

Environmentally Benign Strategies to the Controlled Crystallization of MOF Sorbents

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Abstract: Metal–organic frameworks (MOFs) are a vital class of porous materials with ultrahigh surface areas and tunable pore structures, yet conventional synthesis relies on toxic high-boiling organic solvents, hindering large-scale production and violating green chemistry principles. This work explores green aqueous synthesis of MOF sorbents via controlled nucleation and crystal growth. Using zirconium fumarate (MOF-801) as the model, zirconyl chloride-derived samples show optimal crystallinity and water uptake, reaching 470–490 mg g^{−1} at 96.5–97.5% relative humidity. For aluminum fumarate, a modified aqueous route with controlled ligand addition avoids organic solvents and fluorine-containing reagents entirely. The strategy is extended to MIL-101(Cr) and MOF-199 by tuning crystallization kinetics and separating nucleation/growth stages, yielding highly crystalline porous materials with excellent adsorption performance. These approaches support sustainable MOF production for water purification, atmospheric water harvesting and related applications.

Keywords: MOF; metal–organic frameworks; green chemistry; environmentally benign synthesis; MOF-801; zirconium fumarate; aluminum fumarate; MIL-101(Cr); HKUST-1

Introduction

Metal–organic frameworks (MOFs) represent one of the most important classes of porous crystalline materials, combining exceptionally high specific surface areas, tunable pore architectures, and the possibility of systematic modification of their chemical composition and functionality. Owing to these unique properties, MOFs have attracted considerable attention as adsorbents for water and gas purification, catalysts, separation materials, sensors, and carriers for functional species.

Despite the significant progress achieved in the field of MOF synthesis, the majority of reported preparation methods are still based on the use of toxic high-boiling organic solvents such as N,N-dimethylformamide (DMF), dimethylacetamide (DMA), and N-methylpyrrolidone (NMP). The use of such solvents is associated with the generation of substantial amounts of waste, increased process complexity, and difficulties in industrial scale-up. Furthermore, these

approaches are not fully consistent with the modern principles of green chemistry.

One of the most promising directions in the development of MOF synthesis technology is the transition toward environmentally benign aqueous systems. The use of water as the primary reaction medium significantly reduces environmental impact, simplifies process design, and decreases the costs associated with solvent recovery and purification. However, replacing traditional organic media with water substantially alters the mechanisms of complex formation, nucleation, and crystal growth, thereby requiring the development of new approaches for controlling the synthesis process.

Particular attention has recently been devoted to fumarate-based metal–organic frameworks containing zirconium or aluminum. These materials exhibit excellent chemical and hydrolytic stability, well-developed porous structures, and considerable potential for applications involving water adsorption and purification. Nevertheless, informa-

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Table 1 | Designation and synthesis conditions of zirconium fumarate samples

Sample	Zirconium precursor	Modulator	Temperature	Time
Zr-fum-1	ZrOCl ₂	HCOOH	50 °C	1 hour
Zr-fum-2	ZrOCl ₂	CH ₃ COOH	20 °C	24 hours
Zr-fum-3	Zr(C ₅ H ₇ O ₂) ₄	CH ₃ COOH	20 °C	24 hours
Zr-fum-4	Zr(C ₅ H ₇ O ₂) ₄	HCOOH	20 °C	24 hours
Zr-fum-5	Zr(C ₅ H ₇ O ₂) ₄	HCOOH	50 °C	1 hour
Zr-fum-6	ZrOCl ₂	HCOOH	20 °C	24 hours
Zr-fum-7	ZrOCl ₂	HCOOH	100 °C	24 hours
Zr-fum-8	Zr(C ₅ H ₇ O ₂) ₄	HCOOH	100 °C	24 hours
Zr-fum-9	Zr(C ₅ H ₇ O ₂) ₄	CH ₃ COOH	100 °C	24 hours
Zr-fum-10	ZrOCl ₂	CH ₃ COOH	100 °C	24 hours

tion concerning the formation mechanisms of such materials in fully aqueous media remains limited.

Materials and Methods

Zirconyl chloride octahydrate, zirconium acetylacetonate, aluminum nitrate, fumaric acid, formic acid, and acetic acid of analytical-grade purity were used as starting reagents for the synthesis of metal–organic framework materials. All solutions were prepared using distilled water.

Synthesis of zirconium fumarate

Zirconium fumarate was synthesized entirely in aqueous media. Zirconyl chloride octahydrate and zirconium acetylacetonate were employed as zirconium precursors, whereas formic acid and acetic acid were used as crystallization modulators. The syntheses were carried out at 20, 50, and 100 °C. Upon completion of the synthesis, the products were separated by centrifugation, washed with a water–ethanol mixture, and dried to constant weight.

The synthesis route can be schematically represented as follows:

Zirconium salt solution + water + fumaric acid + modulator (HCOOH or CH₃COOH) → crystallization → Zr-fum (MOF-801)

Synthesis of aluminum fumarate

Aluminum fumarate was synthesized using a modified aqueous procedure that excluded both organic solvents and fluorine-containing reagents. The method was based on the controlled addition of a fumarate-containing ligand solution into an aluminum salt solution under continuous stirring. Particular attention was paid to regulating the reagent addition rate in order to control nucleation and crystal growth processes.

Characterization methods

The phase composition of the synthesized materials was determined by X-ray diffraction (XRD) using a DRON-2.0 diffractometer operating with Co K α radiation in the 2 θ range of 10–90°. The average crystallite size was estimated using the Scherrer equation.

Morphological features were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Infrared spectra were recorded on an AVATAR FTIR-330 spectrometer in the range of 4000–400 cm^{−1}.

Hydrodynamic particle size and ζ -potential values were determined by dynamic light scattering (DLS) using a Zetasizer NanoZS analyzer. Water adsorption measurements were carried out using a quartz crystal microbalance technique.

Textural characteristics and adsorption properties were investigated by low-temperature nitrogen adsorption using an ASAP 2020 MP instrument. Specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method, while pore size distributions and pore volumes were derived from adsorption–desorption data.

Results and Discussion

Effect of synthesis conditions on the formation of zirconium fumarate structure

To investigate the formation mechanisms of zirconium-based metal–organic frameworks in environmentally benign aqueous media, a series of zirconium fumarate samples was synthesized using different zirconium precursors, crystallization modulators, and synthesis temperatures. Zirconyl chloride octahydrate and zirconium acetylacetonate were employed as zirconium sources, while formic and acetic acids were used as crystallization modulators. The syntheses were performed at 20, 50, and 100 °C.

The selection of these parameters was motivated by the need to elucidate the role of zirconium coordination chemistry and crystallization control mechanisms in fully aqueous systems. Unlike conventional synthetic routes for zirconium MOFs, which frequently involve organic solvents and fluoride-containing additives, the present work focused on obtaining highly crystalline materials exclusively through adjustment of the reaction medium composition.

The X-ray diffraction patterns obtained for the synthesized samples (**Figure 1**) demonstrate that synthesis conditions exert a decisive influence on the crystallinity of the resulting materials. Samples Zr-fum-1, Zr-fum-2, Zr-fum-6, Zr-

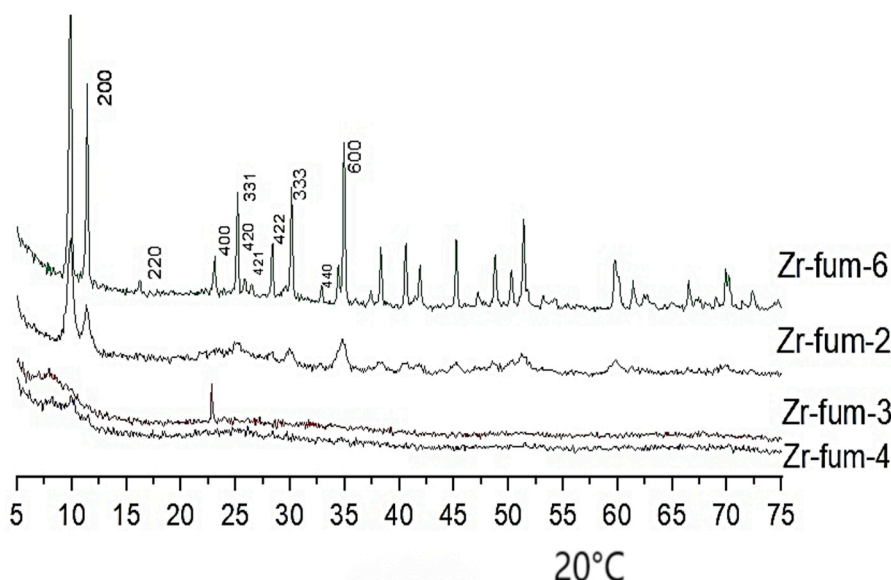


Figure 1 | X-ray diffraction patterns of zirconium fumarate samples synthesized under different conditions

fum-7, Zr-fum-8, Zr-fum-9, and Zr-fum-10 exhibit diffraction peaks characteristic of the MOF-801 structure. In contrast, samples Zr-fum-3, Zr-fum-4, and Zr-fum-5 show no pronounced diffraction maxima and can therefore be classified as amorphous or poorly crystalline materials. These results clearly indicate that the nature of the zirconium precursor significantly affects the mechanism of framework formation.

A comparison of samples prepared from different zirconium precursors reveals substantial differences in crystallization behavior. When zirconyl chloride octahydrate was used, the formation of a crystalline phase occurred much more readily. This observation can be attributed to the rapid hydrolysis of zirconyl chloride in aqueous solution, resulting in the formation of zirconium hydroxo-complexes that serve as direct precursors of the zirconium oxo-clusters constituting the nodes of the MOF-801 framework. Consequently, self-assembly processes proceed more efficiently, increasing the probability of forming a highly ordered structure.

A different behavior was observed for zirconium acetylacetonate. Acetylacetonate complexes are known to exhibit high thermodynamic stability due to the formation of chelate rings. The decomposition of these complexes in aqueous media requires additional time and proceeds through multiple intermediate states. As a result, the formation rate of framework building units decreases, and crystallization begins to compete with the formation of amorphous products. This phenomenon likely explains the amorphous nature of samples Zr-fum-3, Zr-fum-4, and Zr-fum-5.

The nature of the crystallization modulator also exerts a significant influence on the structure and crystallinity of the resulting materials. The experimental results indicate that formic acid promotes the formation of products with higher crystallinity compared with acetic acid. This observation is consistent with contemporary concepts regarding the role of

monocarboxylic acids in the synthesis of zirconium-based MOFs.

Morphology of zirconium fumarate particles and structural features

To evaluate the influence of synthesis conditions on the morphology of the resulting materials, zirconium fumarate samples were examined by scanning electron microscopy (SEM). Analysis of the micrographs revealed that the nature of the zirconium precursor, the type of crystallization modulator, and the synthesis temperature significantly affect particle size, the degree of agglomeration, and the overall microstructural organization of the materials. SEM images of samples Zr-fum-2, Zr-fum-3, Zr-fum-4, Zr-fum-6, and Zr-fum-9 synthesized under different conditions are presented in **Figure 2**. In all cases, the powders consist of aggregates formed by smaller primary particles with submicron dimensions. However, the aggregation behavior and the degree of structural ordering vary considerably among the samples.

The Zr-fum-2 sample, synthesized from zirconyl chloride octahydrate in the presence of acetic acid at room temperature, is characterized by the formation of loosely packed aggregates with irregular morphology. The particles exhibit a relatively broad size distribution and form porous agglomerates. Well-defined crystal faces are largely absent. This morphology is consistent with the XRD results, which indicate a lower degree of crystallinity compared with samples synthesized in the presence of formic acid.

The most pronounced morphological changes are observed when zirconium acetylacetonate is used as the precursor. Sample Zr-fum-3, synthesized in the presence of acetic acid, consists of large irregular aggregates with rough and non-uniform surfaces. Individual structural elements are difficult to distinguish, indicating a low degree of struc-

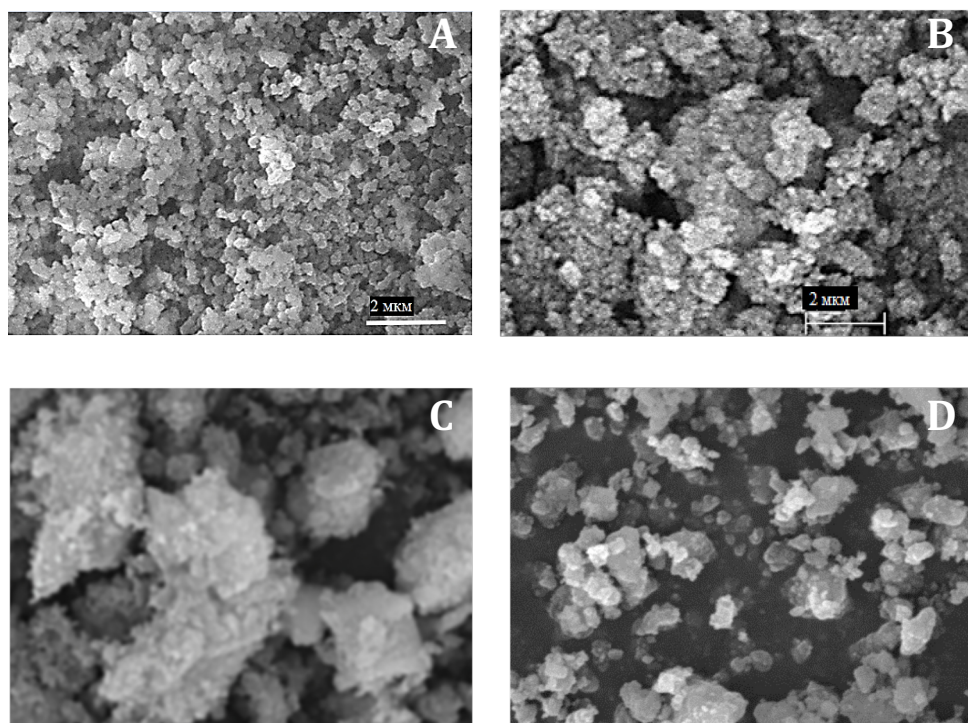


Figure 2 | SEM micrographs of zirconium fumarate samples: (A) Zr-fum-6, (B) Zr-fum-2, (C) Zr-fum-3, and (D) Zr-fum-4

tural organization. These observations are in good agreement with the XRD data, according to which this sample is predominantly amorphous. Therefore, the use of zirconium acetylacetonate at relatively low temperatures significantly hinders the formation of an ordered metal–organic framework.

Interestingly, replacing acetic acid with formic acid while maintaining zirconium acetylacetonate as the precursor leads to noticeable changes in morphology. In sample Zr-fum-4, a more homogeneous distribution of particles and a reduction in aggregate size are observed. Although XRD analysis still indicates a predominantly amorphous structure, the influence of formic acid on the self-assembly process becomes evident at the morphological level. These observations suggest that formate ions promote a more uniform organization of the developing structure, even under conditions where the formation of a well-crystallized framework has not yet occurred.

The most homogeneous microstructure is observed for sample Zr-fum-6, synthesized from zirconyl chloride octahydrate in the presence of formic acid at approximately 20 °C. The powder consists of relatively small aggregated particles with a narrow size distribution. The material appears more uniform and dispersed than the other samples in this series. These observations correlate well with the XRD results, which indicate that Zr-fum-6 possesses the highest degree of crystallinity among the samples synthesized at room temperature. Consequently, the combination of zirconyl chloride octahydrate and formic acid provides the most favorable

conditions for the formation of an ordered MOF-801 structure in aqueous media.

A comparison of the SEM and XRD results reveals a clear relationship between particle morphology and crystallinity. Samples exhibiting higher crystallinity are characterized by a more homogeneous particle distribution and a more developed microstructure. In contrast, a decrease in crystallinity is accompanied by the formation of irregular aggregates and increased structural heterogeneity.

The obtained results confirm that the formation of metal–organic frameworks in aqueous media is governed by the combined effects of precursor chemistry, crystallization modulator, and synthesis temperature. The ability of the precursor to rapidly generate zirconium oxo-clusters required for framework construction appears to be particularly important. Zirconyl chloride octahydrate facilitates the formation of such clusters, whereas zirconium acetylacetonate, owing to the high stability of its chelated coordination environment, slows down the self-assembly process. Formic acid further promotes controlled framework growth, enabling the formation of more ordered materials even at relatively low synthesis temperatures.

Water adsorption and the relationship between structure and adsorption properties

One of the most important practical applications of metal–organic frameworks is their ability to adsorb water vapor from the atmosphere. Consequently, evaluation of water adsorption performance represents a key criterion for

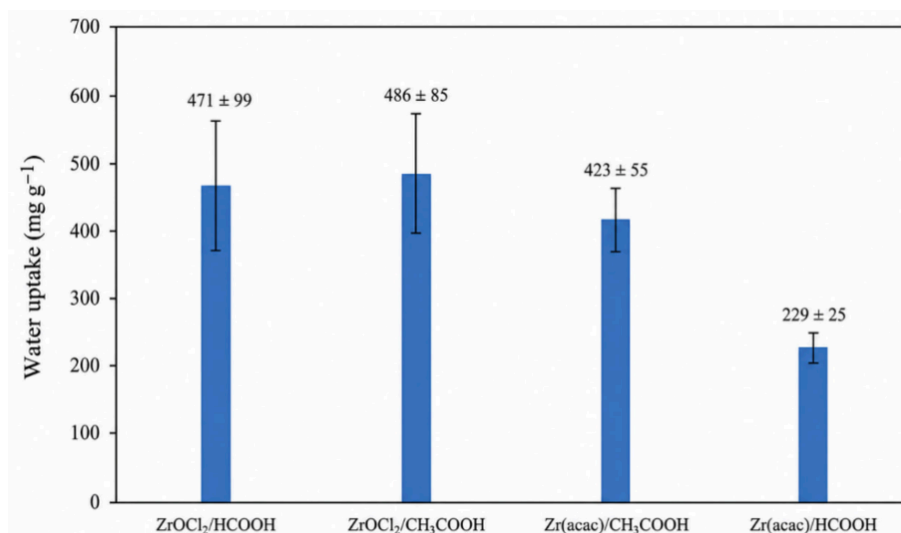


Figure 3 | Water adsorption capacities of zirconium fumarate samples synthesized using different zirconium precursors and crystallization modulators. Error bars represent standard deviations calculated from three independent measurements ($n = 3$).

assessing the suitability of MOF materials for atmospheric water harvesting and related adsorption applications.

The water adsorption performance of the synthesized zirconium fumarate samples was evaluated at a relative humidity of 96.5–97.5% and a temperature of approximately 20 °C. For each sample, three independent measurements were performed. The average water adsorption capacities and corresponding standard deviations were calculated and are presented in **Figure 3**.

As can be seen from **Figure 3**, the highest adsorption capacities were obtained for samples synthesized from zirconyl chloride. For sample Zr-fum-6, prepared in the presence of formic acid, the average water adsorption capacity reached $471 \pm 99 \text{ mg g}^{-1}$. For sample Zr-fum-2, synthesized using acetic acid as a modulator, the water adsorption capacity was $485 \pm 85 \text{ mg g}^{-1}$. These values are in good agreement with those reported in the literature for MOF-801 and indicate the presence of a highly developed porous structure accessible to water molecules.

When zirconium acetylacetonate was used as the precursor, a decrease in adsorption performance was observed. For sample Zr-fum-3, synthesized in the presence of acetic acid, the water adsorption capacity was $423 \pm 55 \text{ mg g}^{-1}$. Although this value remains relatively high, it is noticeably lower than those obtained for samples prepared from zirconyl chloride. The lowest adsorption capacity was observed for sample Zr-fum-4, synthesized from zirconium acetylacetonate in the presence of formic acid. In this case, the average water adsorption capacity was only $229 \pm 25 \text{ mg g}^{-1}$, which is approximately half the value observed for the best-performing samples.

Comparison of the adsorption data with the XRD results reveals a clear relationship between synthesis conditions and adsorption performance. The highest water adsorption capacities were observed for samples exhibiting well-

defined diffraction peaks corresponding to zirconium fumarate. Conversely, a reduction in the intensity of characteristic reflections and an increase in the amorphous fraction were accompanied by lower adsorption capacities.

The results indicate that the nature of the zirconium precursor plays a decisive role in determining adsorption performance. In the case of zirconyl chloride, hydrolysis proceeds readily, promoting the formation of zirconium oxo-hydroxo species required for the construction of the MOF-801 framework. In contrast, the high stability of zirconium acetylacetonate slows down these processes, resulting in lower structural ordering and reduced accessibility of the internal pore system to water molecules.

Overall, the results demonstrate that high water adsorption performance in zirconium fumarate is achieved primarily through the appropriate selection of the zirconium precursor. Under the conditions employed in the present study, zirconyl chloride-based systems proved to be the most effective, yielding materials with water adsorption capacities of approximately $470\text{--}490 \text{ mg g}^{-1}$, comparable to the best MOF-801 samples reported in the literature.

Mechanism of zirconium fumarate formation in aqueous media

The experimental results obtained in the present study make it possible to propose a mechanism for the formation of zirconium fumarate in aqueous media and to explain the influence of the principal synthesis parameters on the structure and properties of the resulting materials. It is well known that the formation of zirconium-based metal-organic frameworks begins with the hydrolysis of zirconium compounds followed by the generation of polynuclear oxo-hydroxo complexes. In the case of MOF-801, the fundamental building units are zirconium clusters of the $\text{Zr}_6\text{O}_4(\text{OH})_4$

type, which are subsequently interconnected by fumarate ligands to form a three-dimensional porous framework.

The first stage of the process involves dissolution and hydrolysis of the zirconium precursor. The rate of this stage is strongly dependent on the chemical nature of the starting zirconium compound. Zirconyl chloride octahydrate readily dissociates in aqueous solution and rapidly forms zirconium hydroxo-complexes. As a consequence, favorable conditions for the formation of zirconium clusters are established at an early stage of synthesis, facilitating the development of an ordered metal-organic framework.

In contrast, zirconium acetylacetonate forms highly stable chelate complexes. The presence of strongly coordinated acetylacetonate ligands significantly retards hydrolysis and subsequent formation of zirconium oxo-hydroxo clusters. This behavior likely explains the formation of amorphous or poorly crystalline products in samples Zr-fum-3, Zr-fum-4, and Zr-fum-5.

A crucial role in framework formation is also played by the crystallization modulator. Formic acid acts as a competitive ligand and regulates the kinetics of framework assembly. In zirconium-based MOFs, monocarboxylic acids are capable of temporarily competing with the primary organic linker for coordination sites within zirconium clusters. This competition decreases the rate of uncontrolled crystal growth and creates favorable conditions for the gradual development of an ordered framework structure. It can be assumed that formate ions temporarily participate in the coordination environment of zirconium during the early stages of synthesis, stabilizing intermediate clusters and suppressing the formation of disordered aggregates. As crystallization proceeds, these formate species are gradually replaced by fumarate ligands, leading to the formation of the final MOF-801 framework. Owing to the relatively small size of the formate ion, this substitution occurs readily and does not introduce significant steric hindrance.

Acetic acid can also function as a crystallization modulator; however, its effectiveness appears to be lower. The larger acetate ion and its stronger coordination interaction with zirconium centers may slow down ligand-exchange processes and hinder the reorganization of the coordination sphere required for framework formation. This interpretation is supported by the XRD results, which demonstrate a lower degree of crystallinity for samples synthesized in the presence of acetic acid.

Temperature represents another important factor controlling framework formation. Increasing the synthesis temperature accelerates zirconium hydrolysis, enhances reagent diffusion, and promotes ligand-exchange processes. As a result, the formation of zirconium oxo-clusters becomes more favorable, increasing the probability of generating a highly ordered framework. This effect is particularly evident for systems based on zirconium acetylacetonate, where increasing the temperature to 100 °C partially overcomes the kinetic limitations observed at room temperature.

The combined analysis of X-ray diffraction, electron microscopy, and water adsorption data indicates that the na-

ture of the zirconium precursor exerts the strongest influence on the formation of zirconium fumarate. The highest water adsorption capacities and the most pronounced crystalline features were observed for samples synthesized from zirconyl chloride.

This behavior can be explained by the relatively facile hydrolysis of zirconyl chloride in aqueous solution, resulting in the formation of hydroxo- and oxo-zirconium species that act as direct precursors of $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters. Under such conditions, self-assembly of the metal-organic framework proceeds efficiently, leading to the development of a highly porous structure with superior adsorption performance. By contrast, zirconium acetylacetonate is a stable chelated complex in which the coordination environment around the zirconium center significantly hinders hydrolysis and oxo-cluster formation. Consequently, the generation of framework building units becomes slower and the degree of crystallinity of the final materials decreases.

The obtained results clearly demonstrate that, under the investigated synthesis conditions, the nature of the zirconium precursor is the dominant factor governing framework crystallization and adsorption performance, whereas the crystallization modulator primarily affects the kinetics of individual crystallization stages.

An additional contribution to crystallization is provided by the use of reflux conditions during synthesis. Continuous return of water and formic acid vapors maintains a constant composition of the reaction medium and prevents concentration changes during the synthesis process. At the same time, convection generated under reflux conditions improves reagent distribution throughout the solution volume and reduces local concentration gradients. Such conditions promote more stable crystal growth and contribute to enhanced crystallinity and improved adsorption characteristics of the resulting materials.

Based on the combined results of X-ray diffraction, electron microscopy, and water adsorption measurements, it may be concluded that the formation of zirconium fumarate in aqueous media is governed by the balance between the rate of zirconium oxo-cluster generation and the rate of framework growth. The combination of zirconyl chloride octahydrate and formic acid provides the most favorable balance between these processes, resulting in the formation of highly crystalline MOF-801 with a well-developed porous structure and high affinity toward water vapor.

Consequently, the proposed aqueous synthesis route enables the preparation of zirconium fumarate without the use of toxic organic solvents or fluoride-containing additives while preserving the possibility of controlling material structure and properties through rational variation of precursor chemistry, crystallization modulator, and synthesis temperature.

Environmentally benign aqueous synthesis of aluminum fumarate

To evaluate the applicability of the developed environmentally benign approaches to other classes of metal-

organic frameworks, the synthesis of aluminum fumarate was investigated. In contrast to most reported preparation methods, which typically involve elevated temperatures, prolonged hydrothermal treatment, or the use of organic solvents, the synthesis in the present work was carried out in aqueous media under relatively mild conditions. A distinctive feature of the proposed method was the preliminary preparation of a soluble fumarate-containing ligand solution through the neutralization of fumaric acid with sodium hydroxide, followed by the controlled addition of this solution into an aluminum salt solution. Unlike conventional procedures based on rapid mixing of reagents, the ligand solution was introduced at a low and controlled rate. It was assumed that such an approach would prevent local pH fluctuations and excessive nucleation rates. As a consequence, the number of crystallization centers formed during the early stages of synthesis decreases, whereas the growth of already formed particles becomes the dominant process. An additional advantage of this method is the reduced probability of incorporating foreign ions into the framework structure.

To investigate the influence of synthesis and post-treatment conditions, three aluminum fumarate samples were prepared. Sample Al-fumarate-1 was synthesized using aluminum sulfate as the aluminum source and subsequently subjected to vacuum drying. Sample Al-fumarate-2 was obtained under similar synthesis conditions but was dried by freeze-drying. In sample Al-fumarate-3, aluminum chloride was used as the precursor.

The X-ray diffraction results revealed a significant influence of both the aluminum salt and the post-synthesis treatment method. The highest degree of crystallinity was observed for Al-fumarate-1 synthesized from aluminum sulfate. The diffraction pattern of this sample shows excellent agreement with both the calculated crystal structure and the reference Basolite A520 material. The main diffraction peaks are characterized by high intensity and good resolution, indicating the formation of a highly ordered crystalline framework. For Al-fumarate-3 synthesized from aluminum chloride, a decrease in diffraction peak intensity and noticeable peak broadening were observed. In addition, extra reflections not characteristic of aluminum fumarate were detected in samples Al-fumarate-2 and Al-fumarate-3. These reflections may indicate the presence of secondary phases or structural defects formed during synthesis and post-treatment.

Particularly interesting results were obtained from water adsorption measurements. The non-activated Al-fumarate-1 sample exhibited almost no water adsorption, with a water adsorption capacity of only $0.003 \pm 0.001 \text{ g g}^{-1}$. Such behavior is typical of porous materials whose pore systems remain occupied by residual solvent molecules or synthesis by-products. Following thermal activation under vacuum, the water adsorption capacity of the same sample increased dramatically to $0.623 \pm 0.004 \text{ g g}^{-1}$. Thus, removal of adsorbed species from the pore structure resulted in more than a 200-fold increase in adsorption capacity.

Even higher adsorption performance was achieved for Al-fumarate-2 after freeze-drying. In this case, the water adsorption capacity reached $0.767 \pm 0.005 \text{ g g}^{-1}$. This result suggests that freeze-drying preserves the porous structure more effectively than conventional thermal treatment, thereby maintaining greater accessibility of adsorption sites.

Sample Al-fumarate-3, synthesized from aluminum chloride and activated under vacuum, exhibited a water adsorption capacity of $0.720 \pm 0.010 \text{ g g}^{-1}$. Although its crystallinity was somewhat lower than that of Al-fumarate-1, its adsorption performance remained high, indicating the preservation of a well-developed porous network.

The obtained results demonstrate that the environmentally benign aqueous synthesis strategy developed in the present work can be successfully extended not only to zirconium-based MOFs but also to aluminum-based frameworks. Furthermore, the results emphasize that high adsorption performance depends not only on the synthesis stage itself but also on appropriate activation procedures that open the internal pore structure and make adsorption sites accessible to water molecules.

Extension of the developed approaches to the synthesis of MIL-101(Cr) and MOF-199 (HKUST-1)

To evaluate the general applicability of the proposed synthetic principles, their implementation in the preparation of other metal-organic frameworks was also investigated. MIL-101(Cr) and MOF-199 (HKUST-1) were selected as model systems because they differ substantially in both metal-center chemistry and framework formation mechanisms.

For MIL-101(Cr), a modified hydrothermal synthesis route incorporating an additional aging stage was developed. Following ultrasonic treatment, the reaction mixture was maintained at 60–80 °C for 2–4 h prior to the main hydrothermal step. This treatment was expected to partially separate nucleation and crystal growth processes, thereby enabling more controlled framework formation. X-ray diffraction analysis demonstrated that the resulting MIL-101(Cr) possessed a high degree of crystallinity. Electron microscopy revealed the formation of well-faceted octahedral particles with an average size of approximately 300 nm. Nitrogen adsorption measurements showed that the synthesized MIL-101(Cr) exhibited a BET specific surface area of $2291 \text{ m}^2 \text{ g}^{-1}$ and a Langmuir surface area of $3179 \text{ m}^2 \text{ g}^{-1}$. The average pore diameter was approximately 2.3 nm, while the total pore volume reached $1.2 \text{ cm}^3 \text{ g}^{-1}$. These values are in good agreement with those reported for highly porous MIL-101(Cr) materials in the literature. In addition, it was found that the sample synthesized without mineralizing agents exhibited the highest water vapor adsorption capacity. For the MIL-101(Cr)–H₂O system, the adsorption capacity reached 2800 mg g^{-1} , exceeding the values reported for samples synthesized using hydrofluoric acid and other modifiers.

A similar strategy was employed for the synthesis of MOF-199 (HKUST-1). The framework was prepared in aqueous media using benzene-1,3,5-tricarboxylic acid and copper sulfate as starting materials. The resulting powders exhibited high crystallinity and consisted predominantly of well-formed crystals with sizes up to 1 μm . For MOF-199, a two-stage temperature protocol was proposed to separate nucleation and crystal growth processes. Unlike conventional synthesis routes performed at a constant temperature, the present method involved two consecutive stages. During the first stage, the reaction mixture was maintained at a relatively low temperature of 40–50 $^{\circ}\text{C}$. Under these conditions, the rate of nucleation remained moderate, leading to the formation of a limited number of stable nuclei. After completion of the nucleation stage, the temperature was increased to 80 $^{\circ}\text{C}$. The higher temperature accelerated diffusion processes and coordination interactions between copper ions and benzene-1,3,5-tricarboxylate ligands. Consequently, crystal growth became the dominant process, whereas the formation of new nuclei was significantly suppressed. It is proposed that such separation of nucleation and growth stages reduces competition between these processes and promotes the formation of larger and more homogeneous crystals with lower structural heterogeneity and a more developed porous structure.

The X-ray diffraction and electron microscopy results confirmed the effectiveness of this approach and demonstrated the formation of highly crystalline HKUST-1. Investigation of adsorption properties revealed a high affinity of MOF-199 toward water vapor. At relative humidities of 90–97%, the water adsorption capacity reached 885 mg g^{-1} , confirming that the developed porous structure was preserved despite the use of environmentally safer synthesis conditions.

Overall, the results demonstrate that the proposed approaches based on nucleation control, regulation of crystal growth conditions, and maximum utilization of aqueous reaction media can be successfully extended to different classes of metal–organic frameworks. These findings confirm the universal nature of the developed environmentally benign MOF synthesis principles and highlight their potential for the preparation of porous sorbents with diverse compositions and applications.

Conclusion

In this work, environmentally benign and modified synthesis methods for metal–organic frameworks based on aqueous reaction media and controlled crystallization processes have been investigated.

It was established that, for zirconium fumarate, the nature of the zirconium precursor exerts a decisive influence on both the structural characteristics and adsorption properties of the resulting materials. Samples synthesized from zirconyl chloride exhibited a higher degree of crystallinity, a more developed porous structure, and superior water adsorption performance compared with materials prepared

from zirconium acetylacetonate. The maximum water adsorption capacities reached 470–490 mg g^{-1} at a relative humidity of 96.5–97.5%.

It was further demonstrated that the application of crystallization modulators, optimization of synthesis temperature, and the use of reflux conditions provide additional control over nucleation and crystal growth processes, resulting in increased structural ordering of the synthesized materials.

For aluminum fumarate, a modified aqueous synthesis method based on the controlled addition of a ligand solution into an aluminum salt solution was developed. It was shown that post-synthesis activation plays a crucial role in determining adsorption performance and enables the achievement of high water adsorption capacities.

The possibility of extending the proposed principles to the synthesis of MIL-101(Cr) and MOF-199 (HKUST-1) was also demonstrated. The introduction of preliminary aging stages and two-step temperature regimes promotes the formation of highly crystalline materials with well-developed porous structures.

The obtained results indicate that controlling the kinetics of nucleation and crystal growth represents an effective strategy for the preparation of MOF sorbents under environmentally benign conditions. The developed approaches may serve as a basis for the creation of new technologies for the synthesis of metal–organic framework materials with diverse compositions and functional applications.

More broadly, the present study demonstrates that environmentally sustainable synthesis routes can successfully replace conventional methods based on toxic organic solvents and hazardous additives without compromising the structural quality, crystallinity, or adsorption performance of the resulting materials. The proposed approaches contribute to the development of green technologies for the production of advanced porous materials and provide a realistic pathway toward the industrial implementation of MOF-based adsorption technologies for water purification, atmospheric water harvesting, gas separation, and related applications.

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