Research Article

Evaluation of Structural Properties and Catalytic Activities in Knoevenagel Condensation Reaction of Zeolitic Imidazolate Framework-8 Synthesized under Different Conditions

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In the present study, the zeolitic imidazolate framework-8 (ZIF-8) was synthesized at both room temperature and high temperatures. The effects of solvents, molar ratios of precursors, reaction time, and temperature on the structural properties of the as-prepared materials were investigated. Moreover, the surface morphologies of the obtained specimens were characterized using X-ray diffraction, scanning electron microscopy, Fourier-transform infrared spectroscopy, and nitrogen adsorption methods. The results show that ZIF-8 was formed in methanol and water at room temperature and in dimethylformamide (DMF) at high temperatures. Further, in methanol, the molar ratios of precursors and reaction time have negligible effects on the morphologies and structures of ZIF-8; however, in DMF, the reaction temperature has a significant influence on the microstructures of ZIF-8. The catalytic activities of the obtained materials were evaluated using the Knoevenagel condensation reaction, and ZIF-8 proves to be an excellent solid base catalyst.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs) belong to the family of metal-organic frameworks (MOFs) and possess unique properties (uniform small pores and high surface area) of both zeolites and MOFs [1, 2]. In ZIFs, divalent metal cations are found to be tetrahedrally coordinated with the imidazolate anions [2, 3]. In recent years, ZIFs have attracted significant attention in gas storage and separation applications [4, 5], catalytic reactions [6], chemical processes [7, 8], and drug delivery systems [9]. ZIF-8 is one of the most studied zeolitic imidazolate frameworks due to its high chemical and thermal stabilities. In addition, ZIF-8 has a large surface area ($S_{\text{BET}} = 1630 \text{ m}^2 \cdot \text{g}^{-1}$) and high porosity ($0.636 \text{ cm}^3 \cdot \text{g}^{-1}$) [2]. In previous studies, ZIF-8 is synthesized in DMF at high temperature and pressure [2, 3]. ZIF-8 can also be synthesized in methanol at room temperature under normal pressure [2, 10–14]. In these two approaches, the

solvents and temperature/pressure have a critical role in the formation of ZIF-8. However, there have not been any studies dealing with this issue.

The Knoevenagel condensation is an important reaction for the formation of carbon-carbon double bonds. The reaction is traditionally catalyzed by conventional bases such as KOH, NaOH, or amine compounds [15]. Today, many researchers have conducted this reaction with different precursors by using solid base catalysts to expand their applicability in the organic synthesis industry [16–18]. Recently, Tran et al. [19] have studied the catalytic activity of ZIF-8 by the Knoevenagel condensation reaction and advocated its feasibility as a catalyst.

In the present work, ZIF-8 was synthesized in two different routes. The effects of solvents, molar ratios of precursors, reaction time, and temperature on the structural properties of the as-prepared materials were investigated. In addition, the catalytic activities of the fabricated materials

were evaluated using the Knoevenagel condensation reaction.

2. Experimental

2.1. Synthesis and Characterization of ZIF-8. ZIF-8 was synthesized via two different routes using zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Fisher) and 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%, Acros) (denoted as meIm) precursors.

- (i) Process A was performed according to Zhu et al. [20]. In a typical process, 8 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 1.4 mol methanol (CH_3OH , 99.9%, Fisher) (denoted as MeOH) (solution 1) and 64.4 mmol meIm was dissolved in 1.4 mol MeOH (solution 2). Solution 2 was then added to solution 1, and the as-prepared mixture was stirred for 8 h. Finally, the obtained ZIF-8 powder (denoted as Z-A(MeOH)) was collected using centrifugation at 3000 rpm, washed three times with MeOH, and dried overnight at 100°C.
- (ii) Process B was carried out according to Bushell et al. [21]. In a typical process, 7.20 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4.48 g meIm were first dissolved in 90 mL dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, $\geq 99.5\%$, Fisher) (denoted as DMF) and the prepared solution was then heated in a Teflon-lined steel autoclave (volume of 200 mL) for three days at 100°C. The as-produced white solid material was collected using filtration, washed in a Soxhlet apparatus for two days with MeOH, and dried at 100°C to obtain ZIF-8 (denoted Z-B(DMF)).

The effects of solvents, molar ratios of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and meIm, reaction time, and temperature on the structural properties of the as-prepared ZIF-8 samples were further studied.

Characterization. X-ray diffraction (XRD) patterns were recorded on a VNU-D8 Advance Instrument (Bruker, Germany) under-Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The N_2 adsorption/desorption isotherm measurement test was performed at 77 K in a Tristar 3000 analyzer, and before setting the dry mass, the samples were degassed at 250°C with N_2 for 5 h. Scanning electron microscopy (SEM) images were obtained using an SEM JMS-5300LV (Japan), and infrared spectra (IR) were recorded in a Jasco FT/IR-4600 spectrometer (Japan) in the range of 4000–400 cm^{-1} .

2.2. Knoevenagel Reaction. The Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate was carried out according to Martins et al. [18]. In the reaction, 1.07 g (10 mmol) benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$, 98%, Acros), 1.04 g (10 mmol) ethyl cyanoacetate ($\text{NCCH}_2\text{CO}_2\text{C}_2\text{H}_5$, 98%, Acros), and 15.42 g toluene ($\text{C}_6\text{H}_5\text{CH}_3$, 99.9%, Duksan) were added to a glass reactor and stirred at 30°C. When the temperature became stable, 0.1 g of ZIF-8 was added. After 6 h of reaction, the solution was centrifuged to remove the catalyst. The compositional analysis of the reactants and

products in the liquid sample was executed using a GC-MS chromatograph (Agilent GC-MS 7890).

The conversion and the selectivity were calculated according to the following equations:

$$\begin{aligned} \text{conversion (\%)} &= \frac{\text{moles of reacted benzaldehyde}}{\text{moles of initial benzaldehyde}} \times 100, \\ \text{selectivity (\%)} &= \frac{\% \text{product of ethyl-2-cyano-3-phenylacrylate}}{\% \text{total products}} \\ &\quad \times 100. \end{aligned} \quad (1)$$

3. Results and Discussion

3.1. Structural Properties of Z-A(MeOH) and Z-B(DMF). Figure 1(a) exhibits the XRD patterns of ZIF-8 synthesized with process A and process B. The diffraction peak (011) at $2\theta = 7.2^\circ$ is observed in both samples, indicating their high crystallinities [2, 10, 12, 20, 22]. However, the intensity of diffraction peaks in Z-B(DMF) is higher than that in Z-A(MeOH), and this means that Z-B(DMF) has higher symmetric planes.

The FT-IR spectra of both Z-A(MeOH) and Z-B(DMF) are displayed in Figure 1(b), and the findings are consistent with earlier reported results [19, 23, 24]. The bands at 3122 cm^{-1} and 2920 cm^{-1} are associated with the aromatic and the aliphatic C-H asymmetric stretching vibrations, respectively. The band at 1668 cm^{-1} is attributed to the C=C stretching mode, and the band at 1574 cm^{-1} is assigned to the C=N stretching mode. The bands at 1300–1460 cm^{-1} are associated with the entire ring stretching, whereas the band at 1140 cm^{-1} is formed from the aromatic C-N stretching mode. Similarly, the bands at 991 cm^{-1} and 748 cm^{-1} could be assigned to the C-N bending vibration mode and to the C-H bending mode, respectively. Moreover, the band at 690 cm^{-1} is developed due to the ring out-of-plane bending vibration of imidazolate. The sharp band at 416 cm^{-1} formed due to Zn-N stretching indicates that zinc atoms are connected to the nitrogen atoms in the 2-methylimidazolate linkers.

The surface morphologies of the materials synthesized with the two approaches are totally different. Z-A(MeOH) comprises cubic crystals, hexagonal-faceted crystals, and rhombic dodecahedrons (with an edge of $\sim 100 \text{ nm}$) (Figures 2(a) and 2(b)). In contrast, Z-B(DMF) has truncated rhombic dodecahedrons with varying particle sizes of 3–20 μm (Figures 2(c) and 2(d)) [19, 22, 25]. Hence, compared with Z-A(MeOH), Z-B(DMF) yields high and sharp diffraction peaks due to its clear crystal planes and large crystal size.

In process A, the formation path of ZIF-8 depends on the reaction time [10, 11]. However, in process B, ZIF-8 was prepared in DMF at 100°C in three days; hence, a fully crystalline ZIF-8 phase was obtained.

Figure 3 displays the nitrogen adsorption/desorption isotherms of Z-A(MeOH) sample and Z-B(DMF) sample at 77 K. According to the classification of IUPAC, the isotherm curves belong to type-I, indicating that Z-A(MeOH) and Z-B(DMF) are microporous materials. The specific

FIGURE 1: (a) XRD patterns and (b) FT-IR spectra of Z-A(MeOH) and Z-B(DMF) samples.

FIGURE 2: SEM images of Z-A(MeOH) (a, b) and Z-B(DMF) (c, d).

surface area of Z-A(MeOH) and Z-B(DMF) is $1279 \text{ m}^2 \cdot \text{g}^{-1}$ and $1415 \text{ m}^2 \cdot \text{g}^{-1}$, respectively (Table 1). These values are higher than those of ZIF-8 synthesized with other routes [23, 26].

3.2. Effects of Solvents. Solvents play an important role in the ZIF-8 synthesis. Earlier studies reported that ZIF-8 can be formed in different solvents: DMF [19, 21], methanol [2, 10–14], and water [25]. Therefore, in our experiment, the effects of different solvents (methanol, DMF, water, and toluene) on the ZIF-8 formation were investigated in detail.

Table 2 describes the characteristics of ZIF-8 obtained from process A and process B with different solvents.

It is clear that toluene is an unsuitable solvent for the ZIF-8 synthesis. This can be attributed to the very small dipole moment of toluene (0.36 D) compared with that of methanol (1.69 D), water (1.85 D), and DMF (3.86 D), and the deprotonation of a melm compound cannot occur to form a melm⁻ ion.

Figure 4 shows that the synthesized samples in water have characteristic diffraction peaks (at $2\theta < 30^\circ$) and

FIGURE 3: Nitrogen adsorption/desorption isotherms of Z-A(MeOH) sample (a) and Z-B(DMF) sample (b).

TABLE 1: Porous properties of ZIF-8 samples.

Sample	BET surface area ($\text{m}^2\cdot\text{g}^{-1}$)	t-plot micropore area ($\text{m}^2\cdot\text{g}^{-1}$)	t-plot external surface area ($\text{m}^2\cdot\text{g}^{-1}$)	t-plot micropore volume ($\text{cm}^3\cdot\text{g}^{-1}$)
Z-A(MeOH)	1279	1237	42	0.604
Z-B(DMF)	1415	1412	3	0.642

TABLE 2: Characteristics of ZIF-8 obtained in different solvents.

Solvent	Product (state, color, and abundance ratio)	
	Process A	Process B
Methanol	Solid, white, medium*	Solid, milk white, very small
DMF	Gel, white	Solid, white, medium**
Water	Solid, white, large	Solid, white, large
Toluene	Solid, gray, very small	Gel, white

*Z-A(MeOH) sample; **Z-B(DMF) sample.

characteristic vibration bands. However, in process B, the diffraction peaks at $2\theta = 31.73^\circ$, 34.4° , 36.23° , and 47.48° and the band at 492 cm^{-1} indicate the existence of ZnO oxides and Zn-O bonds in ZIF-8 [26]. This can be ascribed to the hydrolysis of Zn^{2+} ions in water at high temperatures.

The morphologies of the synthesized samples in water are displayed in Figure 5. In process A, the surface morphologies of ZIF-8 are indeterminate (Figures 5(a) and 5(b)). On the contrary, the microstructures of ZIF-8 synthesized in process B consist of hexagonal cylinders and cubic crystals (Figures 5(c) and 5(d)).

The results in Table 2 indicate that the solvent exchange between the two processes did not lead to the formation of ZIF-8. This is due to large differences in the boiling temperature and dipole moment of the solvents, indicating that solvents play an important role in the synthesis of ZIF-8.

3.3. Effects of Synthesis Time and meIm/Zn Molar Ratios.

Figure 6 displays the SEM images of the synthesized ZIF-8 samples at two different stirring intervals—two days and five

days. Both samples have mainly hexagonal and rhombic dodecahedron crystals of a diameter of $\sim 100\text{ nm}$. Further, their very sharp diffraction peaks appear at 2θ below 10° , indicating the formation of highly crystalline materials (Figure 7(a)).

The XRD patterns of the samples synthesized at different meIm/Zn molar ratios are presented in Figure 7(b). In all cases, the amounts of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and methanol were kept constant. No conspicuous difference was noticed in the XRD peaks of the samples; however, their relative crystallinities slightly decrease as the meIm/Zn molar ratio increases from 64.4/8 to 100/8. These findings are well consistent with those reported by Zhang et al. [24].

3.4. Effects of Synthesis Temperature. The effects of reaction temperature on ZIF-8 synthesized with the process B are depicted in Figure 8. Noticeably, better cohesion of particles in the sample synthesized at 200°C reduces the intensities of diffraction peaks at larger angles. However, as the reaction temperature increases, the intensities of diffraction peaks at angles less than 10° become higher, indicating the formation of ZIF-8 with higher crystallinities.

In conclusion, the meIm/Zn molar ratios, reaction time, and temperature have an impact on the crystallinity of ZIF-8 but do not affect its crystalline structure.

3.5. Catalytic Test. The Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate to form ethyl-

FIGURE 4: (a) XRD patterns and (b) FT-IR spectra of ZIF-8 synthesized in water.

FIGURE 5: SEM of ZIF-8 synthesized in water: process A (a, b); process B (c, d).

2-cyano-3-phenylacrylate (Scheme 1) was used to test the catalytic activities of the synthesized ZIF-8 samples.

The effect of different ZIF-8 samples on the Knoevenagel condensation reaction is illustrated in Figure 9. Evidently, all synthesized samples exhibit excellent catalytic activities in the Knoevenagel condensation reaction (the benzaldehyde conversion in the catalytic reactions is considerably higher than that in the reactions without catalysts). Figure 9(a) shows that the conversion of benzaldehyde depends on the crystallinity of ZIF-8. The conversion is greater when the

intensity of diffraction peaks at $2\theta < 10^\circ$ is higher (Figures 1(a), 7(a), and 8(b)). Specifically, ZIF-8 synthesized with process B at $200^\circ C$ has the highest yield. In addition, the selectivity of ethyl-2-cyano-3-phenylacrylate always remains close to 100% (Figure 9(b)), indicating that the formation of benzoic acid during the catalytic reaction is negligible.

The Knoevenagel condensation reaction is commonly catalyzed by liquid or solid bases. ZIF-8 is a bifunctional catalyst composed of both acidic (Lewis acid Zn^{2+} ions) and basic sites (imidazole groups) [20]. It was noticed that the

FIGURE 6: SEM images of ZIF-8 crystals synthesized with process A as a function of synthesis time: (a) two days; (b) five days.

FIGURE 7: XRD patterns of ZIF-8 crystals synthesized with process A: (a) different synthesis times; (b) different meIm/Zn molar ratios.

FIGURE 8: SEM image (a) and XRD patterns (b) of ZIF-8 samples synthesized with process B at different temperatures.

catalytic activities of ZIF-8 are governed by the basic sites of imidazoles. To evaluate the durability of ZIF-8 catalyst for the Knoevenagel reaction, Tran et al. also test the leaching of

the 2-methylimidazole linker [19]. They conclude that the ZIF-8 solid catalysts remain stable, and no contribution of homogeneous catalysis due to active acid species leaching

SCHEME 1: Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate.

FIGURE 9: Effect of various ZIF-8 samples on the Knoevenagel condensation reaction: (a) benzaldehyde conversion (%); (b) ethyl-2-cyano-3-phenylacrylate selectivity ((1) without a catalyst; (2) Z-A(MeOH); (3) Z-B(DMF); (4) ZIF-8 sample synthesized with process A for five days; and (5) ZIF-8 sample synthesized with process B at 200°C).

TABLE 3: Effect of the different catalysts on Knoevenagel condensation.

Catalyst	Precursors	Reaction condition	Benzaldehyde conversion (%)	References
ZIF-8*	Benzaldehyde (10 mmol) and ethyl cyanoacetate (10 mmol)	30°C, 6 h, 0.1 g of the catalyst	76.5	The present work
ZIF-8	Benzaldehyde (1.9 mmol) and malononitrile (1.9 mmol)	Room temperature, 6 h, 0.02 g of the catalyst	51	[19]
MCM-41	Benzaldehyde (10 mmol) and diethyl malonate (10 mmol)	Room temperature, 24 h, 0.025 g of the catalyst	56–70	[16]
Amine-MCM-41	Benzaldehyde (10 mmol) and diethyl malonate (10 mmol)	Room temperature, 24 h, 0.025 g of the catalyst	78–92	[16]
[CTA ⁺]-Si-MCM-41	Benzaldehyde (4.8 mmol) and ethyl cyanoacetate (4.8 mmol)	30°C, 3 h, 20 mg of the catalyst	57.2	[17]

* ZIF-8 sample synthesized with process B at 200°C.

into the reaction solution is found. Thus, in the ZIF-8 sample synthesized with process B at 200°C, the Lewis acid Zn^{2+} sites may become saturated; hence, the decrease in densities of the Lewis acid sites results in more base sites from the imidazole linkers.

A comparison of the benzaldehyde conversion of the Knoevenagel condensation with different catalysts is shown in Table 3. Although the reaction conditions are different, the benzaldehyde conversion of this study is higher (76.5% compared with 51–70%) or consistent with that of previous studies (78–92%).

4. Conclusions

ZIF-8 was formed in methanol and water at room temperature and in DMF at high temperatures (100–200°C). In methanol, the reaction time and meIm/Zn molar ratio have small effects on the microstructures (uniform particles of ~100 nm diameter) of ZIF-8; however, the diffraction peaks at the angles smaller than 10° had slight variations. In contrast, ZIF-8 synthesized in DMF manifests full crystallinity with varying particle sizes (3–20 μm) with the better cohesion of particles observed at 200°C. All ZIF-8 samples

exhibit excellent catalytic activities in the Knoevenagel condensation reaction because of the base sites of imidazoles. When ZIF-8 are highly crystalline (samples synthesized in MeOH for five days and in DMF at 200°C), the activities of the base sites of imidazole prevail those of the Lewis acid sites of Zn^{2+} , resulting in a higher conversion of benzaldehyde.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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