ISSN: 2633-4828 Vol. 5 No.4, December, 2023

International Journal of Applied Engineering & Technology

A FACILE AND ECO-FRIENDLY IN SITU THERMAL (IST) TECHNIQUE SYNTHESIS OF ZEOLITIC IMIDAZOLATE FRAMEWORKS WITH ENHANCED CRYSTALLINITY

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ABSTRACT

An inventive in situ thermal (IST) technique has been developed for crafting zeolitic imidazole frameworks using a 2-methylimidazole (2-MIM) linker, offering a straightforward and environmentally conscious alternative. This IST method boasts numerous benefits over prior approaches, such as its solvent and additive-free conditions, mild reaction temperature, single-step process, lack of activation prerequisites, and minimal precursor usage. Notably, this pioneering method introduces a fresh avenue for ZIF synthesis, yielding highly porous crystalline structures. Additionally, by adhering to green chemistry principles, the IST approach eliminates the necessity for solvents, activation steps, or post-treatment procedures to clear residual reactants, by-products, and guest molecules. Moreover, the scalability of the IST process underscores its potential for large-scale material fabrication.

Keywords: Zeolitic imidazolate frameworks, in situ thermal (IST), Synthesis, eco-Friendly.

INTRODUCTION

Metal-Organic frameworks, generated by the self-assembly of metal ions or clusters containing organic ligands, have emerged as focal points in environmental green technologies. In the conventional procedure for synthesizing MOFs or ZIFs, the standard method involves dissolving the metal ion and ligand precursor in an organic solvent, followed by heating under specific conditions (referred to as the solvothermal method). This process typically spans from several hours to a week. Commonly utilized organic solvents are preferred for their capability to dissolve precursors and facilitate crystal formation. However, an alternative approach has emerged, where water is utilized as a solvent at room temperature, offering an eco-friendlier option. This results in nanocrystal products with higher yields compared to solvothermal synthesis. Nonetheless, only a restricted number of precursors exhibit solubility in water, leading to fewer successful outcomes in the synthesis of MOFs/ZIFs [1]. To address environmental problems, novel procedures have been developed, such as electrochemistry, spray drying, mechanochemical processes, and microwave irradiation. For instance, microwave-assisted synthesis, albeit requiring complex techniques and specialized equipment, enables the fast crystallization of MOFs. Similarly, unconventional techniques including nucleation agent seeding and electrochemical deposition have been developed especially for ZIF production [2].

Even with the wide range of synthesis techniques available, a number of issues still need to be addressed. These include high energy consumption, the use of costly or dangerous precursors and organic solvents, extended reaction times, high ligand ratios, the requirement for additives (acid/base), and dependence on sophisticated instrumentation. Furthermore, traditional synthesis methods can yield a variety of waste products, which

exacerbates activities that are harmful to the environment [3]. Before MOF materials can be used in a variety of situations, post-treatment processes like purification or activation are usually required to get rid of side products, salt, and solvent residues. Specifically, activation is essential to fully unleashing the functions of the material. These difficulties, which are made worse by the lack of useful information for large-scale synthesis, impede the synthesis and application of ZIFs in novel environments [4]. ZIFs produced by various synthesis techniques have distinct architectures and qualities, opening up possibilities for customized modification to satisfy particular application needs. As a result, there is continuous interest in and difficulty with developing novel synthetic techniques for MOFs/ZIFs that are straightforward and environmentally friendly [5].

Here, we report the creation of a unique approach for the in situ thermal treatment (IST) method of synthesizing ZIFs based on a straightforward and effective one-pot synthesis route. With this method, highly porous crystalline materials can be produced quickly and without the need for additives or solvents during the synthesis process. Comparing the resultant materials to ZIFs that are traditionally synthesized, they show the same isostructural features and qualities, such as porosity, surface area, and thermal stability. Notably, the synthesized materials don't need any post-treatment or activation procedures. Moreover, ZIFs produced using the economical IST technique have significant advantages with regard to their chemical and physical characteristics. These advantages are especially noticeable in applications like catalysis and adsorption. Furthermore, there is encouraging potential for industrial-scale uses of the new IST synthesis process for ZIFs. When taken as a whole, these benefits highlight how much better the IST approach is than conventional or previously documented synthesis methods.

MATERIAL AND METHOD

Materials

Without additional purification, we used zinc acetylacetonate hydrate (99%, Aldrich), cobalt (II) acetylacetonate (≥99%, Aldrich), and 2-methylimidazole (99%, Aldrich).

Method

Cobalt (II) acetylacetonate and 2-methylimidazole were combined to create ZIF-67. The mixture was then physically pulverized in a mortar for five minutes at room temperature. For the production of ZIF-8, the same process was used, but zinc acetylacetonate hydrate was used in place of the cobalt component. In this instance, zinc acetylacetonate hydrate and 2-methylimidazole were mixed and homogenized in a mortar for five minutes at room temperature. The powdered mixture was then placed within an alumina tube inside a muffle furnace with an inert environment after being moved onto an alumina boat. The temperature was raised in two steps: first, over the course of 30 minutes, it was raised from room temperature (R.T.) to 100°C, and then it was raised again, this time to 200°C. Upon cooling, the last ZIFs were gathered.

RESULT AND DISCUSSION

A wide variety of zeolitic imidazole frameworks (ZIFs) have been successfully synthesized up to this point. Of these, the ones that use 2-MIM linkers have garnered a lot of interest because of their diverse range of uses. ZIF-8, ZIF-67, and their derivatives are noteworthy examples that have demonstrated exceptional characteristics and performance in a variety of domains, including adsorption, separation, and catalysis [6]. It takes careful adjusting of important parameters like the nodes-to-linkers ratio, the quantity of precursors used, and variables like temperature and reaction duration to get these ZIFs to behave as desired. Zeolitic imidazole frameworks can be confirmed by analytical techniques such as XRD, BET, and TGA. These frameworks often exhibit high degrees of porosity, crystallinity, specific surface area, and stability. The ratio of metal nodes to organic linkers stands out as the most important variable influencing ZIF synthesis [7]. Samples of ZIF-8 and ZIF-67 were subjected to powder X-ray diffraction (XRD) examination, as shown in Figure 1, to obtain a better knowledge of their crystalline characteristics. ZIF-67 displayed a polyhedral crystal structure, in line with previous findings, while ZIF-8 adopted a body-centered cubic shape. The strength of the first diffraction peak decreased with increasing the 2-MIM concentration in ZIF-8 and ZIF-67. Three main conclusions can be inferred from the absence of additional peaks in the XRD patterns: first, thermal treatment led to solvent-free crystal formation between 2-

MIM and the metal (Co, Zn); second, ZIF-8 and ZIF-67 were successfully synthesized without compromising the integrity of their frameworks; and third, the synthesized products showed a notable degree of purity [8].

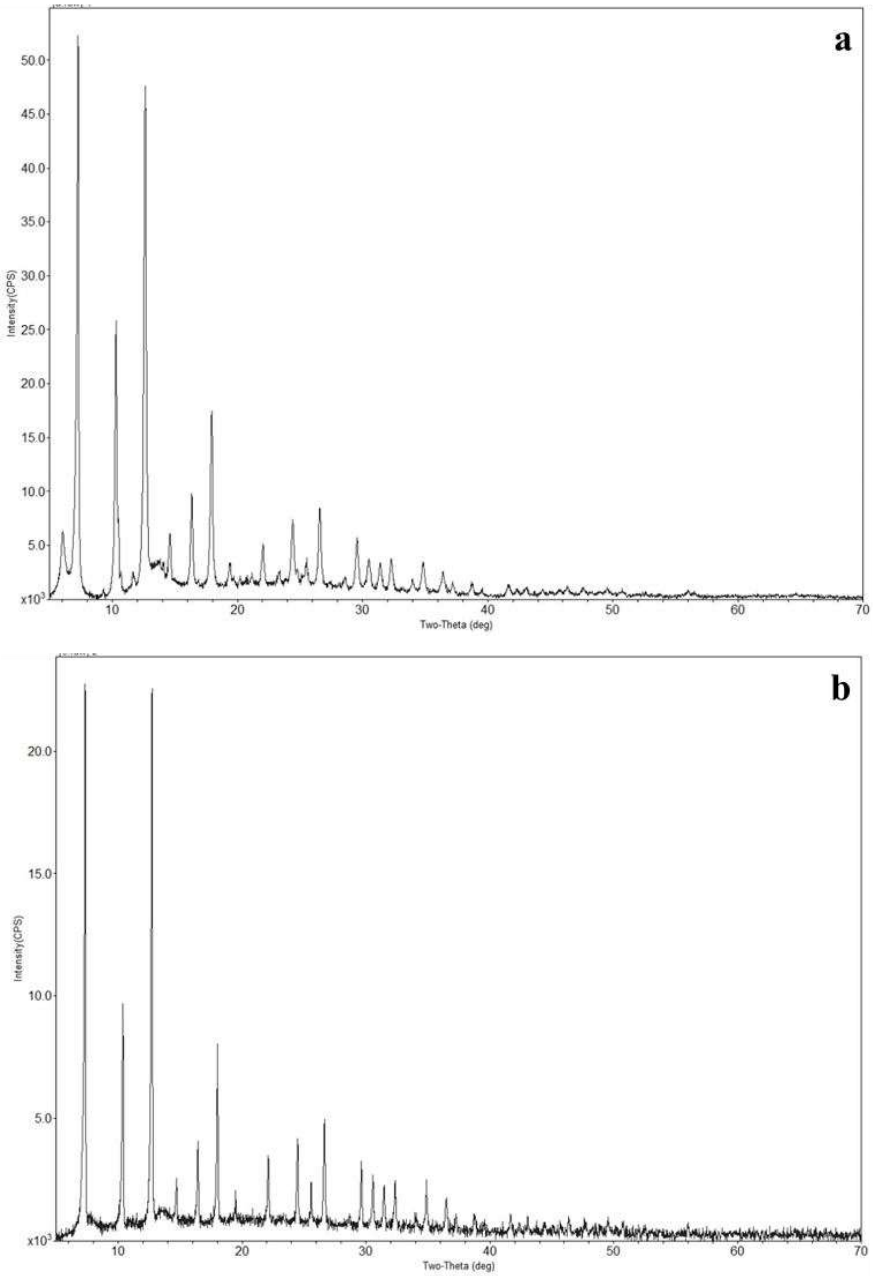

Figure 1 XRD analysis for ZIFs synthesized using the IST approach. a. ZIF-8, b. ZIF-67.

The application of the Brunauer-Emmett-Teller (BET) method to assess the porosity properties of the synthesized ZIFs, including surface area, pore size, pore volume, and Langmuir surface area [9], is shown in Table 1. The trends in surface area were reflected in the porosity features, such as pore volume and pore size (calculated using the Horvath–Kawazoe method). Lowering the 2-MIM molar ratio to zinc and cobalt caused the particles' total pore volume and BET surface area to decrease. This decline was associated with wider dispersion of particle sizes seen at lower 2-MIM/Zn molar ratios, suggesting that smaller particles have higher BET surface areas.

Table 1: Porosity and surface area of ZIF-8 and ZIF-67 samples.

Sample	BET ($m^2.g^{-1}$)	Langmuir	Pore Size (nm)	Pore Volume ($cm^3.g^{-1}$)
ZIF-8	1490.37	1577.82	1.427	0.459
ZIF-67	1585.96	1651.79	1.460	0.409

Thermogravimetric analysis, or TGA, was used to assess the ZIFs' thermal and chemical stability. Variations in the ZIFs' weight were noted at different temperatures in a N_2 atmosphere, with a flow rate of 5 cc/min [10], as Figure 3 illustrates. Two significant weight reductions were found in the ZIF-8 TGA data: one at 187 °C (12%) and another at 590 °C (40%). Likewise, ZIF-67's TGA profile showed two weight changes: at 168 °C (50%) and 510 °C (10%). The first weight loss in ZIF-8 appeared to be related to the removal of adsorbed water or unreacted 2-MIM rather than structural damage, while the second weight loss was related to the breakdown or disintegration of ZIF-8 and ZIF-67 structures.

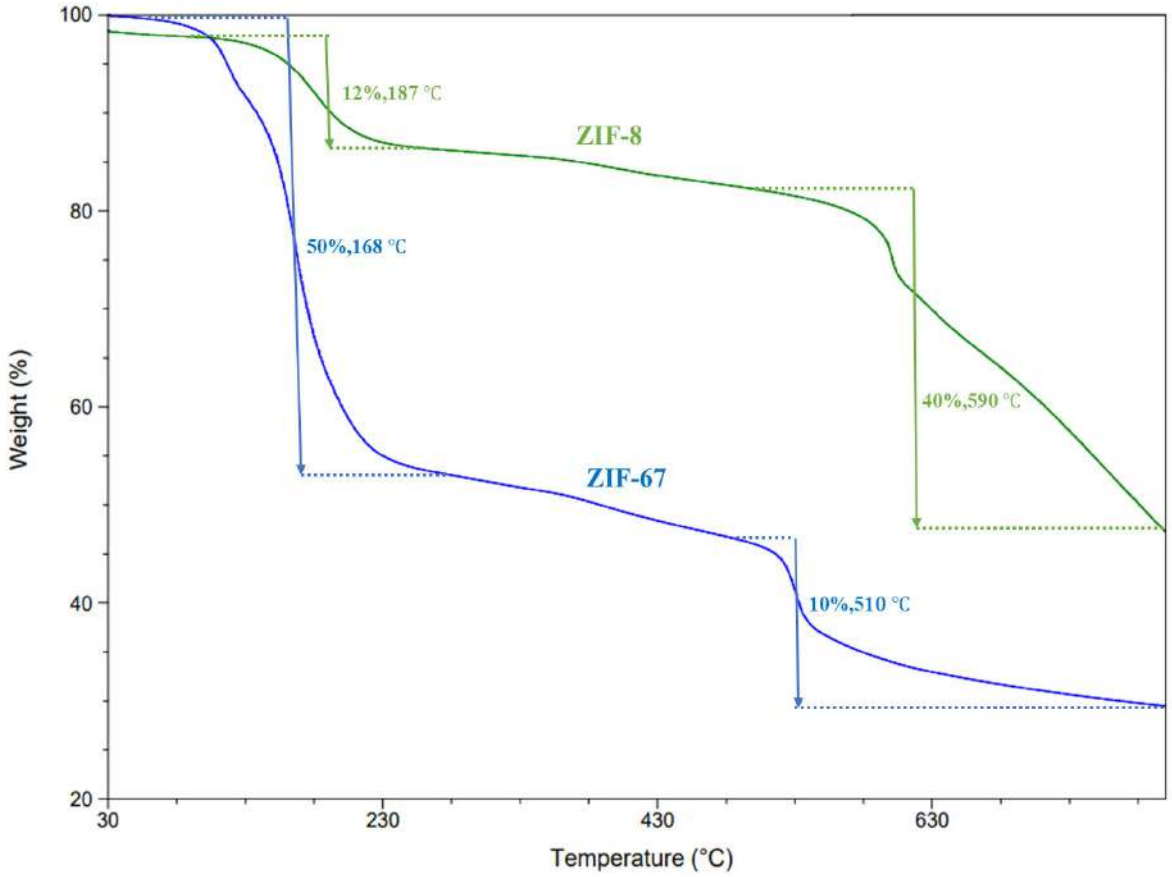

Figure 2: TGA analysis for ZIF-8 and ZIF-67 synthesized using the IST approach.

EDS mapping was employed to investigate the elemental distribution and topological characteristics. Figures 3 and 4 both showed that C, N, Zn, and Co were uniformly distributed throughout ZIF-67 and ZIF-8. These components' existence verified the make-up of both ZIFs. The uniform distribution of metals suggested that ZIF-8 and ZIF-67 had been successfully synthesized.

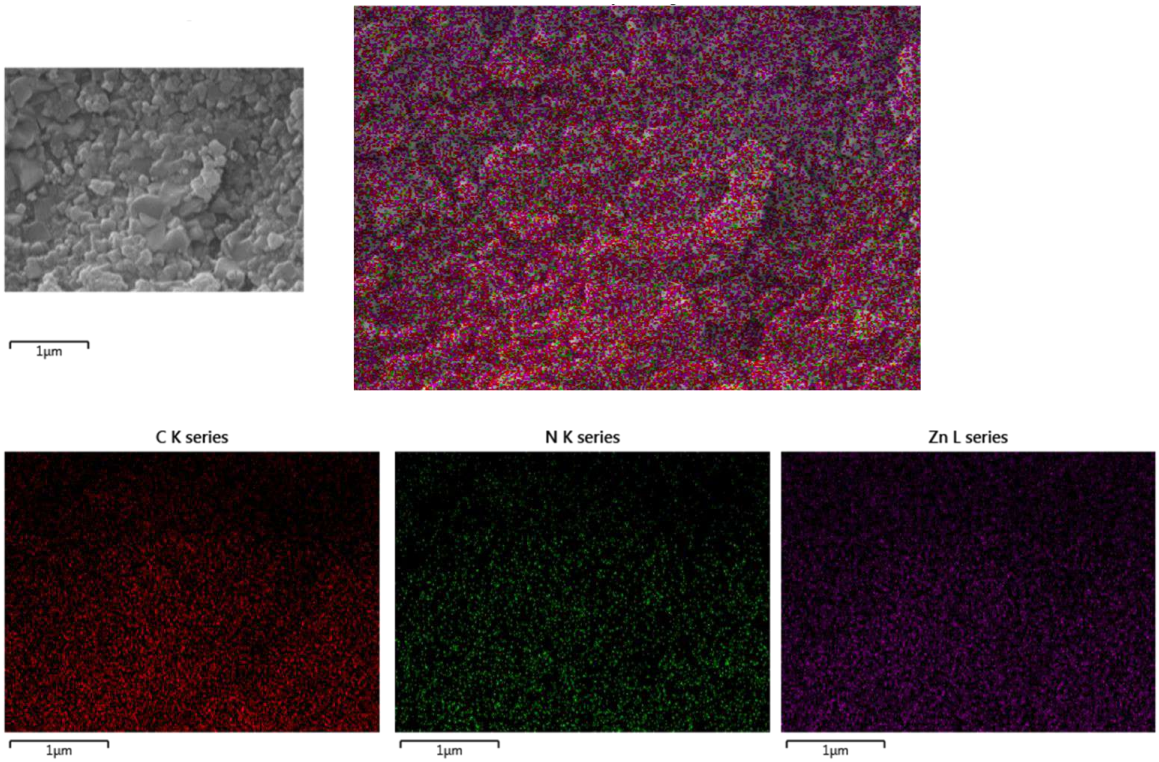

Figure 3: EDS mapping analysis for ZIF-8 synthesized using the IST approach.

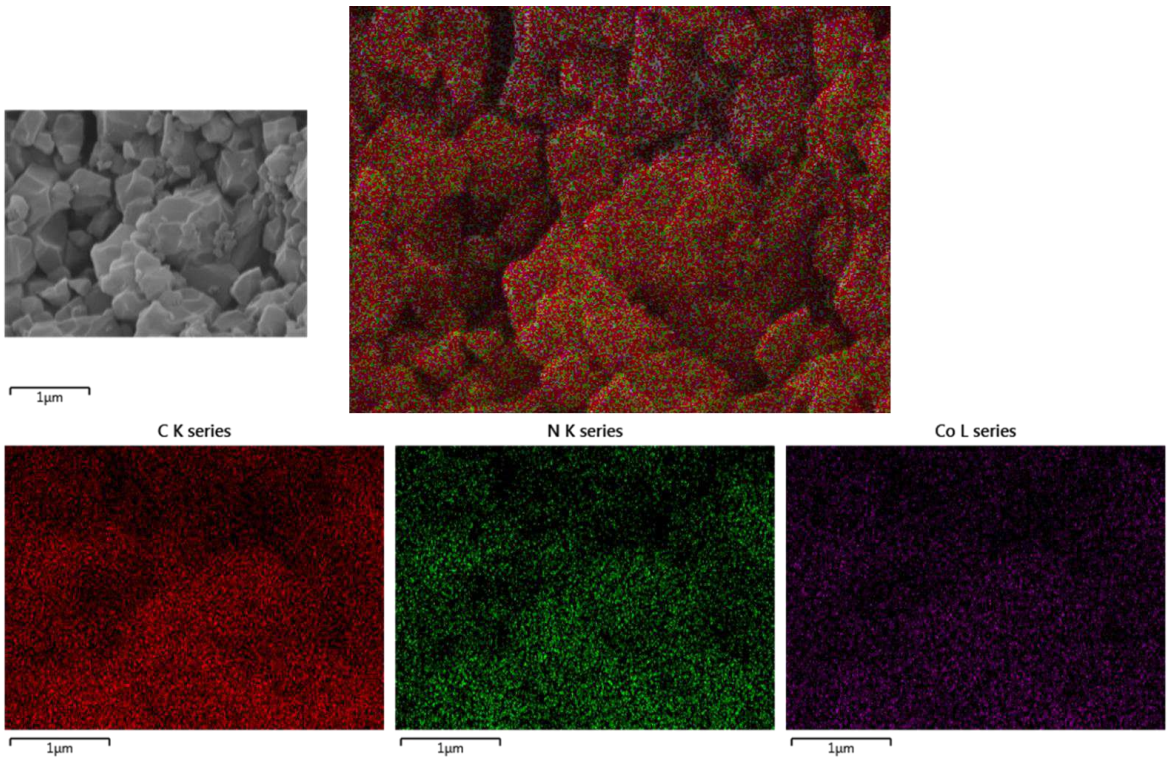

Figure 4: EDS mapping analysis for ZIF-67 synthesized using the IST approach.

Scanning electron microscopy (SEM) examination was used to look further into the morphological traits (form and particle distribution) of ZIF-8 and ZIF-67 (Figure 5). Figures 5a and 5b show a rhombic dodecahedral structure for ZIF-8, while Figures 5c and 5d show a normal rhombic dodecahedron for ZIF-67. Furthermore, the lack of a solvent in the IST approach caused larger particles to aggregate into crystals, which resulted in an uneven dispersion of the material. However, this result is in line with earlier studies in the literature.

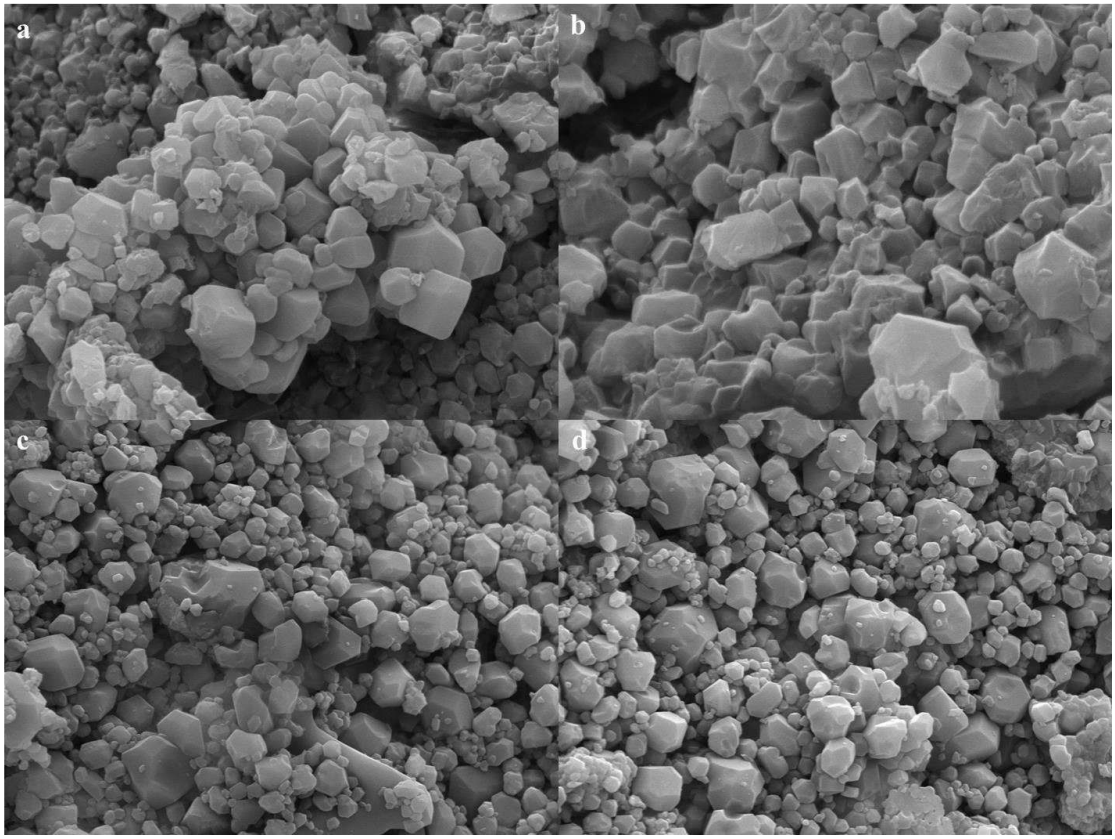

Figure 5: SEM analysis for ZIF-8 (a,b) and ZIF-67 (c,d) synthesized using the IST approach.

CONCLUSION

Specifically, ZIF-8 and ZIF-67, which are high porosity zeolitic imidazole frameworks were produced using an environmentally friendly, straightforward, and effective in situ thermal approach (IST). Rapid and effective synthesis is ensured by the solvent- and additive-free operation of this IST technology. Because of this, it has a lot of potential for large-scale production—as long as it stays affordable. During the production of IST, 2-methylimidazole plays three crucial roles at once: it acts as a ligand, a hydrophilic agent, and a solvent. There is no need for extra activation or purification procedures because the heat process efficiently removes all byproducts and residues, resulting in the development of a crystalline network. In the conclusion, the IST technique shows great promise for large-scale, ecologically benign synthesis of pure metal-organic frameworks.

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