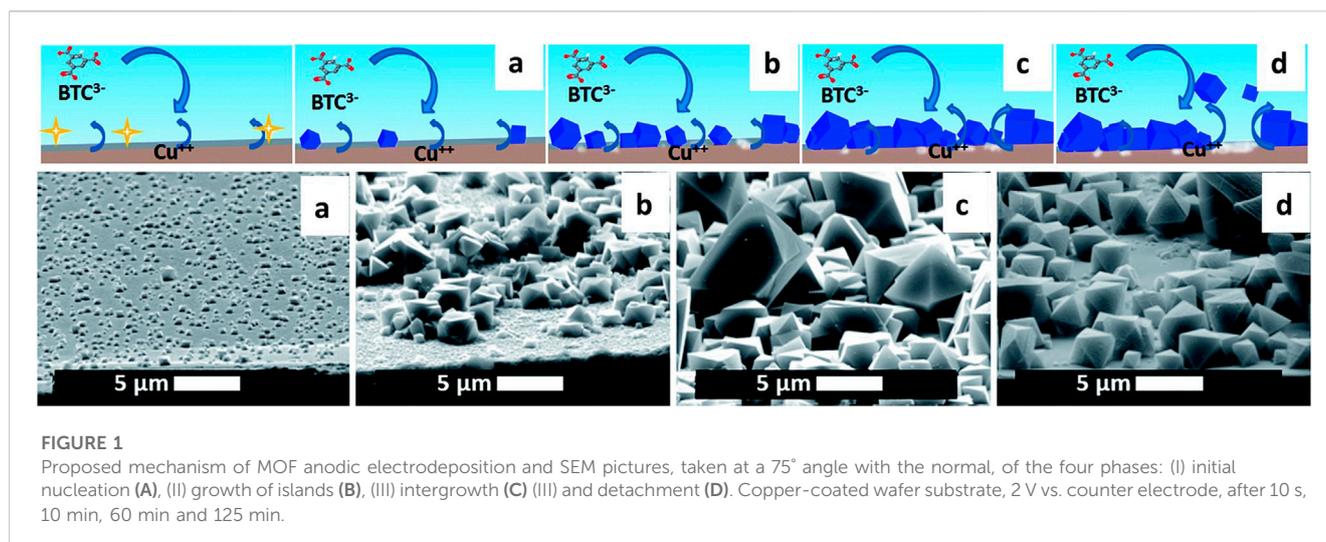
coordination of isopropanol, generated during the hydrolysis of aluminium isopropoxide, with BTC. This coordination inhibits the nucleation and growth process of crystals. Additionally, Me<sub>3</sub>BTC's effect is derived from its slow hydrolysis rate, which limits the release of BTC and subsequently restrains crystal growth.

The input parameters, including reaction time, temperature, molar ratio, and solvent choice, can exert a significant influence on the structure and properties of MIL-96 (Al). These effects manifest in characteristics such as morphology, surface area, crystallinity, particle size, and pore size. It is advisable to conduct further investigations into these input parameters to systematically tailor the structure of the desired materials.

## 2.2 Microwave irradiation reactions

A magnetron is commonly used to convert high-voltage current into high-frequency radiation. This radiation, when interacting with substances like water (H<sub>2</sub>O) due to their dielectric properties, results in the rapid rotation of molecules

and the release of heat through molecular collisions. Microwave heating has gained widespread use in various fields over the past few decades, including applications such as biomass pyrolysis (Foong et al., 2020), fuel recovery (Yek et al., 2021), biochar production (Nguyen et al., 2021), dry reforming syngas production (Pham et al., 2020), oil extraction (Taheri-Shakib and Kantzas, 2021), environmental chemistry (Xia et al., 2022), and nanomaterial synthesis (Wojnarowicz et al., 2020). Regarding the synthesis of MOFs, microwave heating offers distinct advantages, including high production yields, short reaction durations, and rapid kinetics during crystal nucleation and growth (Zornoza et al., 2011). Additionally, the use of continuous flow microwave heating allows for the separate execution of nucleation and growth steps, significantly improving reagent conversion and nucleation kinetics, all achieved under mild pressure conditions. As a result, this technique minimizes the release of residues, secondary products, or by-products into the environment, making it an environmentally friendly and efficient approach for MOF synthesis.



**FIGURE 1**

Proposed mechanism of MOF anodic electrodeposition and SEM pictures, taken at a 75° angle with the normal, of the four phases: (I) initial nucleation (A), (II) growth of islands (B), (III) intergrowth (C) (III) and detachment (D). Copper-coated wafer substrate, 2 V vs. counter electrode, after 10 s, 10 min, 60 min and 125 min.

Application of microwave heating in the fabrication of MIL-96 (Al) has been previously documented. For instance, (Qiu et al., 2015) conducted a study in which they employed hydrothermal synthesis to produce MIL-96 (Al) using microwave irradiation. In this study, deionized water served as the environmentally friendly solvent, and microwave irradiation was carried out at a power level of 150 W. The researchers successfully obtained the final products after subjecting the synthesis to a temperature of 190°C for a duration of 30 min. Moreover, they provided evidence that the synthesis of a pure phase of MIL-96 (Al) using the conventional hydrothermal method posed challenges due to the phase conversion involving MIL-100, MIL-110, and MIL-96 (Al). MIL-100 appeared as the initial phase, and with extended reaction time, both MIL-100 and MIL-110 underwent conversion into MIL-96 (Al). This transformation arises because MIL-100 is the phase controlled by kinetics, whereas MIL-96 (Al) is controlled by thermodynamics. The synthesis process involves dynamic cyclic processes of crystallization, hydrolysis, and recrystallization. The recovery of precursor species from MIL-100, followed by successive crystallization, leads to the conversion of MIL-100 into MIL-96 (Al) (Khan et al., 2012; Lin et al., 2013). To mitigate these issues, Me<sub>3</sub>BTC was introduced as a ligand to slow down the hydrolysis of BTC<sup>3-</sup> and the crystallization process, facilitating the achievement of a pure phase of Al-BTC. Remarkably, their work enabled the synthesis of a pure phase of Al-MIL-96 within just 30 min, a stark contrast to the conventional hydrothermal method, which requires over 24 h. The resulting samples exhibited octahedral morphologies with dimensions of 600 nm in width and 800 nm in length, and the morphologies could be precisely controlled by altering synthesis concentrations.

While the synthesis of MIL-96 (Al) through microwave heating offers accelerated results compared to conventional hydrothermal methods, it is essential to consider certain key factors related to safety and reproducibility. For large-scale production of MIL-96 (Al), a well-equipped system, potentially requiring high-cost safety shields, may be necessary to ensure safe and efficient operations. Additionally, it is crucial to note that the morphology and purity of the synthesized MIL-96 (Al) can be significantly influenced by the

input conditions, emphasizing the importance of strict control over these parameters to achieve desired results consistently.

## 2.3 Other methods

In addition to the aforementioned synthetic techniques, a variety of alternative methodologies, including electrochemical, mechanical, and ultrasonic approaches, are viable for the large-scale fabrication of MOFs materials. Nevertheless, the application of these techniques has been confined to other MOFs and is yet to be documented for MIL-96(Al). Prospective synthesis endeavours could explore the integration of these methods into the production process of MIL-96(Al), potentially facilitating the material's mass production, curtailing the duration of synthesis, diminishing associated costs, and augmenting output.

### 2.3.1 Electrochemical methods

Electrochemistry, the study of the conversion between chemical and electrical energies, merges principles of electricity and chemistry to explore changes induced by electrical currents. For example, an electrodeposition mechanism is presented in Figure 1 with a sketch and SEM pictures. It can be divided in four phases: nucleation, growth of islands, intergrowth and detachment. At the beginning, copper(II) ions are released in solution where the linker is present; when the critical concentration of reagents is reached, nuclei form in solution and on the surface (Phase I: initial nucleation); these nuclei grow to micrometric-sized crystals on the surface next to and on top of each other (Phase II: growth of islands); new crystals keep on nucleating (progressive nucleation) and grow forming an intergrown layer (Phase III: intergrowth). Lastly, parts of the MOF layer lose contact with the substrate and are released into the solution, aided by the internal stress in the MOF layer and the undercut of the crystals (Phase IV: detachment).

Since this initial innovation, electrochemical synthesis of MOFs has garnered significant interest due to several benefits. It facilitates

continuous synthesis, operates under milder conditions than traditional solvothermal or microwave methods, and significantly reduces reaction time—transforming processes that once took hours or days into ones that take minutes or hours. Additionally, electrochemical synthesis allows precise control over MOF formation through the manipulation of current and voltage. This method also enables the creation of uniform thin films or coatings (Li et al., 2016). Building on these advancements, the electrochemical approach holds promise for synthesizing materials like MIL-96 (Al).

### 2.3.2 Mechanochemical methods

Mechanosynthesis, initially a mainstay in metallurgy and mineral processing, has seen a significant expansion into various chemistry fields such as catalysis, inorganic chemistry, and pharmaceutical synthesis in recent decades (Kaupp, 2003; Pichon et al., 2006; Friščić, 2012). This synthesis method relies on initiating chemical reactions by milling or grinding solids, either without solvents or using minimal solvent quantities (Boldyrev, 1993; Stolle et al., 2011). This technique replaces conventional solvothermal MOF reactors with simpler tools like a mortar and pestle or, in more mechanized setups, automated ball mills. The mechanical milling process is not only energy-intensive but also ensures batch-to-batch reproducibility.

Mechanosynthesis typically involves grinding solid precursors in a ball miller without solvents (Neat Grinding, NG), enabling the use of insoluble metal sources—safer and more eco-friendly than conventional MOF synthesis solvents. Hydrated reactants, releasing water during the reaction, enhance NG efficiency. Liquid-Assisted Grinding (LAG) introduces small solvent amounts to improve the synthesis process, enhancing reaction rates and product crystallinity, and extending the range of materials that can be mechanochemically synthesized. Ion- and Liquid-Assisted Grinding (ILAG) combines both liquid and salt, dissolving solid reagents for a homogeneous reaction mixture and intensified substrate reactivity, enhancing efficiency, selectivity, and product quality.

(Liu et al., 2019) developed a novel synthesis strategy for creating various lanthanide (Ln)-containing MOFs. This method involves a short, 5-minute NG of lanthanide nitrate hydrates ( $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ , where Ln can be Europium, Erbium, Dysprosium, Yttrium, or Thulium) with  $\text{H}_3\text{BTC}$ , followed by a 24 h solvent-free thermal treatment at 160°C. The NG process initially produces a mix of amorphous metal complexes and crystal seeds of MIL-78. These seeds then undergo growth during the thermal heating phase, driven by strong chelating interactions. The resulting Ln-MOFs exhibit high crystallinity and a unique morphology. They form accordion-like microrods, which consist of numerous ultrathin nanosheets vertically aligned on the surface of the Ln-MOF crystals. This hierarchical structure is significant as it endows the materials with special room-temperature properties, making them suitable for use as ratiometric luminescent thermometers. The Ln-MOFs' ability to indicate temperature changes through variations in luminescence makes them valuable in the field of temperature sensing.

A key advantage of this approach is the rapid and efficient synthesis of MOFs, often achieving quantitative yields. It allows the use of MOF precursors with low solubility, such as oxides, hydroxides, and carbonates. However, scaling up mechanochemical synthesis poses a challenge; it remains essentially a batch processing technique with

limited production rates. Additionally, while the synthesis itself may be 'solvent-free', subsequent purification steps may require solvents. Despite these limitations, mechanochemical synthesis stands out as an environmentally friendly process for MOF production, potentially reducing manufacturing costs substantially. The application and underlying mechanism of mechanochemical synthesis for synthesizing MIL-96 (Al) remains an area needing more clarity. There is a growing recognition in the scientific community that a detailed and systematic investigation is essential to fully understand and harness this method for MIL-96 (Al) production, particularly if scaling up the process for larger-scale industrial applications is to be achieved.

### 2.3.3 Sonochemical methods

Sonochemistry, leveraging ultrasound power, has emerged as a rapidly evolving field in chemistry. It offers several advantages over traditional energy sources such as electrical heating or microwaves, including simplicity, reduced reaction times, and enhanced energy efficiency. Over the years, its application in organic synthesis has expanded considerably due to these benefits, enabling a wide range of organic reactions to be conducted with high yields and shorter reaction times (Vaitis et al., 2019).

The ongoing evolution in the field of MOFs has been remarkable, with innovations in the choice of metals, custom linkers, synthesis methods, post-synthetic modifications, and specific morphological tailoring for increased application efficiency. The integration of ultrasound in MOF research has significantly contributed to this growth, particularly by enabling the synthesis of smaller particle sizes under milder conditions compared to traditional methods, which often require high temperatures and lengthy reaction times (Vaitis et al., 2019).

An illustrative example of sonochemistry's impact is Haque et al.'s kinetic study comparing three synthesis methods: conventional, microwave, and ultrasound (Haque et al., 2010). They used MIL-53 (Fe) for this study due to its feasibility of synthesis under mild conditions. The findings showed that conventional synthesis took 1.5–3 days at 70°C–80°C, microwave synthesis took 1.5–2.5 h at 60°C–70°C, while ultrasound synthesis only required 0.5–1 h at 50°C–70°C. These results underscore the ultrasound method's potential in reducing reaction times and enhancing productivity.

However, the application of ultrasound methods in the synthesis of MIL-96 (Al) remains unexplored. Given the demonstrated benefits of sonochemistry in other MOF syntheses, its potential to facilitate and possibly scale up MIL-96 (Al) synthesis warrants further investigation. This exploration is essential to determine whether ultrasound can offer similar advantages in terms of reaction efficiency, time reduction, and perhaps even product quality for MIL-96 (Al) as it has for other MOFs.

## 3 Applications of MIL-96(Al)

### 3.1 Environmental remediation

MIL-96(Al) exhibits exceptional proficiency in the removal of pollutants like fluoride ions and heavy metals from aqueous solutions and gaseous pollutants. Its high surface area, adjustable pore size, and strong Lewis acid sites enable efficient fluoride

binding, making it a promising candidate for mitigating excess pollutants (Jiang et al., 2021; Lawrence et al., 2022; Zou et al., 2022). Additionally, the material excels in the removal of diverse pollutants due to its tailored structure, capturing and immobilizing heavy metals effectively (Xu et al., 2021; Zhao et al., 2021; Shamim et al., 2022; Lin et al., 2023). MIL-96(Al)'s selectivity, recyclability, and sustainability further enhance its suitability as a valuable tool for addressing critical environmental and public health challenges (Mokhtari-Shourijeh et al., 2020; Chen et al., 2022a; Chen et al., 2022b; Duan et al., 2022; Chu et al., 2023).

### 3.1.1 Removal of fluoride

Excessive fluoride concentrations in potable water can have detrimental implications for human health. The utilization of aluminium-based materials for fluoride adsorption is gaining prominence due to their widespread availability, cost-effectiveness, and importantly, their enhanced affinity towards fluoride, as explicated by the Hard-Soft-Acid-Base theory. Consequently, the highly water-stable, structurally adaptable MOF, MIL-96 (Al), was synthesized and subsequently modified through the introduction of metal ions dopants to facilitate efficacious fluoride removal from aqueous environments. The adsorption behaviours for each variant of MIL-96 (Al) are systematically elucidated in Table 2.

Four distinct variants of MIL-96 (Al) were synthesized to facilitate the removal of fluoride from aqueous solutions. This approach was initially proposed by Zhang et al., who employed MIL-96 (Al) as an adsorbent to reduce fluoride content to less than  $1.5 \text{ mg L}^{-1}$ . Their research validated both the feasibility and effectiveness of this approach. The adsorption process conformed closely to both the pseudo-second-order model and the Langmuir model, suggesting a predominance of chemisorption and monolayer adsorption (Mahmoodi and Mokhtari-Shourijeh, 2016; Rahimi Aqdam et al., 2021). The synthesized MIL-96 (Al) demonstrated remarkable adsorption performance across a broad pH range, and notably, exhibited substantial resistance to interference from competing ions such as chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ). This can be largely attributed to the unique size-selective properties of the micropores of MIL-96 (Al). The maximum adsorption capacity was quantified at  $31.69 \text{ mg g}^{-1}$ , and it was projected to retain approximately 68.63% of its original capacity after 5 cycles. The principal mechanism of adsorption is hypothesized to involve ion exchange between F and Al-OH. Yang et al. sought to introduce Ce into the interior structure of MIL-96 (Al) for improving the applicability of Ce-based adsorbents over a wider range of pH value. In their study, the synthesized Ce- MIL-96 (Al) adsorbent showed an adsorption capacity of  $38.65 \text{ mg g}^{-1}$  and it was supposed to maintain its original capacity of 70% after 9 cycles. It should be noted that the adsorption behavior is similar to the MIL-96 (Al) supposed by Zhang et al. The key divergence is that the adsorption process of Ce- MIL-96 (Al) toward fluoride is exothermic instead of endothermic and authors also believed the adsorption mechanism is attributable to the ion exchange of F and Ce-OH rather than Al-OH.

Contrary to the pencil-like MIL-96 (Al) powders synthesized by Zhang et al. and Yang et al., Wang et al. altered the molar ratio of the

metal source to organic source from 2.75:1 to 7:1, resulting in the synthesis of rice grain-like MIL-96 (Al) nanoparticles. Remarkably, this adsorbent demonstrated superior fluoride adsorption capacity, reaching  $42.19 \text{ mg g}^{-1}$ , significantly surpassing conventional activated aluminum materials. Moreover, the nanoparticle adsorbent exhibited a noteworthy regeneration capability, recovering 61.8% of its initial adsorption capacity following seven cycles. To address environmental concerns stemming from the accumulation of red mud, and in an effort to curb costs, Wang et al. further synthesized a MIL-96 (Al) variant using red mud as metal salts, designated as MIL-96 (Al) (RM), to supplant  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The morphology of MIL-96 (Al) (RM) diverged significantly from the original MIL-96 (Al), presenting a rougher appearance with several small particles adhering to its surface. This is primarily attributed to the coexistence of multiple metallic elements within the red mud, including Al, zirconium (Zr), and titanium (Ti). Each of these elements is postulated to induce distinct crystal growth behaviors, thereby influencing adsorption performance. Remarkably, MIL-96 (Al) (RM) surpassed the original MIL-96 (Al) in adsorption capacity, achieving a maximum adsorption capacity of  $82.65 \text{ mg g}^{-1}$  under equivalent conditions. Nonetheless, its regeneration capacity diminished somewhat, restoring only 50% of the adsorption capacity after seven cycles.

In summary, it is evident that although MIL-96 (Al) demonstrates outstanding adsorption performance in fluoride ion removal, there is still room for improvement in terms of its cyclic stability. MIL-96 (Al) exhibits commendable structural stability in acidic solutions, but during the desorption process using sodium hydroxide, it is susceptible to a certain degree of structural damage, resulting in decreased efficiency in terms of cyclic utilization. Future research endeavors should prioritize enhancing its stability, considering the varying binding affinity between different crystal facets and fluoride ions. Additionally, it is important to recognize that different crystal facets exhibit varying degrees of stability, which may manifest differently during the adsorption-desorption processes.

### 3.1.2 Removal of heavy metals

In addition to the removal of fluoride anions, MIL-96 (Al) also possesses promising capabilities for efficient heavy metal extraction from aqueous solutions, a potential attributable to several key advantages. Firstly, the abundant presence of weak Lewis acid sites facilitates strong coordination bonding with water molecules, hydroxyl groups, or other hard base groups present within the aqueous medium. Secondly, the propensity for proton release within the structure of MIL-96 (Al) fosters the generation of negative charges, consequently augmenting the material's affinity for cationic ions.

Considering these inherent advantages of MIL-96 (Al), a magnetically recyclable  $\text{Fe}_3\text{O}_4/\text{MIL-96 (Al)}$  nanoparticle (Mehdinia et al., 2018) has been successfully synthesized and utilized for highly efficient removal of Pb(II) ions from aqueous solutions. It has been postulated that the  $\text{H}_3\text{BTC}$  ligand exhibits a tendency to coordinate with Fe(III) sites on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles. Following a hydrothermal reaction, MIL-96 (Al) crystals can proliferate in the vicinity of  $\text{Fe}_3\text{O}_4$  nanoparticles. The results of adsorption have indicated that the  $\text{Fe}_3\text{O}_4/\text{MIL-96 (Al)}$

TABLE 2 Removal of fluoride from aqueous solution with different type of MIL-96 (Al) adsorbents.

Sample	BET, (m <sup>2</sup> ·g <sup>-1</sup> )	Adsorption capacity, (mg·g <sup>-1</sup> )	Initial concentration, (mg·L <sup>-1</sup> )	Regeneration	Adsorption behaviours	Ref.
MIL-96 (Al)	272	31.69	~32.5	~68.63% after 5 cycles	Pseudo-second-order, Langmuir, Endothermic and spontaneous	Zhang et al. (2014)
Ce- MIL-96 (Al)	18.28	38.65	100	~70% after 9 cycles	Pseudo-second-order, Langmuir, Exothermic and spontaneous	Yang et al. (2017)
MIL-96 (Al)	220	42.19	150	~61.8% after 7 cycles	Pseudo-second-order, Langmuir, Endothermic and spontaneous	Wang et al. (2019a)
MIL-96 (Al) (RM)	168.26	82.65	150	~50% after 7 cycles	Pseudo-second-order, Langmuir, Endothermic and spontaneous	Wang et al. (2020)

nanoparticle exhibits a considerable adsorption capacity towards Pb<sup>2+</sup> ions, exceeding 301.5 mg g<sup>-1</sup>. This enhanced capacity is primarily attributed to the ability of positively charged hydrated Pb<sup>2+</sup> ions to interact with the anionic structures of MIL-96 (Al) via electrostatic interactions. Furthermore, water molecules, which represent Lewis acid sites on the MIL-96 (Al) surface, can react with Pb<sup>2+</sup> ions in accordance with the hard and soft acid base theory. The adsorption process of the adsorbate-adsorbent system can be more comprehensively elucidated through the utilization of the Temkin model, and this process is exothermic and spontaneous. This model suggests that the adsorption phenomenon primarily relies on electrostatic interactions between positively and negatively charged species, aligning with the ion exchange adsorption mechanism.

Owing to its unique capabilities, MIL-96 (Al) can serve a dual role, not only as a primary body for heavy metal removal from aqueous solutions, but also as a supporting material for the growth of functional groups due to its extensive specific surface area and exceptional water stability. In a study conducted by (Zhou et al., 2019), an attempt was made to embellish the surface of MIL-96 (Al) with α-MnO<sub>2</sub> to catalyze a synergetic removal effect on Hg<sup>0</sup>. The MIL-96 (Al) nanoparticles with regular-shaped forms were synthesized and α-MnO<sub>2</sub> particles dispersed and adhered to the surface of MIL-96 (Al). The resulting composite materials displayed a highly promising performance in the removal of mercury. The outcomes of the study underscore that MIL-96 (Al) can effectively amplify the availability of active sites for mercury binding, a phenomenon attributed to the augmentation of its specific surface area. The loading of MnO<sub>2</sub> in varying quantities exhibited a negligible impact on the crystal structure of MIL-96, with MnO<sub>2</sub> nanoparticles primarily serving the Hg<sup>0</sup> adsorption process. The oxidation of Hg<sup>0</sup> to HgO and the concurrent reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup> were identified as critical factors influencing removal efficiency. Moreover, the presence of O<sub>2</sub> and NO gases was found to promote mercury removal positively, whereas the presence of SO<sub>2</sub> resulted in a converse effect.

### 3.1.3 Removal of VOCs

VOCs present a considerable hazard to human health and contribute significantly to environmental issues such as global warming, ozone layer depletion, and the formation of photochemical smog (Ramos et al., 2010; Yamamoto et al., 2010;

Dou et al., 2011). MOFs, characterized by their customizability and extensive surface area, have garnered substantial interest across various applications. Specifically, the MIL-n series of MOFs, renowned for their superior hydrothermal stability and Lewis acid sites, demonstrate particular efficacy in the selective adsorption of sulfur- and nitrogen-bearing VOCs (Chen et al., 2012; Qiu et al., 2015; Sun et al., 2015).

(Qiu et al., 2015) attempted the synthesis of MIL-96 (Al) particles utilizing a microwave reactor, a method demonstrated to significantly diminish the required reaction time. The employed molar ratio of the metal source to the organic source was 12:1. It was shown that these synthesized MIL-96 (Al) particles exhibited superior adsorption capacity for pyridine. The adsorption process adhered closely to the pseudo-second-order kinetics model and Langmuir model, indicating that the process is largely governed by typical monolayer chemisorption. Additionally, thermodynamic calculations portrayed the adsorption process as spontaneous and exothermic. However, the adsorption capacity retained approximately 40% of its initial value after four cycles, primarily attributed to acid washing, which impairs the structural integrity of MIL-96 (Al). The adsorption mechanism for MIL-96 (Al) is attributed to its weak Lewis acid sites, which serve as effective adsorption sites. When a molecule, characterized by a lone pair of electrons and high polarity, comes into contact with MIL-96, it occupies the vacant sites created by the activation of Al-MIL-96's pores. This process occurs as the weaker bonds in the material are broken due to heating.

### 3.1.4 Removal of carbon dioxide

The Paris Agreement mandates significant reductions in carbon emissions to limit global warming to well below 2°C above pre-industrial levels, with an aspirational target of 1.5°C. According to Article 4.1, the goal is to rapidly reduce emissions after reaching a global peak as early as possible, aiming for a balance between human-caused emissions and natural absorption by the latter half of the century, effectively reaching net-zero emissions. The Intergovernmental Panel on Climate Change (IPCC) emphasizes the need for net global CO<sub>2</sub> emissions to drop to zero by approximately 2050 for a 1.5°C limit and by 2070 for a 2°C limit. This net-zero concept has become a practical focal point for countries, including major economies like the UK, Canada, France, China, and Japan, who have aligned their emissions reduction targets with the IPCC's 1.5°C guideline (Iyer et al., 2021).

Achieving net-zero emissions necessitates rapid decarbonization across energy, industrial, and land sectors, coupled with extensive implementation of carbon dioxide removal (CDR) strategies (Clarke et al., 2009; Weyant and Kriegler, 2014). Discussed CDR approaches range from terrestrial methods like afforestation, reforestation, enhancing coastal blue carbon, and soil carbon enrichment through biochar, to subsurface techniques such as sequestering atmospheric CO<sub>2</sub> in geological formations using bioenergy with carbon capture and storage (BECCS) and direct air capture (DAC) (Sohi, 2012; Wilberforce et al., 2021).

MOFs, extensively studied for their ability to capture greenhouse gases from gaseous mixtures, have emerged as a promising solution. The industrial application of adsorption techniques for the sequestration of these gases is a practical approach widely recognized for its effectiveness. Conventional porous materials, such as activated carbon, zeolites, and metal oxides, have been reliable adsorbents in curbing greenhouse gas emissions (Pellerano et al., 2009; Hernandez et al., 2015). However, recently, MOFs have captivated scientific interest, propelled by their tremendous potential across a range of industrial applications, notably including greenhouse gas storage and separation (Stock and Biswas, 2012). While MOFs do exhibit limited thermal and chemical stability when compared to their conventional counterparts, they possess larger surface areas, tunable pore sizes and volumes, and easy functionalization. These features render them attractive alternative adsorbents, ideally suited for deployment across various environmental fields. Their unique characteristics underscore the potential of MOFs to revolutionize our approach to combatting global warming and achieving broader environmental sustainability.

MIL-96 (Al) has recently received significant attention due to its remarkable chemical stability and strong CO<sub>2</sub> adsorption capacity. In an intriguing study (Abid et al., 2020), embarked on an endeavor to synthesize pure MIL-96 (Al) and MIL-96 (Al) modified through secondary metal coordination with calcium (Ca). The authors employed a hydrothermal reaction, maintaining a molar ratio of 3.33:1 between the metal and organic sources. Calcium coordination was achieved by introducing varying quantities of CaCO<sub>3</sub> into the reaction mixture. Their research revealed that the use of Ca<sup>2+</sup> as a secondary metal in the single pot synthesis induced substantial morphological changes in the resultant MOF, significantly influencing the crystal anisotropy. Notably, the secondary metal, Ca<sup>2+</sup>, did not supplant the primary metal, Al<sup>3+</sup>, but instead likely coordinated with an active site of the Al<sup>3+</sup> metal center. In terms of CO<sub>2</sub> adsorption, the parent sample demonstrated a capacity of 8.09 mmol g<sup>-1</sup>. However, this capacity noticeably enhanced when MIL-96 (Al) was modified with Ca<sup>2+</sup> coordination. Even a small amount of Ca<sup>2+</sup> coordination was found to augment the BET surface area, pore volume, and micropore content of MIL-96 (Al), thereby proving advantageous for CO<sub>2</sub> adsorption.

(Azhar et al., 2018) synthesized three variants of MIL-96 (Al), using water, methanol, and ethanol as solvents. They maintained a molar ratio of 5:1 between the metal and organic source. Interestingly, all three samples exhibited similar XRD peak characteristics, though the intensities varied, potentially due to differences in crystal size. Hexagonal crystal shapes were consistent across all samples, but crystal lengths differed. All

three versions of MIL-96 (Al) showed high adsorption capacity for both CO<sub>2</sub> and N<sub>2</sub>, albeit with less selectivity. This research highlights the role of solvent choice in influencing the characteristics and performance of synthesized MIL-96 (Al).

In addition to its adsorption capacity, the stability of MOFs under high humidity conditions serves as another crucial evaluation criterion (Qian et al., 2017). In the case of MIL-96 (Al), it demonstrates robust stability while maintaining a notable adsorption rate within a relative humidity range spanning from 3% (resulting in an adsorption of 1.6 mmol g<sup>-1</sup>) to 10% (1.1 mmol g<sup>-1</sup>) (Benoit et al., 2018). Of particular significance is the consistent adsorption performance of MIL-96 even under the latter condition. This noteworthy behavior can be attributed to the specific adsorption mechanisms involved: H<sub>2</sub>O is initially absorbed within cavities formed by H<sub>2</sub>O–Al (Trimer), terminal-OH-Al, and terminal-H<sub>2</sub>O-Al, whereas CO<sub>2</sub> is adsorbed within a separate, independent cavity. This segregation of absorption sites ensures the stable capture of CO<sub>2</sub> even in the presence of high humidity levels.

(Sakai et al., 2023) introduced a novel one-pot synthesis method for MIL-96 (Al) monoliths. The method involves hydrothermal treatment of an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> monolith in a solution containing H<sub>3</sub>BTC and HNO<sub>3</sub>, without adding a metal source. The effects of synthesis temperature and HNO<sub>3</sub> concentration on the crystallization of MIL-96 (Al) were examined. The study found that HNO<sub>3</sub> enhances the dissolution of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the growth of MIL-96. The crystallization required a synthesis temperature above 453 K. The synthesized MIL-96 (Al) monoliths showed comparable CO<sub>2</sub> adsorption capacity to that of well-grown MIL-96 (Al) powdery crystals and demonstrated good stability, retaining adsorption properties even after 2 months of storage under atmospheric conditions.

(Andrés et al., 2018) details the fabrication and characterization of ultrathin films of MIL-96(Al) nanoparticles. It optimized MOF dispersions in chloroform to create dense, high-quality monolayer films without nanoparticle agglomeration. These films could be deposited on various solid substrates. The MIL-96(Al) films are of interest for CO<sub>2</sub> capture due to their interaction with CO<sub>2</sub> molecules, facilitated by Al<sup>3+</sup> Lewis centers and hydroxyl groups. A comparative study using different film fabrication procedures revealed that CO<sub>2</sub> uptake depends significantly on the method and storage conditions. Notably, the CO<sub>2</sub> adsorption capacity of Langmuir-Blodgett (LB) films increased by 30% after a simple water immersion treatment. The study also confirmed the stability of LB MOF monolayers across multiple CO<sub>2</sub> adsorption/desorption cycles.

MIL-96 (Al) offers several advantages for CO<sub>2</sub> capture, making it a promising candidate for environmental applications. Its key strengths lie in its effective CO<sub>2</sub> adsorption capability, as demonstrated in studies where MIL-96 (Al) monoliths and ultrathin films showed comparable CO<sub>2</sub> uptake to well-grown MIL-96 (Al) powdery crystals. This attribute is crucial for efficient CO<sub>2</sub> capture in various industrial processes. Moreover, MIL-96 (Al) exhibits remarkable stability, maintaining its adsorption properties even after prolonged storage periods, ensuring long-term usability. The versatility in its fabrication, evidenced by the development of ultrathin films, expands its applicability across different CO<sub>2</sub> capture settings, potentially

enabling integration into diverse systems and technologies. However, MIL-96 (Al) also faces some challenges. The synthesis process is intricate, requiring careful control of environmental conditions such as temperature and the concentration of nitric acid, which influence the crystallization and growth of MIL-96 (Al). This complexity can pose difficulties in scaling up production for commercial applications.

## 3.2 Catalysis

MIL-96 (Al) is an effective catalyst due to its distinct structural characteristics, including large surface areas, adjustable pore sizes, and a stable framework that can support and disperse various metal nanoparticles. This adaptability is exemplified in its application in different catalytic processes:

For example, Wen et al. demonstrated that bimetallic Ni-Pt nanoparticles, grown on MIL-96 using a simple liquid impregnation method, exhibit enhanced catalytic activity for hydrogen generation from hydrazine at room temperature. Ni<sub>64</sub>Pt<sub>36</sub>/MIL-96 (Al) showed the highest catalytic activity among tested catalysts, with a turnover frequency of 114.3 h<sup>-1</sup> and 100% hydrogen selectivity. This high performance is attributed to the synergistic effect between the MIL-96 support and NiPt nanoparticles (Wen et al., 2015).

Similarly, (Lu et al., 2017) provide a detailed investigation into the enhanced catalytic capabilities of RuCo nanoparticles when supported on the MIL-96(Al) framework. They demonstrate that the Ru<sub>1</sub>Co<sub>1</sub>@MIL-96 catalyst significantly outperforms its monometallic counterparts in catalysing the hydrolysis of ammonia borane, a reaction crucial for hydrogen generation. Key findings include the uniform and effective distribution of RuCo nanoparticles on MIL-96(Al), leading to a synergistic effect between ruthenium and cobalt that greatly enhances catalytic activity. The catalyst not only shows a remarkably high turnover frequency but also maintains its structural integrity and performance over multiple cycles, highlighting its durability and potential for efficient hydrogen generation in practical applications. These findings underscore the importance of the structural and chemical properties of MIL-96(Al) in facilitating and optimizing the performance of supported metal nanoparticles in catalysis.

(Xue et al., 2018) demonstrate that MIL-96(Al), is exceptionally effective in dispersing platinum particles, leading to the creation of Pt<sub>x</sub>MIL-96 (Al) catalysts with varied platinum contents. Their findings show that these catalysts, particularly Pt<sub>5</sub>MIL-96 (Al)/CP, achieve impressive NO removal efficiencies of up to 100% at 60 °C when used in a gas diffusion reactor for low-temperature H<sub>2</sub>-SCR. This study highlights the potential of MIL-96(Al) as a robust catalyst support, maintaining the structural integrity of both the platinum and the framework itself, indicating its suitability for efficient low-temperature catalytic applications.

MIL-96 (Al) stands out as a catalyst due to its unique combination of high surface area and porosity, which allows for efficient dispersion and accessibility of active catalytic sites. This structure, coupled with its thermal stability, makes it suitable for various catalytic reactions, especially those requiring the support of metal nanoparticles, enhancing both activity and selectivity. However, MIL-96 (Al) faces challenges in practical applications. Its stability might be compromised under certain chemical

conditions or in high humidity environments. The complexity and potential costliness of its synthesis, particularly for tailored catalytic applications, pose additional hurdles. Furthermore, scalability and recovery of the catalyst in industrial settings remain challenging, potentially limiting its widespread adoption despite its notable advantages in laboratory-scale experiments.

## 3.3 Batteries

The MOFs materials with porous structure are attracting tremendous attention for function as host materials to anchor sulfur in Li-S batteries owing to their high theoretical capacity (1,675 mAh g<sup>-1</sup>) (Li et al., 2018; Baumann et al., 2019). More importantly, they have the potential to reduce the shuttle effect of lithium polysulfides (LPS, chemical formula: Li<sub>2</sub>S<sub>x</sub>, 4 ≤ x ≤ 8) from the cathode to the anode with the aids of the Lewis acidic metal sites in MOFs, which is helpful in mitigating the irreversible loss of sulfur during the discharge process (Liang et al., 2019; Tian et al., 2019; Zhang et al., 2021; Geng et al., 2022a). It has been reported that the regulation of shape could affect the growth of planes and then change the adsorption capacity for LPS, implying that the planes with larger amounts of active sites are able to enhance the catalytic activity and cyclic stability (Wen et al., 2018; Bai et al., 2020). In this regard, Geng et al. synthesized MIL-96 with different shape and particle size and tried to reveal the relationship between shapes/sizes of an individual MOF and its cyclic performance for Li-S battery application.

The MIL-96 (Al) nanoparticles with hexagonal platelet crystals (HPC), hexagonal bipyramidal crystals (HBC), and hexagonal prismatic bipyramidal crystals (HPBC) were synthesized through adding different organic solvents including N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) to affect the growth of the specific planes. The results demonstrate that the introduction of different polar regulators can dominate the growth of planes and affect the distribution of particles size, the primary exposed planes for HPC, HBC and HPBC are (002), (101), and (100), respectively. Among which, (101) plane has the largest density of Lewis acidic sites, followed by (100) and (002) planes, demonstrating that (101) plane exhibits the strongest adsorption ability. Moreover, a smaller particle size has a more superior ability to inhibit LPS diffusion because of the improved plane area.

The authors concluded that the sulfur-loading effect and the interaction with LPS demonstrate that a huge quantity of exposed (101) planes would enhance the adsorption ability and cyclic performance, especially mitigate the shuttle effect. Furthermore, particles with smaller size have a faster Li<sup>+</sup>/electron transfer rate and a higher cyclic stability.

Similarly, to inhibit the shuttle effect and mitigate the volume expansion, MIL-96 (Al) with HBC shape was synthesized and applied as the skeleton to prepare a core shell structure through coating poly pyrrole (PPy). The morphology of MIL-96 (Al) remained unchanged before and after the sulfur loading. A PPy shell with a thickness of 175 nm was then coated through an *in situ* oxidation polymerization process, which is beneficial for offsetting the volume expansion of the sulfur cathode during the electrochemical reaction process and the shell is able to physically confine LPS inside MIL-96 (Al)-S-PPy (Liu et al.,

2019). Based on the experimental results it could be concluded that MIL-96 (Al)-S-PPy exhibited a strong chemical adsorption affinity towards  $S_8$  and  $Li_2S_x$  as it can encapsulate  $S_8$  and  $Li_2S_x$  into its large internal void space compared to that of MIL-96 (Al)-S. More importantly, a high specific capacity of  $1233.8 \text{ mA h g}^{-1}$  at 0.5 C could be realized regarding on the MIL-96 (Al)-S-PPy cathode (Wang et al., 2019).

MIL-96(Al) in lithium-sulfur batteries offers a blend of promising advantages and notable challenges. Its high porosity and surface area enhance energy density by accommodating more sulfur, while its good conductivity and chemical stability contribute to efficient and durable battery performance. Additionally, its ability to trap polysulfides addresses the common issue of capacity fading. However, the complexity and cost of its synthesis, potential for volume expansion during use, and limited scalability pose significant challenges. Furthermore, concerns about its thermal stability and the limited research on its long-term performance in lithium-sulfur batteries highlight the need for further exploration and optimization before it can be widely adopted in this application.

## 4 Future perspectives and conclusion

This thorough review systematically collates a range of synthesis techniques for generating MIL-96 (Al) crystals. It covers established methods such as hydrothermal and microwave reactions, and introduces emerging synthesis approaches like the electrochemical, mechanochemical, and sonochemical methods. These novel methods, already proven effective in synthesizing other MOFs, hold promise for scaling up the production of MIL-96 (Al) for industrial applications. The review emphasizes the importance of rational design in synthesis, highlighting the selection of metal and organic sources, the molar ratio, and the choice of solvent as key factors for precise control over the growth, shape, and facet development of MIL-96 (Al) crystals. Beyond synthesis strategies, the review extensively examines the applications of MIL-96 (Al) in environmental remediation, catalysis, and battery technology. MIL-96 (Al) demonstrates exceptional efficacy in removing pollutants like fluoride ions and heavy metals from water, as well as in capturing gaseous pollutants. Its application extends to catalysis and battery technologies. The material's high surface area, tunable pore size, and robust Lewis acid sites position it as a versatile and promising candidate for a wide array of applications.

Nevertheless, the broader application of MIL-96(Al) does face certain challenges. Primarily, the process of scaling up the synthesis of this MOF to industrial levels poses substantial difficulty. Cost-effective, efficient, and reproducible large-scale synthesis is an area

that requires more focused research and development. In addition, the longevity of MIL-96(Al) under different environmental conditions is yet another critical area of concern. Studies exploring its long-term stability, recyclability, and performance under diverse operational conditions are of paramount importance to ensure its reliability in sustained pollution control.

The prospects of MIL-96(Al) are, nonetheless, promising. Research endeavors should concentrate on fine-tuning synthesis methodologies for industrial scale-up and investigating novel strategies to enhance the material's stability and recyclability. Moreover, a comprehensive assessment of its environmental impacts, stability, safety, and real-world efficiency should be undertaken. It is crucial to bridge the gap between laboratory-based research and real-world applications, underscoring the need for more in-depth, application-oriented studies that evaluate the performance of MIL-96(Al) in real settings.

## Author contributions

HZ: Conceptualization, Formal Analysis, Investigation, Methodology, Writing—original draft, Writing—review and editing. QC: Investigation, Methodology, Writing—review and editing. ZC: Conceptualization, Formal Analysis, Investigation, Methodology, Writing—review and editing. B-JN: Conceptualization, Formal Analysis, Supervision, Writing—review and editing.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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