



Synthesize Al-ZIF-8 & Al-ZIF-67 Composite via in Situ Thermal (ISI) Approach for Green Applications

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Abstract

To effectively manufacture ZIF-8 and ZIF-67 with different amounts of copper, an environmentally friendly and efficient in-situ thermal (IST) method based on 2-methylimidazole (2-MIM) as an organic linker was used. This IST technique has various benefits in comparison to earlier research, such as a reaction environment devoid of solvents and additives, gentle temperature conditions, a simpler single-step process, no activation needs, and the use of the lowest precursor ratio (M/L). Because of their large specific surface area, good porosity, and structural stability, Al/ZIF-8 and Al/ZIF-67 exhibit extraordinary catalytic activity when used in click chemistry. This may be ascribed to the click catalysts. The characteristics that were required in the catalysts were accomplished via the process of optimizing variables including time, temperature, gas environment, and precursor ratio. In order to verify the characteristics of the produced catalysts, a number of different approaches for characterizing them were used. In general, this environmentally friendly synthesis approach offers a mechanism for the production of metal-organic frameworks that is both scalable and sustainable, and it does so without the need of extra activation or treatment. In addition, the click reaction was carried out using water as a solvent, which not only contributed to the ecologically benign character of the technique but also resulted in high yields. Water was used as a solvent. Therefore, this novel technique has significant promise not just for use in academic research but also in applications on a wide scale in the industrial sector.

Keywords: In-situ thermal approach, Metal-organic frameworks, Aluminum-containing catalysts, Green synthesis.

1. Introduction

MOFs, which have a crystalline and porous structure and are made up of metal nodes and organic linkers, are the subject of current study owing to the unique qualities that they possess. These characteristics include a pore size that can be adjusted, great stability, and a large surface area. They have the potential to be used in a broad variety of sectors, including storage, medicine delivery, and catalysis, among others. Zeolitic-imidazole frameworks, also known as ZIFs, are a form of metal-organic framework (MOF) that feature metal centers that are coordinated with organic linkers. ZIFs have a tetrahedral structure with sodalite topology and may be produced utilizing a variety of metals in conjunction with organic linkers. The selection of metal centers, organic linkers, and reaction conditions are what ultimately decide the qualities possessed by ZIFs. Because of their high porosity and thermal stability, ZIFs have the potential to be useful in a variety of applications, including catalysis, the manufacture of biofuels, the administration of drugs, and separation. In these kinds of applications, a number of studies have shown that ZIFs may perform better than other types of materials, such as activated carbon, zeolites, and metal oxides [1, 2].

There are several different ways to synthesize MOFs and ZIFs, each of which may be used for a specific purpose. In the classic solvothermal process, metal sources and organic linkers are dissolved in an organic solvent prior to the heating step. This process takes place under a variety of different reaction conditions. However, this method does have a few downsides, including lengthy reaction durations, the use of organic solvents such as THF, DMF, and DEF, and restrictions on the usage of water as both a green solvent and a precursor. In addition, further treatment is required to be performed on the ZIFs that were obtained in order to eliminate any residual solvent molecules and achieve optimum application compatibility. Mechanochemical, microwave-assisted, and electrochemical synthesis are some of the most recent and cutting-edge technologies that have evolved as more environmentally friendly alternatives. Nevertheless, they come with their own set of drawbacks, such as the need of specialized equipment and intricate processes, the use of organic solvents and an excessive amount of energy, extended reaction periods, and the utilization of additives. As a consequence of this, there is a need for an environmentally friendly, innovative, and user-friendly way of synthesizing ZIFs on a wide scale, which is anticipated to be a problem for scientists in the foreseeable future [3, 4].

The use of zeolitic imidazole frameworks (ZIFs) as a catalyst has lately garnered a lot of interest in the scientific community. Metal-organic frameworks, in particular ZIFs, have the potential to be used in a wide variety of settings owing to their one-of-a-kind qualities and characteristics, as well as their little impact on the natural world and economical production procedures. Due to the presence of both acidic (metal nodes) and basic (imidazole) sites, ZIFs are suited for a diverse array of catalytic processes. It is possible to boost the catalytic activity of ZIFs by increasing the number of uncoordinated sites, also known as defect structures. This may be accomplished by increasing the pace at which the ZIFs crystallize. When compared to more conventional techniques of synthesis, a quick crystallization process carried out using the solvent-free In Situ Thermal (IST) approach may result in the formation of many defect structures. The IST technique is an environmentally benign, one-step process that creates highly porous crystalline ZIFs without the need for a solvent, activation, or post-

treatment to remove unreacted residue, side-products, and guest molecules. This method makes ZIFs in a manner that is single-step and requires just one process. This technique offers many benefits in comparison to more conventional approaches to synthesis, including a shorter processing time, the lowest precursor ratio (M/L), and the absence of a necessity for a solvent. In order to produce a material with superior crystalline and porosity characteristics, a number of synthesis parameters, including temperature, time, precursor, and gas environment, were subjected to optimization. The synthetic materials were put through a variety of tests to determine their chemical and physical characteristics, and the results revealed that they had potential for use in applications involving adsorption and catalysis. It is a revolutionary way for synthesizing ZIFs on a wide scale since the single-step IST procedure can be scaled up to a greater degree than other methods [5-8].

The synthesized ZIFs have a high porosity and the presence of basic imidazole sites, which makes them potential candidates for green catalytic applications such as the gas adsorption of CO₂ and CH₄ or the removal of micropollutant from the environment. In addition, the fact that Al-ZIF-8 and Al-ZIF-67 may be reused as heterogeneous catalysts is another evidence of the materials' high level of thermal and chemical resilience. Following the completion of four cycles, XRD and SEM measurements were used to investigate the structural soundness of the catalysts. The XRD, FTIR, EDS, TEM, BET, TGA, and ICP-OES methods were used to further study the physical, chemical, and structural characteristics of the ZIFs that were synthesized.

2. Material and Method

Materials

There was no need for purification of the following compounds: aluminum (III) acetylacetonate, zinc acetylacetonate hydrate, 2-methylimidazole, cobalt (II) acetylacetonate, or tetracycline. These compounds were employed as received.

The synthesis of Al-ZIF-8 and Al-ZIF-67

A combination of cobalt (II) acetylacetonate, 2-methylimidazole, and aluminum (III) acetylacetonate was manually produced in a mortar under ambient circumstances in order to synthesis Al/ZIF-67. This preparation took place at room temperature. For the synthesis of Al/ZIF-8, a process somewhat identical to this one was used, with the exception that the cobalt source was replaced by zinc acetylacetonate hydrate. After that, the powder combinations that were produced were moved to an alumina boat and put through a two-step temperature program in a muffle furnace while the environment in the furnace was composed of nitrogen. The final ZIF materials were gathered once the stipulated heating and cooling cycles had been completed.

3. Result and Discussion

An investigation of ZIF-8 and ZIF-67 samples containing varied amounts of aluminum was carried out using powder X-ray diffraction (XRD) methods, as shown in Figure 1. This was done in order to improve one's understanding of the crystalline properties. Figure 1 shows the results of this investigation. According to the findings of the XRD examination, both Al-ZIF-8 and Al-ZIF-67 had a crystal structure that was either body-centered cubic or polyhedral, respectively, which aligned very well with the information that had been previously provided. Adsorption of nitrogen dioxide was used to figure out the microporous structure, lasting

porosity, and stability of the samples that were manufactured. As shown in Figure 3, the nitrogen isotherm type I was present in all of the samples that were analyzed. Notably, Al-ZIF-67 and Al-ZIF-8 displayed hysteresis in the N₂ isotherm owing to variations in pore diameters, notably the existence of mesoporous with capillary condensation. This was the cause of the hysteresis. The quantity of copper that was included into the framework structure was shown to have a correlation with this occurrence. When the copper concentration was more than 30 weight percent, hysteresis was seen in the N₂ isotherm; however, the hysteresis loop was not present when the incorporation level was lower than 30 weight percent. The Brunauer–Emmett–Teller technique (BET) was used in order to ascertain the porosity qualities of the ZIFs that were manufactured. These values include surface area, pore size, pore volume, and Langmuir surface area. Both ZIF-8 and ZIF-67 saw a reduction in their surface area and porosity characteristics when the framework included a greater quantity of copper than before. This reduction may be ascribed to impurities, which can induce structural changes and possibly alter the opening and shutting of particular pores. Impurities can cause a decrease in the amount of pores that are available. In addition, the surface area followed a pattern that was mirrored by the porosity parameters, including pore volume and pore size (both of which were determined using the Horvath–Kwazoe technique). In order to evaluate both the chemical and thermal stability of the Al-ZIFs, a thermo gravimetric analysis (TGA) was carried out. As shown in Figure 2, weight fluctuations of the aluminum ZIFs were detected when exposed to an environment containing N₂. These observations were made at a range of temperatures. The Al-ZIF-8 sample had two distinct weight decreases during the TGA examination. The findings that were obtained by the use of energy dispersive spectrometry (EDS), which was used to measure the metallic content of the ZIFs (Zn, Co, and Al), are shown in Table 1. In addition, EDS was used in order to ascertain the amount of aluminum present in both ZIF-67 and ZIF-8.

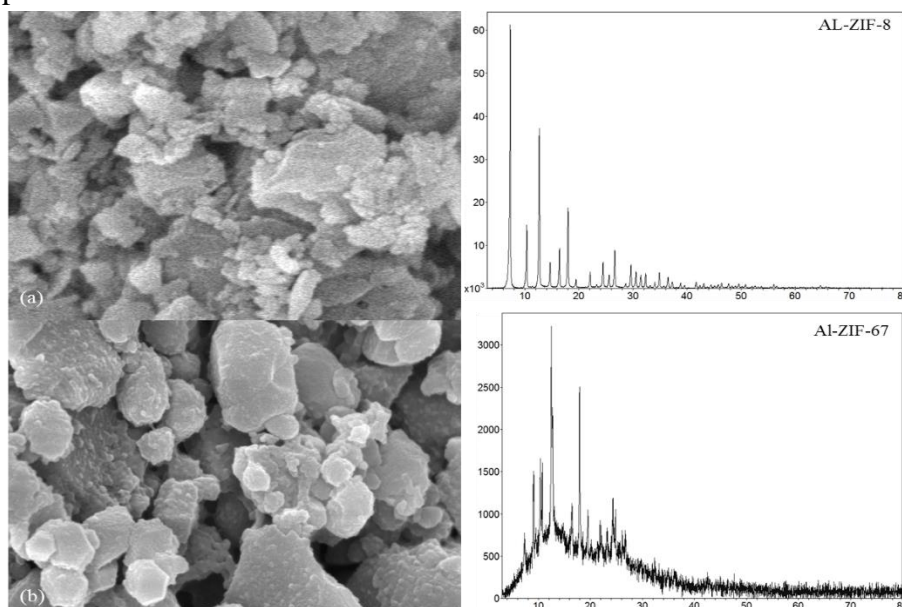


Figure 1 XRD analysis for AL-ZIFs synthesized using the IST approach.

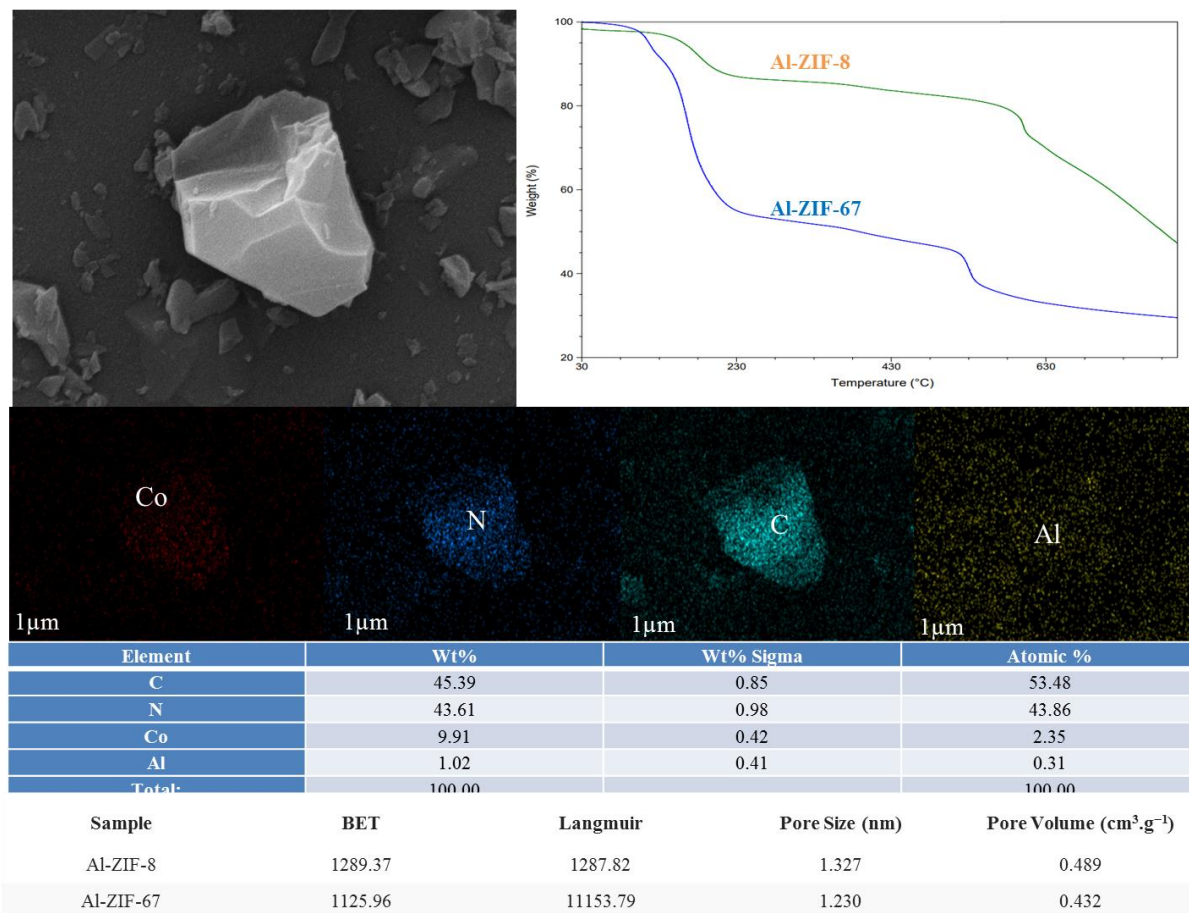


Figure 2 different analysis for AL-ZIF-67 synthesized using the IST approach.

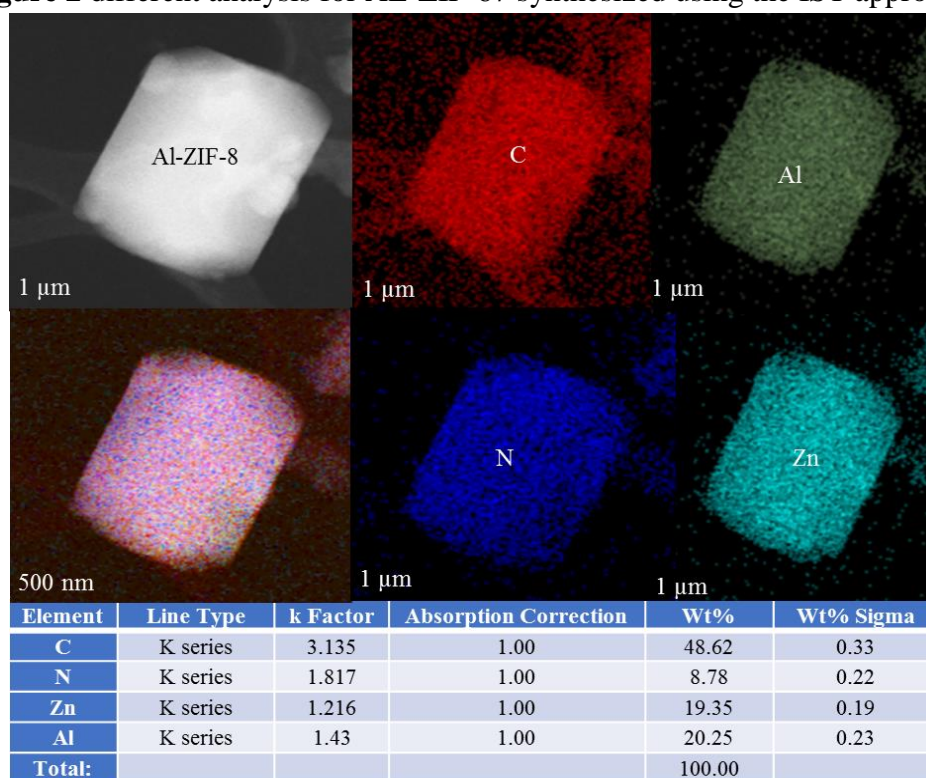


Figure 3. SEM mapping analysis for AL-ZIF-67 synthesized using the IST approach.

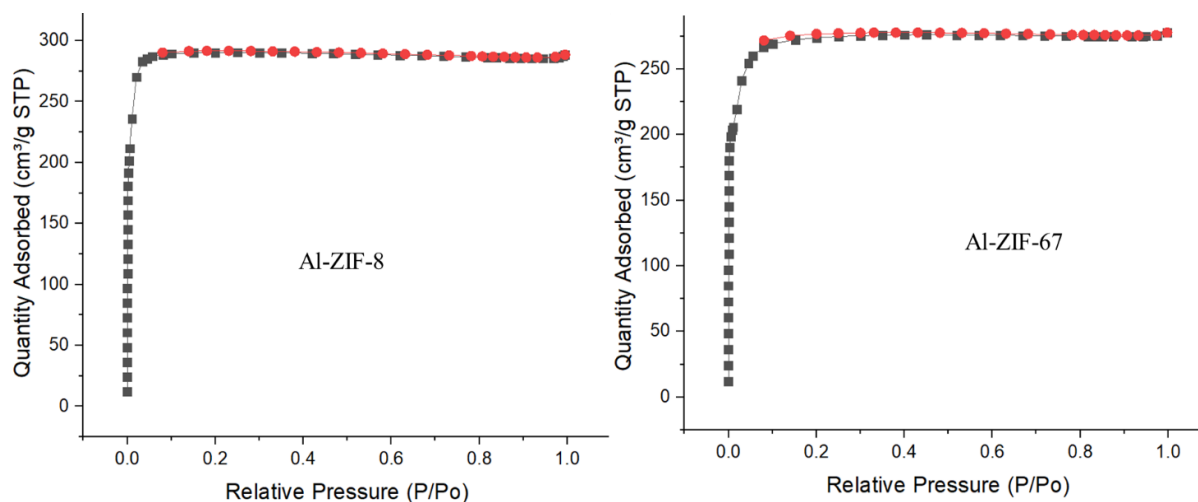


Figure 4. N_2 Isotherm for ZIFs synthesized using the IST approach.

4. Conclusion

Aluminum-infused zeolitic imidazole frameworks (Al/ZIF-8 and Al/ZIF-67) with good porosity were synthesized by using an environmentally friendly, uncomplicated, and efficient in situ thermal technique (IST). In the IST process, no solvents nor additives were employed; as a consequence, a high yield was accomplished in a relatively short amount of time. As a consequence of this, there is a substantial potential for the use of this method to synthesis on a big scale provided that it is economical. Notably, it was discovered that 2-methylimidazole served as a solvent, a hydrophilic agent, and a ligand all at the same time during the IST synthesis. This is an important finding that warrants more investigation. The use of heat allowed for the total removal of any potential byproducts or residues, which subsequently facilitated the development of a crystalline structure with clear boundaries. As a direct consequence of this, there was no need for any further activation or purification processes. The aluminum-containing ZIFs that were produced as a consequence showed extraordinary effectiveness when used as an agent for eliminating micropollutants from their natural environments. In the end, it becomes clear that the IST technique is a good contender for an ecologically benign, large-scale synthesis of pure metal-organic frameworks.

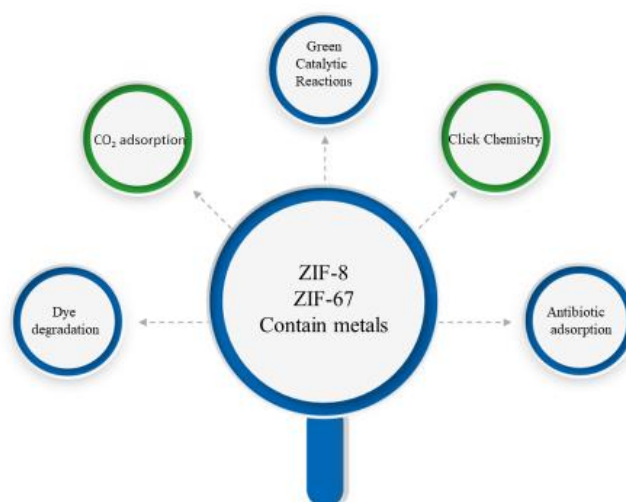


Figure 3. Different applications of ZIFs synthesized using the IST approach.

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