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Exploring the Influence of the Reused Methanol Solution for the Structure and Properties of the Synthesized ZIF-8

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Abstract: The zeolitic imidazolate framework-8 (ZIF-8), as a kind of MOF, is widely used in sensors, gas storage/separation, drug delivery, and catalysis due to its adjustable porous structure, high surface area, and excellent chemistry tunability. ZIF-8 is constructed by Zn^{2+} and 2-methylimidazole and synthesized in the methanol solution. In this paper, we explored the influence of the reused methanol solution for the structure and properties of the synthesized ZIF-8. The as-synthesized ZIF-8 was characterized by an X-ray diffraction instrument (XRD), a scanning electron microscope (SEM), a specific surface area analyzer (BET), and Fourier transform infrared spectroscopy (FT-IR). The results show that the reused methanol solution does not change the phase, porous structure, and BET surface area of ZIF-8. However, the particle size of ZIF-8 increases from 50 nm to 5 um and the productive rate decreases to 7.4% when the methanol solution is reused four times. This work provides new insight into the reuse of dissolvents for the synthesis of MOFs.

Keywords: ZIF-8; methanol solution; particle size; productive rate

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1. Introduction

Metal organic frameworks (MOFs), constructed by metal ions or metal clusters and organic ligands, are a kind of porous organic or inorganic hybrid material with a periodic network structure, and has drawn much attention as a fascinating material for the researchers [1–3]. The chemical composition and periodic network structure of MOFs can be adjusted within a certain range, which makes the synergistic combination of properties a reality [4,5]. They are widely used in sensor, gas storage/separation, drug delivery, and catalysis due to their adjustable chemical compositions, periodic network structure, good crystallinity, high surface area, and excellent chemistry tunability [6–9].

As a kind of MOF, zeolitic imidazolate frameworks (ZIFs) are composed of Zn^{2+} or Co^{2+}, as well as imidazole or imidazole derivatives, and exhibit a zeolite skeleton structure. Until now, ZIFs have been widely used in many fields, such as CO_2 capture, H_2 storage, and catalysis, due to their outstanding properties [10–12]. Zeolitic imidazolate framework-8 (ZIF-8) is constructed by Zn^{2+} and imidazole (Im) units, exhibits the zeolite sodalite (SOD) topology, and generates a resistant structure with large cages interconnected via narrow six-ring windows [13]. Compared with other MOFs, ZIF-8 has higher chemical and hydrothermal stability. For example, ZIF-8 can also retain its structure properties when it is treated at high temperatures, even up to 500 °C. Furthermore, ZIF-8 can also maintain its high crystallinity and porous structure properties when it is put into water and organic solvents [14]. The pore sizes and structure of ZIF-8 is also tailorable [15]. Now, ZIF-8 is widely applied in many forms, such as membranes, colloid, and powders [16–18].

Methanol is the most commonly used solvent for the fabrication of ZIF-8. It weakly interacts with the ZIF-8 and can be removed more easily than more pore solvents such as DMF [19]. For example, Aleksandra Schejn and his co-workers used methanol as an organic solvent to synthesize ZIF-8 and control its nano- and microcrystal formation and reactivity though zinc salt variations [20]. That, the wide use of methanol can cause great waste and pollution for the environment. Nilay Keser Demir and his co-workers used mother liquor to synthesize ZIF-8 by adding only the initial amount of Zn^{2+} to the liquor, adjusting the pH of the mother liquor [21]. However, they did not report the influence of mother liquors to the structure and properties of the synthesized ZIF-8 by adding the same content of 2-methylimidazole and zinc nitrate hexahydrate. In this paper, we used the methanol solution as dissolvent to synthesize ZIF-8, collected the methanol solution and used it as dissolvent to synthesize ZIF-8 four times. We used XRD, SEM, FT-IR, and BET technologies to characterize the synthesized product and explored the influence of the reused methanol solution for the structure and properties of the synthesized ZIF-8. We hope this study can provide a reference for the following researchers applying themselves to synthesize MOFs with economical and environmental friendly methods.

2. Materials and Methods

2.1. Materials and Regents

Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$], 2-methylimidazole ($C_4H_6N_2$), methanol, and ethanol were all the analytical reagents and purchased from the Sinopharm Chemical Reagent Co., Ltd. (China, Shanghai). All reagents were directly used without any additional purification.

2.2. Synthesis of ZIF-8 by the Reused Methanol Solution

ZIF-8 was synthesized by the following procedure. Firstly, 22.5 g of $Zn(NO_3)_2 \cdot 6H_2O$ was absolutely dissolved into 100 mL of methanol. Secondly, the above solution was poured into another 100 mL of methanol containing 19 g of $C_4H_6N_2$. The mixture was stirred 5 min and then aged at 60 °C for 15 h. Then, the white precipitate was centrifuged, washed by ethanol and dried at 60 °C to obtain the ZIF-8. Following, the above methanol solution was retrieved to synthesize ZIF-8 by the same method. In order to make comparison, the synthesized ZIF-8 was labeled as ZIF-8(X) (X represents the reused time of the methanol solution).

2.3. Characterization

The X-ray diffraction of all synthesized samples was characterized on a Bruker D8 Advance, using Cu-Ka radiation and operating at 40 kV and 40 mA. Scanning electron microscopy (SEM) was carried out on a Tescan-VEGA3SBH at an accelerating voltage of 10 kV. N_2 adsorption–desorption isotherms were obtained from a Bei Shi De (3H-2000PS4) instrument at −196 °C after degassing the samples at 150 °C for 8 h. FT-IR examination was performed on a spectrophotometer (Bruker VERTEX 70 & ALPHA) in the 400–4000 cm^{-1} range. The mass of the synthesized sample was directly measured on an electronic balance (3H-2000PS4).

3. Results and Discussion

3.1. XRD Patterns Analysis

Figure 1 shows the XRD patterns of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4). All samples almost show the same XRD patters and exhibit six obvious peaks at 7.53°, 10.58°, 12.93°, 14.84°, 16.67° and 18.24°, corresponding to the (011), (002), (112), (022), (113), and (222) planes of ZIF-8, respectively (JCPDS 00-062-1030) [22,23]. This indicates that all samples have the same phase of ZIF-8 and the reused methanol solution does not affect the structure of the synthesized ZIF-8.

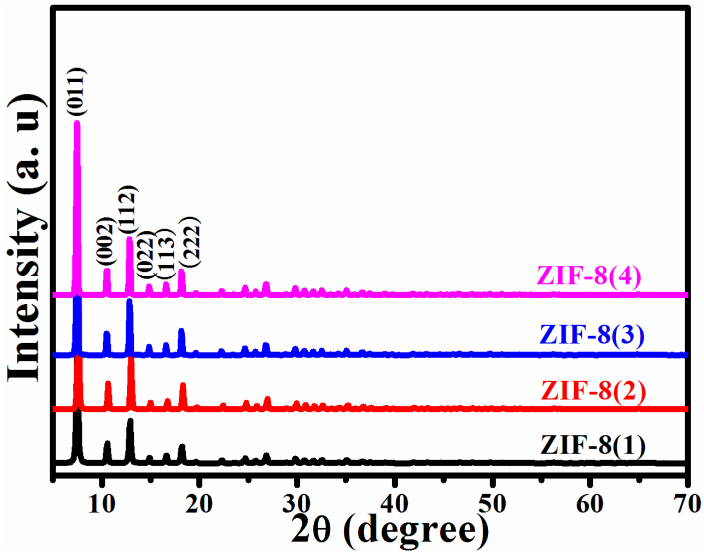

Figure 1. XRD patterns of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4).

3.2. SEM Image Analysis

The morphology of all samples was directly observed on the scanning electron microscopy and the results are shown in Figure 2. Figure 2a shows the SEM image of ZIF-8(1), which exhibits a polyhedral structure with a particle size of about 50 nm. Then, the above methanol solution was retrieved and used to synthesize the ZIF-8(2). Figure 2b shows the SEM of ZIF-8(2). Compared with ZIF-8(1), ZIF-8(2) also exhibits a polyhedral structure. However, its particle size increases to about 800 nm. Figure 2c shows the SEM image of ZIF-8(3). The morphology of ZIF-8(3) is more regular than ZIF-8(1) and ZIF-8(2) and its particle size further increases to about 2 um. Figure 2d shows the SEM image of ZIF-8(4), which shows a strip structure. The particle size of ZIF-8(4) is about 5 um. This reveals that the reused methanol solution is beneficial to the growth of the lattice plane of ZIF-8 at the same condition.

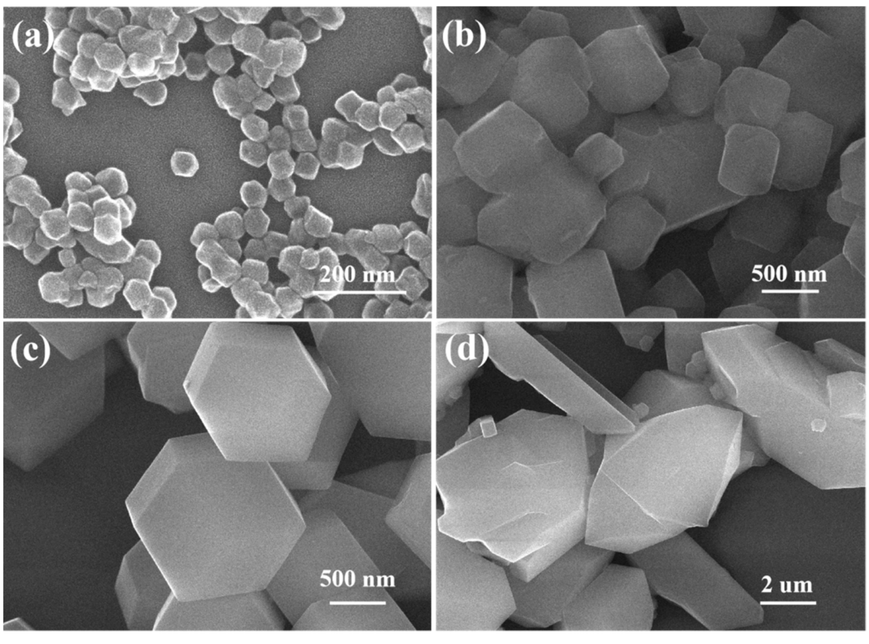

Figure 2. SEM images of (**a**) ZIF-8(1), (**b**) ZIF-8(2), (**c**) ZIF-8(3), and (**d**) ZIF-8(4).

3.3. FT-IR Spectra Analysis

The FT-IR spectra of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4) are illustrated in Figure 3. As shown in Figure 3, ZIF-8(1) exhibits peaks in the bands of 2500–3500 cm^{-1}, which are ascribed to the stretching vibration of the functional groups, such as -OH, $-CH_3$, and -NH- [24]. The peaks at 1585 and 422 cm^{-1} are axial deformations of C = N and Zn-N, respectively [25]. The peaks in the 1300–1500 cm^{-1} bands originate from the stretching of imidazole ring [26]. The above signals are ascribed to the characteristic peaks of the ZIF-8 framework. ZIF-8(2), ZIF-8(3), and ZIF-8(4) have almost the same FT-IR spectra with ZIF-8(1). This confirms the existence of the framework of ZIF-8 in ZIF-8(2), ZIF-8(3), and ZIF-8(4).

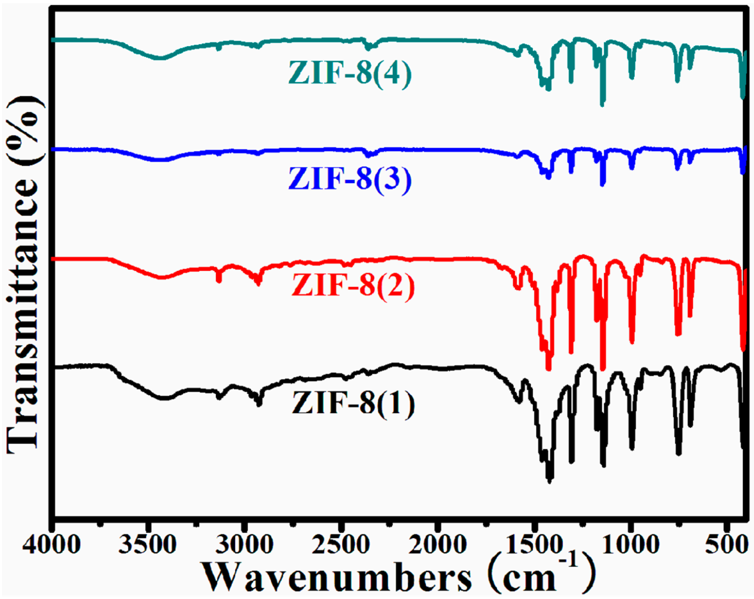

Figure 3. FT-IR spectra of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4).

3.4. N_2 Adsorption–Desorption Isotherms Analysis

Figure 4 shows the N_2 adsorption–desorption isotherms of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4). All samples exhibit a significant high uptake in the $P/P_0 < 0.1$ region, which is ascribed to the type I isotherm, indicating the presence of microporosity in ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4). The corresponding textural parameters of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4) are shown in Table 1. All samples almost have the same pore size property and BET surface area. This indicates that the reused methanol solution does not change the textural parameters of the synthesized ZIF-8.

Table 1. Textural parameters of (a) ZIF-8(1), (b) ZIF-8(2), (c) ZIF-8(3), and (d) ZIF-8(4).

Sample	S_{BET} [a]	V_{total} [b]	V_{micro} [c]	D [d]
ZIF-8(1)	1308.5	0.651	0.643	0.551
ZIF-8(2)	1292.3	0.642	0.639	0.551
ZIF-8(3)	1331.7	0.667	0.658	0.551
ZIF-8(4)	1322.9	0.663	0.653	0.551

[a] BET surface area (m^2/g), [b] total pore volume (cm^3/g), [c] t-plot micropore volume (cm^3/g), [d] median pore width (nm).

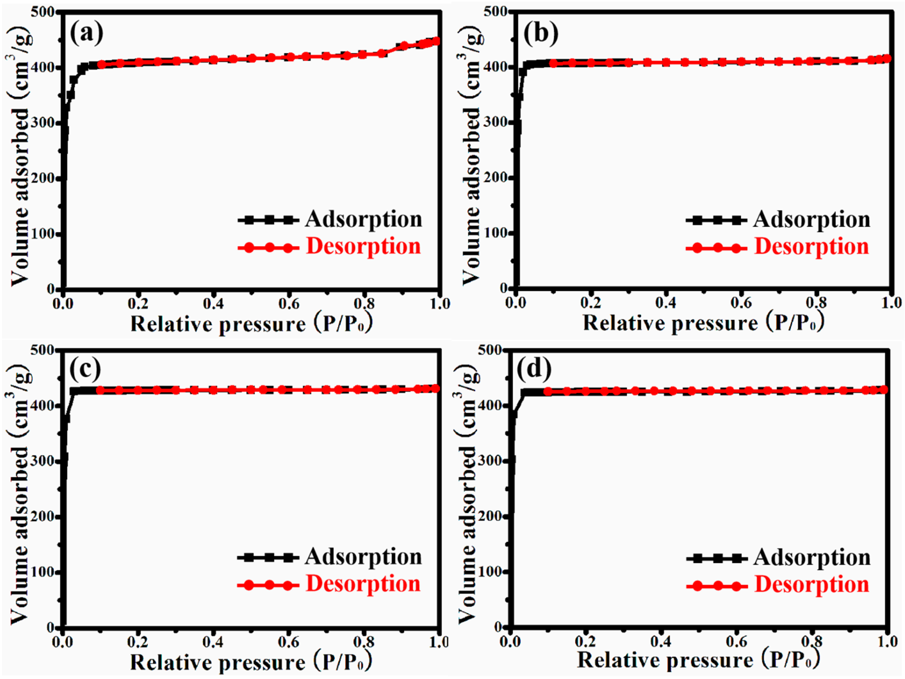

Figure 4. N_2 adsorption–desorption isotherms of (**a**) ZIF-8(1), (**b**) ZIF-8(2), (**c**) ZIF-8(3), (**d**) ZIF-8(4).

3.5. The Production and Productive Rate Analysis

Figure 5 represents the production and productive rate of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4). The production of ZIF-8(1), ZIF-8(2), ZIF-8(3)and ZIF-8(4) is 4.58 g, 1.63 g, 0.53 g, and 0.34 g, respectively. Compared with ZIF-8(1), the productive rates of ZIF-8(2), ZIF-8(3), and ZIF-8(4) are 35.6%, 11.6%, and 7.4%, respectively. This indicates that the production of ZIF-8 is directly affected by the reused methanol solution and productive rate of ZIF-8 is significantly reduced in the reused methanol solution.

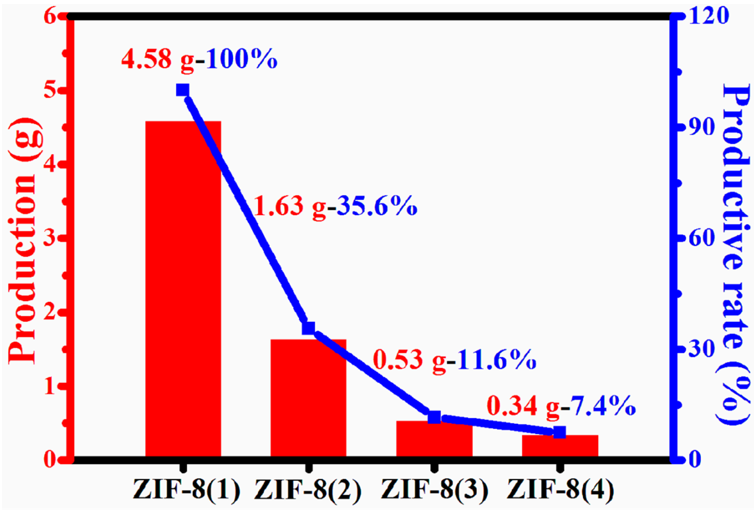

Figure 5. The production and productive rate of ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4).

4. Conclusions

In conclusion, ZIF-8 was successfully synthesized in the methanol solution and the collected methanol solution could be used as a dissolvent to synthesize ZIF-8(X) (X represents the methanol solution that is reused for X times to synthesize the ZIF-8). ZIF-8(1), ZIF-8(2), ZIF-8(3), and ZIF-8(4) exhibit the XRD patterns of ZIF-8. ZIF-8(2), ZIF-8(3), and ZIF-8(4) have almost the same pore size property and BET surface area with ZIF-8(1). When the methanol solution is used four times to synthesize ZIF-8, the particle size of the obtained product increases from 50 nm to 5 um and the productive rate decreases to 7.4%.

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