Microporous and Mesoporous Materials 234 (2016) 287–292

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Synthesis of ZIF-8 and ZIF-67 using mixed-base and their dye adsorption

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ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form
16 May 2016
Accepted 25 July 2016
Available online 26 July 2016

Keywords:
Zeolitic imidazolate framework
ZIF-8
ZIF-67
Triethylamine
Dye adsorption

ABSTRACT

ZIF-8 and ZIF-67 were prepared by using mixed-base ammonium hydroxide and triethylamine (TEA). These two bases could promote the ZIF synthesis, and the yields are significantly improved. The texture structure and morphologies of ZIF prepared with mixed-base also have obvious changes. Three typical dyes, neutral rhodamine B (RB), anionic methyl orange (MO) and cationic methylene blue (MB), were examined for the dye adsorption by using various ZIFs. ZIF-8 and ZIF-67 prepared with TEA have enhanced RB adsorptions that are 2.3–3.8 times of those prepared without TEA, and ZIF-8 exhibited better adsorption performance than ZIF-67. For MO adsorption, ZIF-67 crystals have better adsorption performance than ZIF-8, and ZIF-67 prepared with TEA has a decreased MO adsorption. For MB adsorption, the addition of TEA does not change the MB adsorption for both ZIF-8 and ZIF-67.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs), a subclass of crystalline porous metal-organic frameworks (MOFs), are formed from tetrahedral metal ions (e.g. Zn, Co) bridged by imidazolate [1,2]. ZIFs display unique and highly desirable properties from both zeolites and metal organic frameworks, and therefore the exploration of ZIF preparation has attracted considerable interest. Addition of base agents to the synthesis solution is one of the most promising methods to accelerate the preparation procedure and reduce the environmental impact [2]. The use of a base in the ZIF synthesis can be traced back to the first synthesis of single crystal ZIF-7 and ZIF-8 via the liquid phase-diffusion method by using ammonia (ammonium hydroxide) solution [3,4]. Beldon et al. reported that NH_4^+ ions were particularly beneficial for the ball milling synthesis of ZIFs at room temperature [5]. In our previous work, ZIF-7, ZIF-8, ZIF-9, ZIF-67, ZIF-11 and ZIF-12 were fast prepared by addition of ammonium hydroxide to deprotonate the organic ligands [2,6–8]. The resulting ZIFs could be formed in several minutes from stoichiometric metal and ligand precursor solution. Organic amines, such as triethylamine (TEA) [9–11], polyamine [12] and n-butylamine [13] have also been used to deprotonate the organic ligands and thus to promote the synthesis of ZIFs. Gross et al. prepared ZIF-8 and ZIF-67 in an aqueous solution by addition of TEA, which accelerated the deprotonation of 2-methylimidazle and the molar ratio of metal ion to organic ligand could be reduced to as low as 1:(4–16) [14] ZIF-78 micro-crystals with a hexagonal rod shape were prepared with the assistance of TEA [15]. By using mixed-base NaOH and TEA, Cho et al. reported the large scale synthesis of ZIF-8 in the pH-adjusted synthesis conditions without compromising its textural properties [16]. Therefore, the use of organic amines is one of the hot topics in the synthesis of ZIFs [2].

MOFs have been widely studied in the removal of several hazardous organic compounds such as dyes, benzene and bisphenol-A [17–20]. Adsorption is regarded as an attractive technique, because it is simple, has a low-operating temperature/pressure, and does not need expensive reagents and catalysts [17]. ZIF-8 is a promising material because of its high stability, and it has been used in the adsorptive removal of phthalic acid [21], benzotriazoles [22], As(III) [23] and rhodamine B [24]. In order to improve the adsorption performance of ZIF-8, surfactants [24,25] and amino acid [26] were used to modify its textural property. Mesoporous or hierarchical ZIF-8 has then been prepared to adsorb mercaptan [25], arsenate [26] and arsanilic acid [17]. The morphology of adsorbents also has positive effect on the adsorption. For example, two-dimensional layered titanium carbide [27], NiFe layered double hydroxide [28],

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http://dx.doi.org/10.1016/j.micromeso.2016.07.039
1387-1811/

and self-assembly of bismutite nanocrystals into three-dimensional nanostructures [29] were reported for the adsorption and separation of dyes. In this work, SOD-type ZIF-8 and ZIF-67 were prepared by using mixed-base ammonium hydroxide and TEA. Both of the bases could promote the ZIF synthesis. The yield was significantly improved and the structure properties of ZIFs were modified. Three typical dyes, neutral rhodamine B, anionic methyl orange and cationic methylene blue, were investigated for the dye adsorption by using various ZIFs prepared under different conditions.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate (≥99%, $Zn(NO_3)_2 \cdot 6H_2O$) was purchased from Tianjin Kemiou Chemical Reagent, China. 2-Methylimidazole (Hmim, $C_4H_6N_2$), cobalt nitrate hexahydrate (≥98.5, $Co(NO_3)_2 \cdot 6H_2O$) and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent, China. Ammonium hydroxide solution (NH_3, 25–28%) was provided by Nanjing Chemical Reagent Co. Ltd., China.

2.2. Synthesis of ZIF-8 and ZIF-67 using mixed-base

ZIF-8 was prepared by the addition of ammonium hydroxide and TEA based on our previous report [7]. In a typical synthesis, 0.594 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was dissolved in 3 g of deionized water; 0.328 g of Hmim and 0–8.9 ml of triethylamine were added in 3.76 g of ammonium hydroxide solution. After that zinc nitrate and Hmim solutions were mixed together. The final synthesis solutions had Zn^{2+}: Hmim: NH_3: TEA: H_2O molar compositions of 1: 2: 32: (0–32): 157. The solution immediately turned into milk-like suspension, and stirred for 10 min at room temperature to complete the crystallization. The sample was collected by centrifugation and washing with deionized water three times until the final product had pH value of ~7, then dried at 60 °C overnight. The resulting samples are named as ZIF-8-Tx, where x stands for the molar ratio of TEA/Zn^{2+} in the precursor solution. For example, ZIF-8-T0 and ZIF-8-T2 are the samples prepared without TEA and with TEA/Zn^{2+} molar ratio of 2, respectively. ZIF-67 was prepared by the same procedure as ZIF-8 only replacing zinc nitrate hexahydrate with cobalt nitrate hexahydrate, and the resulting products are named as ZIF-67-Tx (x = 0–32). The yield of products is calculated based on the following equation:

$$\text{Yield} = m_r/m_t \times 100\%$$

Where m_r is the actual yield whereas m_t is the theoretical yield of ZIF-8 based on the chemical formula of $Zn^{2+} + 2\text{mim}^- \rightarrow Zn(\text{mim})_2$.The yield of ZIF-67 is calculated by the same method.

2.3. Characterization

X-ray diffraction (XRD) patterns were taken on an Ultima IV diffractometer with Cu Kα radiation at a scan rate of 2°/min with a step size of 0.02°. Nitrogen adsorption-desorption isotherms were measured by using a volumetric adsorption analyzer (Micromertics ASAP 2020) at liquid nitrogen temperature (77 K). The surface areas were determined by the Brunauer-Emmett-Teller (BET) method. The microscopic morphology of ZIFs was examined by field emission scanning electron microscope (FESEM, Hitachi S-4800II, Japan).

2.4. Dye adsorption

Three typical dyes including neutral rhodamine B (RB), anionic methyl orange (MO), and cationic methylene blue (MB) were studied for adsorption. 15 mg of ZIF sample was added into 15 ml of 24 mg/L RB (MO or MB) solution and the muddy solution was dispersed with an ultrasonic instrument for 1–2 min then magnetically stirred for 2 h at room temperature. After that, the remaining dye solution was collected and analyzed. A UV-240 UV–vis spectrometer was used to record the absorbance change of the dye solution.

3. Results and discussion

3.1. Preparation of ZIF-8 and ZIF-67

ZIF-8 crystals were prepared by using mixed-base, ammonium hydroxide and triethylamine. Fig. 1a shows XRD patterns of ZIF-8 prepared with different molar ratios of TEA/Zn^{2+}. For the sample prepared without TEA, pure SOD-type ZIF-8 phase is formed that is exactly the same as our previous work [30]. By addition of triethylamine with TEA/Zn^{2+} molar ratios of 2–32, all the samples show the ZIF-8 phase with similar peak intensity, which is a little weaker than that prepared without TEA (ZIF-8-T0). The yield of ZIF-8-T0 is about 52%. With the increase of TEA usage, the yields of ZIF-8 increase quickly, from 77% for ZIF-8-T2 to nearly 100% for ZIF-8-T8, ZIF-8-T16 and ZIF-8-T32. The addition of TEA favors the crystal formation of ZIFs but does not change the chemical structure and the functional groups of final products. Fig. 1b shows nitrogen adsorption-desorption isotherms of various ZIF-8. For ZIF-8-T0 prepared without TEA, there is a high sorption step at the low relative pressure, indicating a type I isotherm with micropores. The BET surface area is about 1007 $m^2\ g^{-1}$. For the ZIF-8 samples prepared with TEA, their corresponding nitrogen sorption all decrease to almost the same level. Their BET surface areas decrease to 441, 407, 437, 409 and 395 $m^2\ g^{-1}$ for ZIF-8-T2, ZIF-8-T4, ZIF-8-T8, ZIF-8-T16 and ZIF-8-T32, respectively. The micropore volume of ZIF-8, ZIF-8-T2, ZIF-8-T4, ZIF-8-T8, ZIF-8-T16 and ZIF-8-T32 is 0.44, 0.14, 0.14, 0.14, 0,13 and 0.14 $cm^3\ g^{-1}$ whereas the mesopores volume is 0.04, 0.12, 0.10, 0.13, 0.13 and 0.14 $cm^3\ g^{-1}$ respectively.

Fig. 2 shows SEM images of ZIF-8 prepared with different molar ratios of TEA/Zn^{2+}. ZIF08-T0 has a uniform cubic structure that is exactly the same as the previous report [30]. By introducing TEA in the synthesis solution, the resulting ZIF-8 particles (Fig. 2b–f) are aggregated crystals with a submicrometer size; therefore more mesopores were formed between the interparticles with increased mesopores volume, which is in agreement with the above N_2 adsorption and desorption results. Compared to samples without TEA addition, the ZIF-8 particles are much smaller when TEA was used during the synthesis. In our previous study [31], we found that the addition of ammonium hydroxide facilitates the deprotonation of 2-methylimidazole, and thus favors ZIF-8 crystal formation. Similarly, the addition of TEA is more favorable for ZIF-8 crystal formation and more nuclei were formed; therefore, smaller particle size was observed when TEA was used.

ZIF-67 crystals were prepared by the same procedure as ZIF-8 with mixed-base ammonium hydroxide and triethylamine. XRD patterns in Fig. 3a indicate that ZIF-67 prepared without the addition of TEA (ZIF-67-T0) has the SOD-type ZIF-67 phase. Similar to ZIF-8, with the addition of TEA, the XRD peak intensity of all ZIF-67 becomes weak, indicating a relatively low crystallinity. The yield of ZIF-67-T0 is about 21%, which is quite low as compared to that of ZIF-8-T0 (52%), indicating cobalt ions has a weaker coordination force with 2-methylimidazole than zinc ions [6]. The yields of ZIF-67 sharply increase to 53% for ZIF-67-T2 and 75% for ZIF-67-T8.