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Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) in aqueous solution via microwave irradiation

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ABSTRACT

Herein we report a new strategy to synthesize zeolitic imidazolate framework-8 (ZIF-8) at a relatively low molar ratio of ligand to metal ion in aqueous solution under microwave irradiation for the first time. The products possess high surface area and large micropore volume. The molar ratio of ligand to metal ion and the salt anion play an important role on the size and shape of ZIF-8.

Zeolitic imidazolate frameworks (ZIFs), a novel class of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), possess zeolite-like topologies in which the tetrahedral Si or Al and the bridging O are replaced by transition metals and imidazolate-derived ligands [1]. Interestingly, ZIFs have exceptional chemical and thermal stability [1–3], which make ZIFs capable of diverse applications, such as gas storage [2–5], separation [6,7], heterogeneous catalysis [8,9] and chemical sensing [10,11]. ZIF-8 is one of the most widely investigated materials among them, which consists of Zn and 2-methylimidazole (Hmim). It exhibits a sodalite (SOD) topology with internal cavities of 1.16 nm in diameter which are accessible through small apertures with a diameter of 0.34 nm [1].

Currently, a majority of methods were reported to synthesize ZIF-8 in organic solvents, such as dimethylformamide (DMF) [1] or methanol [12,13]. These organic solvents are expensive, environmentally unfriendly and toxic. A great deal of efforts has been made to develop environmentally friendly methods to prepare ZIF-8. Recently, Tanaka and his coworkers synthesized ZIF-8 in aqueous system at room temperature with the molar ratio of Hmim to Zn^{2+} at 40–100 [14], and the ZIF-8 possessed large surface area and micropore volume. Gross's group reported an aqueous room temperature method with a lower concentration of Hmim, in which triethylamine (TEA) was used to deprotonate imidazole ligands [15]. However, the product exhibited non-uniform shape and size, the surface area and micropore volume were much smaller than the ideal ZIF-8 [15].

Compared with conventional heating method, the microwave irradiation is a more promising method, which can significantly accelerate the reaction rate while the size and shape of the products can be well controlled [16,17]. So far, there are only two literature reports using microwave to synthesize ZIF-8. Bux and his coworkers succeeded in preparing pure-phase ZIF-8 under microwave irradiation in methanol solution, but the reaction time was up to 4 h [18]. Yang and his coworkers also synthesized ZIF-8 by microwave irradiation using ionic liquids as structure directing agent, but the ionic liquids will increase the cost [19].

In this paper, we applied microwave irradiation to synthesize ZIF-8 in an aqueous solution for the first time [20], which is environmentally friendly and cost saving. Moreover, the products exhibit similar high surface area and large micropore volume compared with literature reports. In addition, the influence of ligand to metal ion ratio and the salt anion were also investigated.

X-ray diffraction (XRD) patterns were measured to examine the crystallinity and phase purity of products (Fig. 1). The sample obtained in hydrothermal process was assigned to the dia framework (dia(Zn)), a 3D framework like dia topology [21], and the diffraction peaks of both simulated (Fig. 1a) and experimental (Fig. 1c) samples matched well at corresponding positions. However, the diffraction pattern of the sample obtained under microwave irradiation (Fig. 1d) fitted well with simulated ZIF-8 pattern (Fig. 1b), which indicates that it is a pure phase of ZIF-8. Peak broadening was observed from the XRD pattern, indicating a smaller crystallite size compared to literature report [1].

The SEM pictures of the samples prepared from different methods are shown in Fig. 2. The sample prepared under hydrothermal condition (Fig. 2a–b) showed irregular shape and variable size. Most of them were presented as blocks and seem quite dense. Meanwhile, the sample prepared under microwave irradiation (Fig. 2c–d) was homogeneous with a hexagonal shape and the average particle size was about 350 nm.

The possible crystallization processes of these two methods were discussed as following. All the starting reagents were dissolved into aqueous solutions. Less reaction time was needed under microwave

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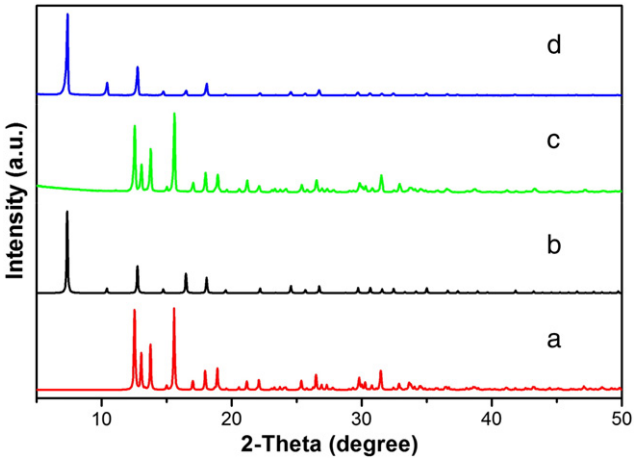

Fig. 1. XRD patterns of the products: (a) the one simulated from dia(Zn) crystal structure date, (b) the one simulated from ZIF-8 crystal structure date, (c) the hydrothermal products, and (d) the microwave irradiation products.

irradiation. Therefore the crystal nucleation and crystal growth would be much faster than the hydrothermal method. We suppose that the crystallization process was under kinetic control for microwave irradiation while the crystallization process of hydrothermal method was under thermodynamic control. Leoni [22] and Ruiz-Salvador [23] both had put forward a theory of the relationship between total energy and the crystal structure on the basis of DFT calculation. They concluded that the dia(Zn) structure had a lower energy than the ZIF-8 structure, which was consistent with our speculation.

The N_2 sorption isotherm of ZIF-8 prepared under microwave irradiation showed a type I isotherm (Fig. S1). The increase at the relatively low pressure indicates the presence of micropores, and the second uptake near $P/P_0 = 1$ is due to the interparticle porosity formed by packing of nanoparticles. The Brunauer–Emmett–Teller (BET) and Langmuir surface areas are 1075 and 1416 $m^2\ g^{-1}$, respectively. The micropore volume based on t-plot method is about 0.49 $cm^3\ g^{-1}$. These porous data are close to the highest literature values [14], which are higher than most ZIF-8 prepared in aqueous solution at room temperature [15,24]. This was possibly due to the homogenous nucleation in the solution. Therefore, smaller particles and narrower size distribution could be obtained, which resulted in a higher surface area [25].

The XRD patterns of the samples prepared at different Hmim/Zn^{2+} molar ratios are shown in Fig. S2. No SOD structure was found under the ratio of 2. ZIF-8 structure was found at the ratio of 5, however, the peak intensity was very weak, indicating a poor crystallinity. When the ratio reached 10 or higher, all the XRD patterns showed excellent agreement with the simulated ZIF-8 pattern. Fig. 3 shows the SEM images of the samples prepared at different Hmim/Zn^{2+} molar ratios. At the ratio of 2, the sample showed variable sizes and inhomogeneous shapes. The sample shape became homogeneous when the ratio reached 5, but the sample surface was rough. When the ratio was higher than 10, the samples maintained homogeneous hexagonal shapes, and the average sizes were about 350 nm and 190 nm, respectively.

We also investigated the effect of different anions on the shape and size of ZIFs. $Zn(NO_3)_2 \cdot 6H_2O$ was used to replace $Zn(OAc)_2 \cdot 2H_2O$

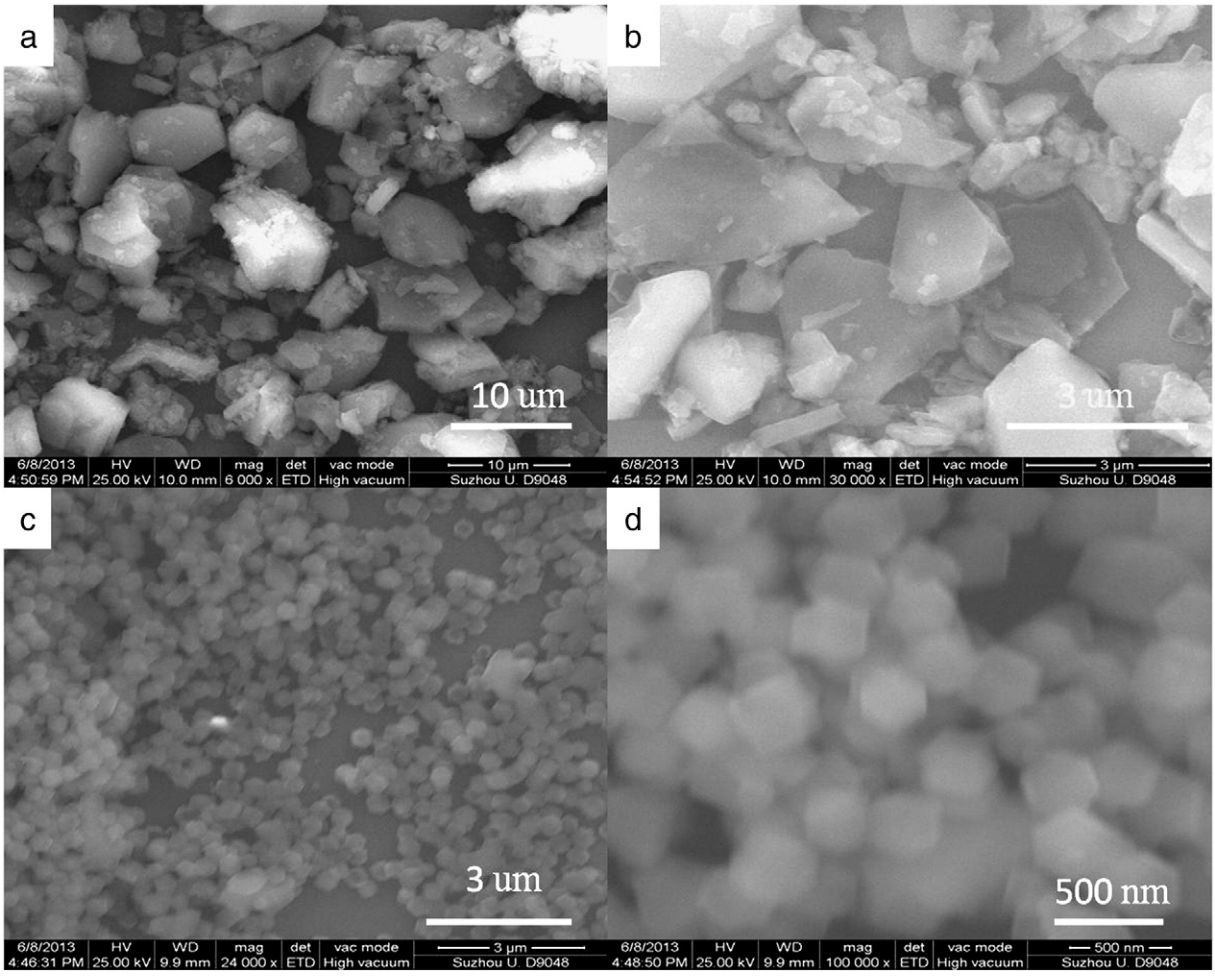

Fig. 2. SEM images of the products: (a, b) the hydrothermal products, and (c, d) the microwave irradiation products.