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COMMUNICATION

Synthesis of ZIF-11 Crystals by Microwave Heating

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We demonstrate the synthesis of zeolitic imidazolate framework 11 via microwave assisted approach. The resultant 2 – 7 µm crystals were synthesized in minutes, and display BET surface areas as high as 745 m²/g. The state-of-the-art ZIF-11 synthesis techniques are summarized. XRD, SEM, and porosimetry, were used as pivotal characterization techniques.

Introduction

Zeolitic imidazolate frameworks represent a subclass of metal organic frameworks formed by linking zinc or cobalt ions with nitrogen atoms of imidazole based groups resulting in microporous crystalline structures with diverse and distinctive topologies [1,2]. Due to the size of their limiting pore apertures, enhanced mechanical and thermal stability, and topological diversity, zeolitic imidazolate frameworks have been recognized as highly appealing materials (in membrane form) for challenging molecular gas separations [3-6]. In particular ZIF-11 is a suitable candidate to molecular sieve industrially relevant gases. ZIF-11 is a microporous zeolitic imidazolate framework consisting on Zn atoms coordinated with nitrogen atoms of benzimidazole forming a crystalline structure with RHO type topology, with limiting pore apertures of 3 Å [7].

ZIF-11 crystals have been prepared via conventional solvothermal approach [1], centrifugation [8], room temperature synthesis [9-15], sono-crystallization [16], and refluxing [17, 18]. Microwave heating represents an alternative synthesis approach. Microwave heating offers the following general advantages as compared to conventional solvothermal approaches [19]: (a) higher heating rates as compared to conventional heating; (b) no wall or heating diffusion effects; (c) selective heating due to the presence of microwaves; (d) more uniform heating due to the lack of hot spots. Typically, microwave heating leads to smaller and uniform crystals with narrow size distribution, which is highly desirable for many functional applications. Several porous crystalline materials, including zeolites [20-22], mesoporous oxides [23], metal organic frameworks [24-26] and recently porous organic cages [27] have been synthesized via microwave. Herein, we report the successful synthesis of ZIF-11 crystals via microwave. To our best knowledge, we demonstrate for the first time the synthesis of this zeolitic imidazolate framework by microwave approach.

Two solutions were prepared. The first solution consisted of 0.24g benzimidazole dissolved in the solvent mixture of 6.4g methanol, 9.2g toluene, and 2.4g ammonium hydroxide. The other solution consisted of 0.22g zinc acetate dihydrate, dissolved in 3.2g of methanol. Both solutions were combined, and stirred at room temperature for 2 hours. The resultant solution was placed in a Teflon liner, sealed, and placed in the microwave (CEM Mars 5). The temperature was ramped to 100°C, and held for 15 min, and 1 hour. The microwave power was set to 400w. The resultant solution was filtered, rinsed 3x with methanol, and dried overnight at 80°C. An additional experiment was done, where the two solutions were mixed for

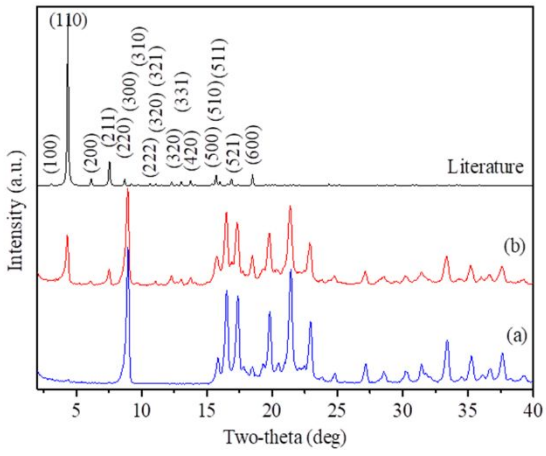

Figure 1. PXRD patterns of ZIF-11 crystals synthesized via microwave for heating time of (a) = 15 minutes, and (b) = 60 minutes. For comparison, the simulated XRD pattern of ZIF-11 is shown.

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only 2 minutes before addition to the microwave. Details on characterization are available in the SI.

Figure 1 shows the PXRD patterns of two representative microwave synthesized ZIF-11 crystals at two different heating times. The resultant PXRD patterns of these two samples correspond to the typical RHO topology of ZIF-11 [1]. The synthesis of ZIF-11 crystals via traditional approaches (solvothermal, room temperature, and sono-chemical) requires several hours, while the synthesis of these crystals via microwave took place only in several minutes. Both microwave synthesized samples displayed a slight XRD peak displacement as compared to simulated XRD pattern, suggesting a small change in the unit cell dimensions of ZIF-11. Specifically, the samples exhibited a small shift in XRD peaks to higher two theta angles, indicating a decrease in interplanar spacing. When comparing the two samples, the relative degree of crystallinity (presence of sharper peaks) is higher for the sample synthesized at longer heating times. The observed slight change in interplanar spacings suggests framework flexibility, a distinctive feature that is common in several microporous crystals [29], including zeolitic imidazolate frameworks [10, 30]. The higher intensity of some of the peaks corresponding to the microwave samples (as compared to the simulated pattern) may suggest preferential exposure of that particular crystallographic plane, and/or a different degree of relative crystallinity in the resultant samples. The relative crystallinity of the two samples as compared to the simulated powder pattern has been calculated (SI). The relative crystallinity of the 15 minute, and 60 minute sample when integrating for the area under the peak at 2θ°=4.3, is 2.8%, and 90.7% respectively. The intensity of the main peak corresponding to the (110) plane of ZIF-11 is much lower for the microwave synthesized samples. This suggests a higher degree of local structural disorder and lower degree of relative crystallinity as compared to the simulated pattern. This local structural disorder has been observed for metal organic frameworks.[28] Shorter solution mixing is possible with this system. Figure S1 illustrates a PXRD pattern of a sample which was mixed with all ZIF-11 components for only two minutes before being introduced to the microwave. This sample shows excellent crystallinity and RHO topology. Figure S2 is a representative SEM image of this sample.

Figure 2 illustrates representative SEM images of the microwave synthesized ZIF-11 crystals. The samples display highly crystalline faceted rhombohedra. Crystals synthesized for 15 minutes, and 60 minutes exhibited crystals with an average size of 4.33 ± 1.67 µm, and 4.14 ± 1.85 µm respectively. Figure S3 shows the size distributions for these samples. The relatively small crystal size of the microwave synthesized ZIF-11 crystals can be associated to the high nucleation rate provided by the microwave heating. It is known that microwave leads to a high dissolution of reactants at very short times, promoting to the formation of an increase concentration of small nuclei. Subsequent crystallization of these nuclei due to the rapid consumption of the reactant leads to small crystals with narrow size distribution.

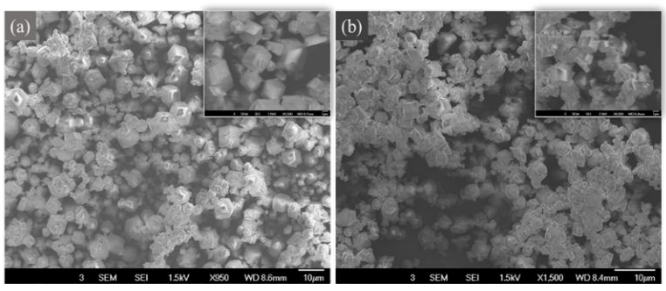

Figure 2. Representative SEM images of ZIF-11 crystals synthesized via microwave heating time: (a) 15 min, and (b) 1 hr. Insets scale bars are 1 µm.

Figure 3 shows the nitrogen adsorption-desorption isotherms for the ZIF-11 microwave samples. The insets show the pore distributions of the samples within the microporous range. The observed hysteresis loops of these crystals exhibit the shape that is characteristic of microporous type materials [31-32]. The BET surface areas extracted from these isotherms were 713 m^2/g and 745 m^2/g for the samples synthesized for 15 min, and 1 hour, respectively. Nitrogen isotherm collection took more than 2 days for the microwave synthesized ZIF-11, because it is known to be fairly "non-porous" to nitrogen [1,8,11] due to its limiting aperture size of 3 Å. Our reported values corroborate ZIF-11's high pore flexibility suggested earlier [10]. The slight increase in surface area for the 1 hour sample, may be due to its enhanced relative crystallinity. In principle, the increase in surface area for several metal organic frameworks can be related to an increase in long range order.

Figure S4 shows the FTIR spectra of ZIF-11 synthesized via microwave for 15 minutes. A characteristic Zn-N stretch at 427 cm^{-1} [33] indicates the successful bond formation between zinc ions and the benzimidazole organic linker. The C=C bending around 730 cm^{-1}, C-H bending around 1450 cm^{-1}, C=C stretching around 1600 cm^{-1}, and C-N stretch at 1250 cm^{-1} are all frequencies associated with the bonds contained within the benzimidazole molecule.

Figure S5 shows the TGA profile of ZIF-11 synthesized via microwave for 15 minutes. ZIF-11 is stable up to ~520°C. This thermal stability is consistent with previous literature [34].

Table 1 compares the synthetic approaches that have been employed to synthesize ZIF-11 crystals. Most of the reported ZIF-11 crystals have been synthesized at room temperature under stirring conditions for up to 4 hours.[9-15] The shortest synthesis time shown, is for ZIF-11 synthesized via centrifugation for up to 1 minute, though

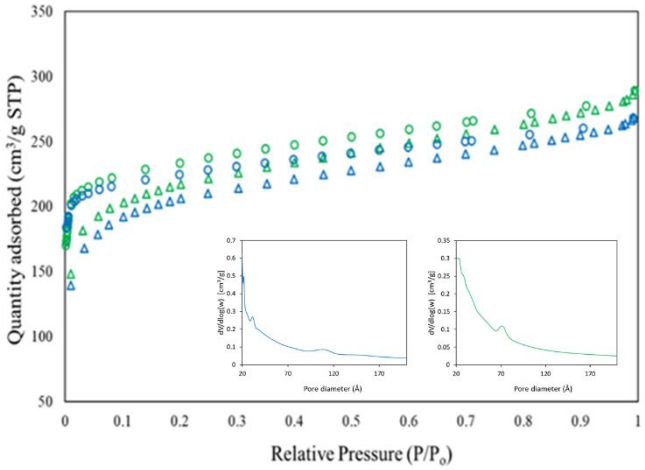

Figure 3. Nitrogen adsorption (triangles) - desorption (circles) isotherms at 77K of ZIF-11 crystals synthesized via microwave: (blue) 15 minutes, (green) 1 hour. Insets indicate pore size distributions.

overall crystallization is somewhat compromised [8]. Crystal size distributions vary for each method (with the exception of Ref.15), and although microwave synthesis is known for the production of narrowly distributed crystals,[35] we do not accomplish this with the ZIF-11 system. BET surface areas are scarcely reported due to nitrogen diffusion limitations within ZIF-11 pores.

Table 1. State-of-the-art synthetic approaches and general properties of ZIF-11 crystals

Synthesis approach	Synthesis time and temp	Crystal size (μm) N_2 surface area (m^2/g)	Ref.
Solvothermal	4 days, 100°C	Not reported 1,676 m^2/g (simulation)	[1]
Centrifugation	1-30 min, 18°C	~0.04 - 16.61	[8]
Room temp	Stirring 3h, 23°C	~2 - 8	[9]
Room temp	Stirring 3h, 23°C	Not reported (97 m^2/g)	[10]
Room temp	Stirring 3h, 23°C	~1 - 6	[11]
Room temp	Stirring 4h, 23°C	~ 0.5 – 4.5	[12]
Room temp	Stirring 2h, 23°C	~ 0.5 – 2.5	[13]
Room temp	Stirring 3h, 23°C	~1 – 3	[14]
Room temp	Stand for 4h, stirred 2h, 4h	22, 36	[15]
Sono-crystallization	6 – 12h, 60°C	~ 1 - 5	[16]
Refluxed	100°C	Not reported	[17]
Refluxed	6 - 96 h, 60°C, 100°C	~2 - 4.5	[18]
Microwave	15 & 60 min, 100 °C	~ 2- 7 (745 m^2/g)	This work

Conclusions

Summarizing, a prototypical zeolitic imidazolate framework denoted as ZIF-11 was prepared via microwave heating. The rapid and localized heating provided by microwave, led to the formation of regular ZIF-11 crystals with narrow size distribution. ZIF-11 crystals in the ~5 μm, and 3 μm size range were obtained at microwave times of 15 and 60 minutes respectively. The synthesized ZIF-11 crystals displayed BET surface areas in the 713-745 m^2/g range. The PXRD patterns confirmed the formation of RHO topology, typical of ZIF-11. To the best of our knowledge, this study represents the first example on the successful synthesis of ZIF-11 crystals via microwave approach.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare

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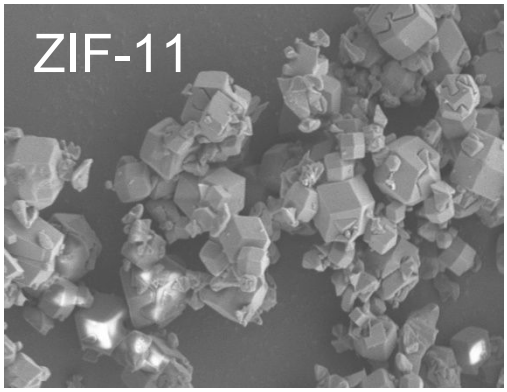

Zeolitic imidazolate framework ZIF-11 displaying crystal sizes within the ~2-7 micron size range were synthesized via microwave.