Materials Letters 206 (2017) 233–236

Contents lists available at ScienceDirect

Materials Letters

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

Controllable synthesis of zeolitic imidazolate frameworks with rod-like or delta-shaped morphologies at oil-water interface

Yingya Zhang [a], Yingjie Zhao [a], Xuebin Ke [b,*], Lixiong Zhang [a,*]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering and College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, PR China
[b] School of Engineering and Computer Science, University of Hull, HU6 7RX, UK

ARTICLE INFO

Article history:
Received 8 June 2017
Received in revised form 30 June 2017
Accepted 1 July 2017
Available online 1 July 2017

Keywords:
Zeolitic imidazolate framework
Interface synthesis
Morphology
Rod
Delta

ABSTRACT

Zeolitic imidazolate framework (ZIF-8) has attracted extensive application in gas adsorption, membrane separation and catalysis. It has been demonstrated that the morphology is crucial for the physical and chemical properties. In this work, ZIF-8 crystals with rod or delta morphology are regulated by interface synthesis. The preferred growth of specific crystalline face is controlled at oil-water interface and results in uniform ZIF-8 crystals with various morphologies. Solvents types and feeding concentrations play crucial roles in crystalline growth. This method can be extended to other materials synthesis, such as ZIF-1 and ZIF-67 crystals. The interface synthesis approach may provide insight to promote advanced materials fabrication and achieve better materials function.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are a sub-class of metal-organic frameworks which have zeolite-like structures and exhibit regular crystalline lattices with well-defined pore structures [1]. ZIF-8 is one of such ZIFs which constructed from zinc ions and 2-methylimidazole (Hmim), and has received extensive interests because of its excellent thermal and hydrothermal stability. The synthesis strategies, including microfluidic approach [2], of ZIF-8 have been explored and their functionalities can be exploited in terms of adsorption separation [3,4], gas storage [5–7], and catalysis [8,9]. Generally, the ZIF-8 crystals synthesized from conventional methods commonly exhibit rhombic dodecahedron morphology. By changing zinc sources and the molar ratio of Hmim to Zn^{2+}, the morphology of ZIF-8 crystals can be tuned [10–12]. Nevertheless, current regulation of their morphology is mainly achieved by employing various additives during the synthesis [13,14].

In this work, we present a feasible interfacial synthesis to prepare ZIF-8 crystals with controllable morphologies of rods or delta. A tunable oil-water interface is formed by dispersing zinc nitrate aqueous microdroplets in Hmim contained isooctanol through a co-axial microfluidic device. ZIF-8 crystals are produced at the interface. The morphologies of the resultant ZIF-8 crystals can be regulated by changing the interface conditions, mainly including the types of alcohols and the concentrations of feedstock. Other two synthetic examples of ZIF-1 and ZIF-67 are demonstrated to illuminate a general methodology to regulate crystalline aspects through interface synthesis.

2. Experimental section

2.1. Synthesis of ZIF-8 crystals with various morphologies

All the chemicals were supplied from Sigma-Aldrich without further purification. A home-made co-axial microfluidic device was used to conduct the interfacial reaction (Fig. S1). Typically, 0.14 M $Zn(NO_3)_2$ aqueous solution and isooctanol dissolved with Hmim (0.1 M), acted as disperse phase and continuous phase, were supplied by syringe pumps set at 0.4 and 4 ml h^{-1}, respectively. The formed microdroplets flowed through the PTFE tube within a residence time of 100 s at a controllable temperature of 35 °C. The effluent was collected in a beaker containing methanol. The collected solution was centrifuged and the obtained powders were washed with fresh methanol three times by centrifuging. Rod-like ZIF-8 powder was obtained after drying at ambient temperature. Decreasing the concentration of two phases to 1/4 folds, same as above, we could get delta-like ZIF-8 crystals.

2.2. Characterization

Fourier transform infrared (FT-IR) spectra were obtained using a Nexus 870 FT-IR spectrometer. Samples were mixed and ground with KBr (at a mass ratio of 1:10) for the FT-IR measurements,

* Corresponding authors.
E-mail addresses: x.ke@hull.ac.uk (X. Ke), lixiongzhang@yahoo.com (L. Zhang).

http://dx.doi.org/10.1016/j.matlet.2017.07.002
0167-577X/

which were performed within the wavelength range of 4000–400 cm^{-1}. The morphologies of ZIFs crystals were observed using a Hitachi S-4800 scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were recorded using a Bruker D8-Advance powder diffractometer with a Ni-filtered Cu Kα radiation source at 40 kV and 40 mA at a scan rate of 5° min^{-1} and a step size of 0.05°.

3. Results and discussion

We conduct the synthesis of ZIF-8 crystals at the oil-water interface between the Zn^{2+} aqueous droplet and isooctanol containing Hmim. The SEM images illustrate that the obtained ZIF-8 crystals are with rod or delta morphologies, which is quite different from that of ZIF-8 crystals with conventional polyhedron morphology, with a specific surface area of 667 cm^3/g and 424 cm^3/g (Fig. S2), respectively. The rod-like ZIF-8 crystals can be seen clearly with length of 2.2 μm and width of about 0.2 μm (Fig. 1a). While delta-like ZIF-8 has a length of 0.6 μm and width of 0.3 μm and 50 nm at two ends (Fig. 1b). The overall XRD patterns are in good agreement with that the commonly synthesized ZIF-8 crystals [1,15], indicating formation of pure phase ZIF-8. Compared to the stimulated one, the peak intensity at 2θ of 7.3° for rod-like and delta-like ZIF-8 is weaker, suggesting the growth of the (011) face is restricted (Fig. 1c). Furthermore, for delta-like ZIF-8 crystals, the peak intensity at 2θ of 14.6° and 16.4° are stronger, indicating that more (022) and (013) face are exposed. The FT-IR spectrum is in well agreement with those in previous reports [16] (Fig. 1d).

The interfacial action is significant to form ZIF-8 crystals. While Hmim has a better solubility in water than that in alcohols, the diffusion of Hmim is much easier than Zn^{2+} towards the two-phase interface. To examine the effect of the diffusion, the alcohols, such as isobutanol, isoamyl alcohol, cyclohexanol and decanol, are used in replacement of isooctanol. Their solubility in water decreases with increasing carbon numbers. Various morphologies evolve with different alcohols. When isobutanol is used, two phases are miscible and cannot form stable interface. The resulting ZIF-8 crystals are particles of 50–100 nm (Fig. 2a). The isoamyl alcohol, cyclohexanol, and isooctanol, can constitute stable two-phase interface, leading to rod-like ZIF-8 crystals (Fig. 2b–d). But there exist some nonuniformity in size for the ZIF-8 crystals synthesized with isoamyl alcohol and cyclohexanol, respectively. In the case of decanol, two phases are distinctly immiscible and impede the axial growth, thus the cube-like ZIF-8 crystals overlap together (Fig. 2e). The XRD patterns indicate that ZIF-8 crystals are synthesized with a good crystallinity (Fig. 2f).

The precursor concentrations have strong influence on the morphology of ZIF-8 crystals. The interfacial syntheses are conducted by simultaneously changing concentrations of the two phases without altering other synthesis conditions. The results indicate that ZIF-8 crystals can be synthesized while the molar ratio of Hmim: Zn^{2+}: isooctanol: H_2O is 7: 1: 455x: 384x, with change of the solvent amounts from x = 16 to x = 1/8 folds (Fig. S3). Decreasing the Hmim concentration to 0.00625 M (x = 16) leads to mixed ZIF-8 crystals of 5 μm rhombic dodecahedron and 500 nm spheres (Fig. 3a). High concentrations (x = 1/8) promote the synthesis of ZIF-8 crystals but with heterogeneous sizes (Fig. 3h). Changing the solvent amounts between x = 8 and x = 1/2 folds leads to the formation of rod-like ZIF-8 crystals with length from 400 nm to 4.7 μm (Fig. 3b–f). It is concluded that the growth of ZIF-8 crystals primarily relies on mass diffusion of reactants between two-phase interfaces.

Based on the above results, we propose the formation mechanism of ZIF-8 crystals with rod or delta morphology by interface synthesis. The liquid-liquid interfacial reaction for synthesis of ZIF-8 crystals includes precursor diffusion from one liquid to the other, nucleation and crystallization. As Zn^{2+} diffuses from the aqueous phase to the oil phase, a concentration gradient towards the fringe of W/O droplet will be built up and Hmim is more dispersed in water/alcohols interface. Right after the diffusion of Zn^{2+}, the coordination of Hmim to Zn^{2+} occurs and nuclei are formed immediately at the W/O interface. Since the concentration of Zn^{2+} at the oil side of the droplet is lower than that in the water

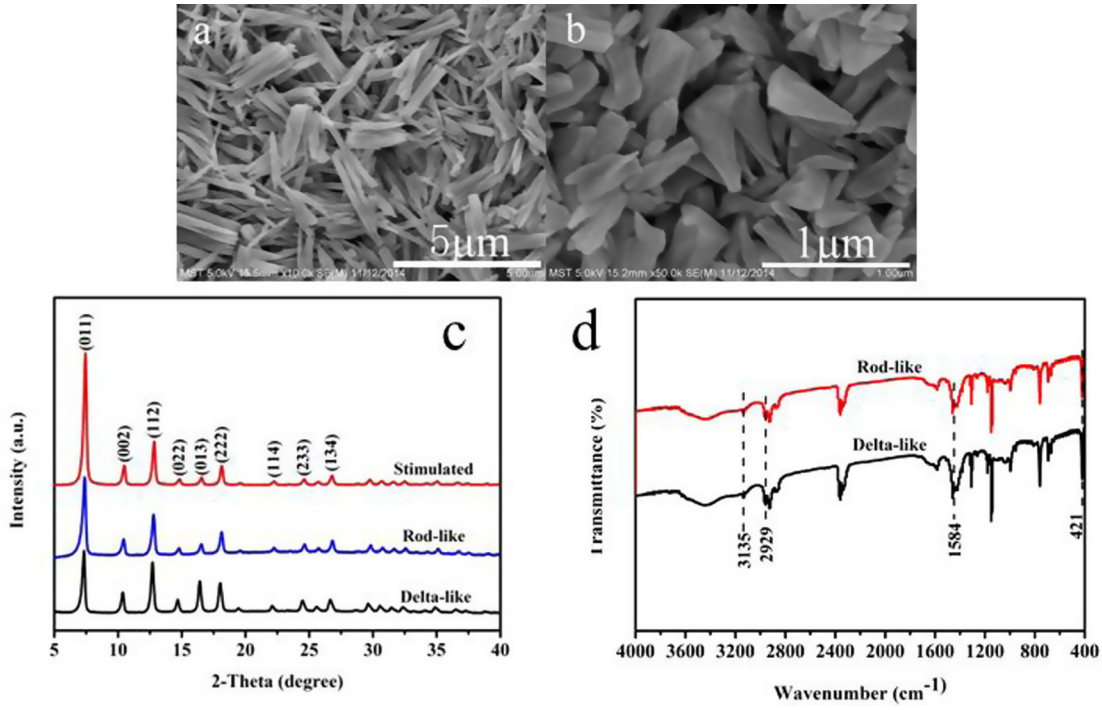

Fig. 1. SEM images of rod-like (a) and delta-like (b) ZIF-8 crystals, XRD patterns (c), and FTIR spectra (d), corresponding to W/O interface synthesis.