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Effect of the Solvent and Imidazole to Zinc Source Ratio on the Synthesis of Zeolitic Imidazolate Framework-8

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Abstract

Zeolite Imidazolate Frameworks (ZIFs) are a subset of Metal-Organic Framework (MOFs) with zeolite topology that has the desired properties of both zeolite and MOFs. They are a unique kind of nanoporous material combining rigid characteristics of inorganic compounds and the flexibility of organic linkers. In the manufacturing of electronic devices, MOFs have opened new ways to overcome issues of conventional materials. In this study, to investigate the effect of synthesis conditions in morphology, size distribution, and phase crystallinity, ZIF-8 was fabricated in aqueous or alcoholic media with different ratios of ligand/metal. It was revealed that morphology, size distribution, and phase crystallinity depended mostly on the type of solvent. The ZIF-8 nanoparticles obtained in methanolic media with a 1:35 molar ratio of 2-methyl imidazole: zinc nitrate, have the best quality.

Introduction

MOFs are crystalline microporous materials that form a broad crystalline network through strong bonds between metal ions and organic ligands [1- 6]. ZIFs are a popular class of MOFs with porous structures similar to zeolites that are made on quadrilateral networks attached to imidazolate ligands [7-11]. They have both the advantages of zeolite (stability) and MOF (adjustability), resulting in novel crystalline adsorbents [12, 13]. ZIF-8 is a type of extensively studied ZIF, that has a zeolite-like structure, composed of zinc ions and imidazolate [14]. ZIF-8 has a high specific surface area, adjustable pore size, chemical stability, and also relatively high-temperature stability [14]. ZIF-8 is produced on a large scale due to its excellent features, ease of preparation, and wide applications [15] such as catalyst [6], adsorption [17], gas storage and separation [18], sensors [19], biological applications (drug delivery) [20] and removal of contaminants [21]. ZIF-8 synthesis methods include hydro-solo thermal [22], microwave [23], ultrasonic [24], electrochemical [23], mechanical-chemical [25], diffusion [6] and solvent evaporation [26]. The room temperature synthesis methods, which ZIF-8 can be synthesized at a temperature lower than the boiling temperature of the solution, are suggested which are much easier and low-cost because of the omission of expensive autoclaves [22-27].

The synthesis conditions such as type of solvent and ligand/metal ratio have a strong impact on the physicochemical properties of ZIF-8, such as the morphology, crystallinity, and particle size. In this study, to investigate the synthesis conditions in morphology, crystallinity, and size distribution, ZIF-8 was synthesized with different molar ratios of raw materials and solvents, and then the samples were characterized and compared.

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Experimental

The chemicals used in this study were of analytical grade without any further purification. 2-methyl imidazole and zinc nitrate hexahydrate were prepared from Merck. ZIF-8 was synthesized under different conditions, according to Table 1. For a defined amount of 2-methylimidazole, 25 mL of the solvent was added and the resulting solution was stirred for 15 min. Then, a certain amount of zinc nitrate hexahydrate was added to 15 mL of the solvent (methanol or deionized water) and mixed for 15 min. The two prepared solutions were mixed for 20 hr. The resulting milky solution was centrifuged for 20 min and then washed. Finally, the remaining material was dried in an oven at 60 °C for 24 hours and the final product was obtained. X-ray diffraction (XRD) analysis was used to identify the crystalline structure using device model PW1730, topography, and morphology were determined by scanning electron microscope (FESEM) model MIRA3.

Table 1: Synthesis of ZIF-8 under different conditions.

Sample	$(ZnNo_3)_2$ $6H_2O$: 2 – Methyl Imidazole (molar ratio)	Solvent
ZIF(1)	1: 35	DI water
ZIF(2)	1: 35	methanol
ZIF(3)	1: 8	methanol
ZIF(4)	1: 8	DI water

Results and discussion

The FESEM results in **Figure 1,** indicate the morphology and particle size distribution of synthesized ZIF-8 samples. According to the FESEM images, in the ZIF(1) sample, a crystalline structure and there are no agglomerate particles and also an octagonal crystal is observed. In the ZIF (2), the sample has the pores and crystalline structure with a hexagonal crystal system as expected [28] and there is uniform particle size distribution. In ZIF (3) the crystalline structure is almost observable but the particles do not have a uniform size distribution. In ZIF (4) the particles are completely agglomerated and no crystalline structure is observed. The aggregation process derived by inter-crystal forces can be due to the weak separation level of the nucleus in a high polar aqueous system suggesting the structure-directing role of the solvent [21]. The histogram of the synthesized samples is given to investigate the particle size distribution. According to **Figure 2**, the maximum particle size frequency is about 100, 70, 90, and 120 nm, for ZIF (1), ZIF(2), ZIF(3), and ZIF(4), respectively. It can be said that samples ZIF (1) and ZIF(4) which synthesized from aqueous solvent have higher average particle size compared to samples ZIF(2) and ZIF(3) which is from the alcoholic solvent, also the histograms of these two samples don't have a uniform particle size distribution, while the two samples ZIF(2) and ZIF(3) have a homogeneous particle size distribution. Comparing the FESEM images of ZIF (1) with ZIF(2), and ZIF(3) with ZIF(4), it can be said that the use of methanol as solvent improves the uniformity of particle size distribution and so deionized water was removed from the conditions. Furthermore, the samples synthesized in an alcoholic medium illustrated more uniform mono-dispersed nanoparticles. Finally, by comparing the SEM images of ZIF(1) and ZIF(2) with the SEM images of ZIF(3) and ZIF(4), it can be said that the shape of ZIF-8 nanoparticles is variable by changing the molar ratio of metal ion and binder (2-methyl imidazole) [29]. The molar ratio of 1:35 was chosen as the best molar ratio. As a result, according to the results, the best ionic structure and uniform and homogeneous distribution are of ZIF(2), it can be said that the best conditions include a 1: 35 molar ratio and methanol solvent.

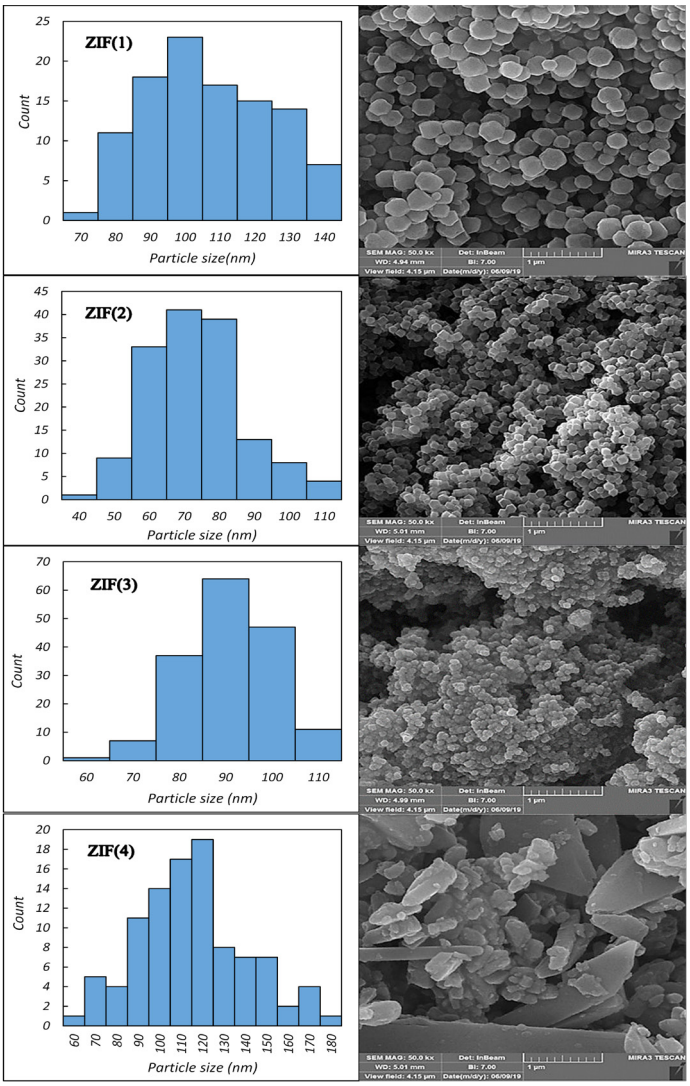

Figure 1: FESEM (left) and particle size distribution histogram (right), for the synthesized ZIF-8 samples.

To identify the crystalline structure of the particles, an X-ray diffraction pattern was taken from the samples. Then, compared with the standard diffraction pattern, and crystalline phase is identified. **Figure 2** shows the XRD pattern different conditions of ZIF-8 synthesized. According to the XRD results, ZIF(1), ZIF(2), and ZIF(3) samples showed characteristic reflections at 2θ angles at about 7.3, 10.4, 12.7, 16.4, 18.0° correspond to sodalite structure of ZIF-8 [12]. Characteristic peaks of ZIF(4) peaks were observed at 2θ = 11.6, 13.4, 15.8, 17.7, 18.6, 25.2, and 29.7, which illustrate its different structure to the other samples. On the other hand, the crystallinity of the samples was investigated according to XRD results. Relative crystallinity of the ZIF-8 samples is based on the major peak at 2θ value of about 7.3° and the crystal surface (110), which is defined by the formula (1) as follows:

$$\text{Relative crystallinity} = \frac{\text{Peak intencity of sample at (110) plane}}{\text{Peak intencity of reference at (110) plane}} \quad (1)$$

The relative crystallinities were obtained about 86.3, 100, 92.7, 2 percent for ZIF(1), ZIF(2), ZIF(3), and ZIF(4) samples, respectively. The results illustrate that the samples synthesized in an alcoholic medium have higher crystallinity compared with the ones produced in an aqueous medium that is consistent with the FESEM results.

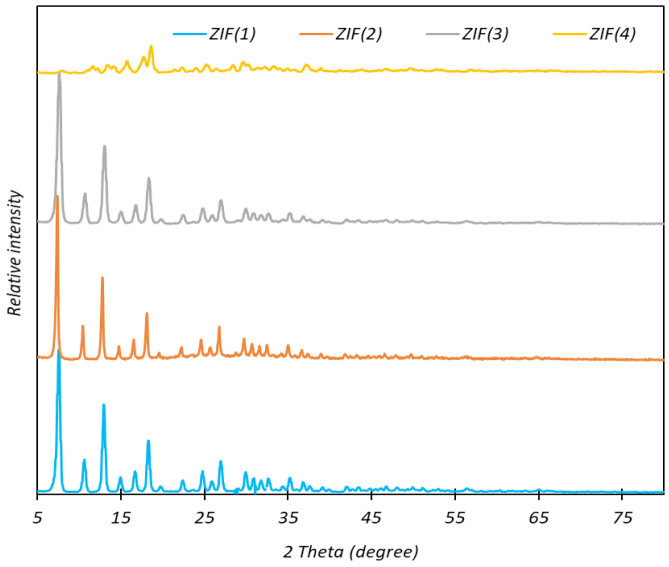

Figure 2: XRD analysis of ZIF-8 samples.

Figure 3 shows a proposed scheme that leads to the formation of ZIF-8. The proposed mechanism consists of three steps: linker coordination of zinc ions centers, deprotonation of the 2-methylimidazole linker, and finally oligomerization by linking together different centers through deprotonated 2-methylimidazole ligands. The methanol and water solvents are polar with different degrees of hydrogen bond donation characteristic and dielectric constants in solvating zinc ion, ligand, and acetate units. The structure-directing agent role of the solvents confirm by formation the hydrogen bonds between pyrrolic hydrogen of imidazole ring in ligand and electronegative oxygen head of solvent during ZIF-8 formation. The solvents act as mold in directing the structure through non-covalent interactions in bridging and stabilizing pores during the growth of cages [21]. The deprotonating 2-methylimidazole (mim- ions) in the solution is required to bridge the solvated zinc ions to form building units. However, the deprotonation of 2-methylimidazole is not able to occur in water because of its high pKa value equal to 14.2. Instead, the ligand 2-methylimidazole mostly runs a hydrolysis reaction in an aqueous solution. In an aqueous medium, reversible hydrolysis of linker takes place initially which produces (H2-methylimidazole)$^{+}$ and consequently increases the pH. Then complexation of zinc ions with 2-methylimidazole linker occurs simultaneously with reverse hydrolysis because of continuous consumption of 2-methylimidazole and shift of equilibrium to the left side of the hydrolysis reaction. The increase in the linker concentration and decrease in metal/linker ratio gives rise to an increase in the rate and extent of ligand exchange reactions between 2-methylimidazole linkers and methanol/water/nitrate ligands around zinc ions. Hence a higher linker concentration will lead to a zinc ion coordination sphere, which is more abundant in 2-methylimidazole linkers, established in a shorter time. As a result, a higher concentration of linker coordinated zinc ion complexes will result in an increased reaction rate of 2-methylimidazole deprotonation. These deprotonated zinc ions complexes are vital for nucleation since a single deprotonated 2-methylimidazole ligand can bridge two zinc ions centers, leading to oligomerization and therefore nucleus formation. It is thus expected that the nucleation rate increases for higher linker concentrations owing to the increase in the deprotonation rate, eventually yielding more nuclei/particles for higher linker concentrations, and more formed nuclei lead to smaller particles. This can be rationalized by the fact that metal and linker constituents in the solution are to be distributed amongst a larger number of nuclei for lower metal/linker ratios, leading to smaller particles [31-33].

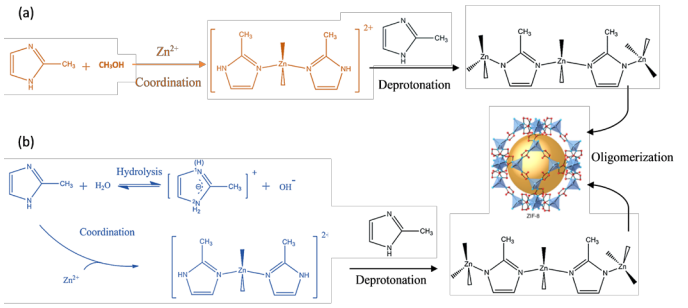

Figure 3: The suggested mechanism of formation of ZIF-8 crystals in **(a)** alcoholic and **(b)** aqueous solvents.

Conclusion

Here, to obtain the best quality of ZIF-8 in morphology, size distribution, and phase crystallinity, it was synthesized in aqueous or alcoholic media with different ratios of ligand/metal. The samples were characterized by X-ray diffraction and field emission scanning microscope. It was revealed that morphology, size distribution, and the phase crystallinity of final products depend mostly on the type of solvent. The ZIF-8 nanoparticles obtained in methanolic media with a 1:35 molar ratio of 2-methyl imidazole: zinc nitrate, have the best quality.

Conflict of interest

The authors have no conflict of interest to declare.

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Data availability: Not applicable.

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