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Synthesis of ZIF-11 crystals by microwave heating†

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We demonstrate the synthesis of zeolitic imidazolate framework ZIF-11 via a microwave assisted approach. The resultant 2–7 lm crystals were synthesized in minutes and displayed BET surface areas as high as 745 m ^{2} g ^{1}. 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 for molecularly sieving industrially relevant gases. ZIF-11 is a microporous zeolitic imidazolate framework consisting of Zn atoms coordinated with nitrogen atoms of benzimidazole forming a crystalline structure with RHO type topology and with a limiting pore aperture of 3 Å.[7]

ZIF-11 crystals have been prepared via conventional solvothermal approaches,[1] centrifugation,[8] room temperature synthesis,[9–15] sonocrystallization,[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, and (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 a microwave assisted approach. Herein, we report the successful synthesis of ZIF-11 crystals via a microwave assisted approach. To our best knowledge, we demonstrate for the first time the synthesis of this zeolitic imidazolate framework by a microwave assisted approach.

Two solutions were prepared. The first solution consisted of 0.24 g benzimidazole dissolved in a solvent mixture of 6.4 g methanol, 9.2 g toluene, and 2.4 g ammonium hydroxide. The other solution consisted of 0.22 g zinc acetate dihydrate, dissolved in 3.2 g 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 a microwave oven (CEM Mars 5). The temperature was ramped to 100 1C and held for 15 min and 1 hour. The microwave power was set to 400 W. The resultant solution was filtered, rinsed 3 with methanol, and dried overnight at 80 1C. An additional experiment was carried out, where the two solutions were mixed for only 2 minutes before microwave heating. Details on characterization are available in the ESI.†

Fig. 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 sonochemical) requires several hours, while the synthesis of these crystals via a microwave assisted approach took only several minutes. Both microwave synthesized samples displayed a slight XRD peak displacement as compared to the simulated XRD pattern, suggesting a small change in the unit cell dimensions of ZIF-11. Specifically, the samples exhibited a small shift in their XRD peaks to higher two theta angles, indicating a decrease in their interplanar spacing. When comparing the two samples, the relative degree of crystallinity (presence of sharper peaks) is higher for the

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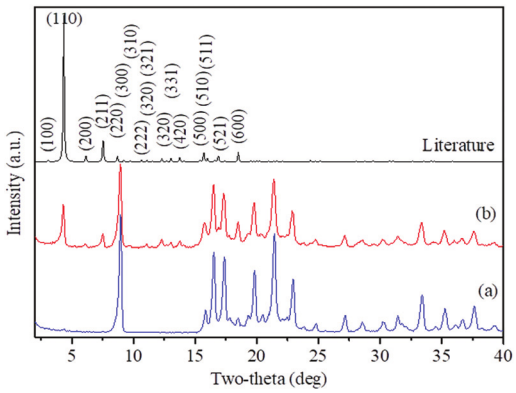

Fig. 1 PXRD patterns of ZIF-11 crystals synthesized via a microwave assisted approach with heating times of (a) 15 minutes and (b) 60 minutes. For comparison, the simulated XRD pattern of ZIF-11 is shown.

sample synthesized at longer heating times. This observed slight change in their interplanar spacings suggests framework flexibility, a distinctive feature that is common in several microporous crystals,[28,29] including zeolitic imidazolate frameworks.[10,30] The higher intensity of some of the peaks corresponding to the micro-wave 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 (ESI†). The relative crystallinity of the 15 minute and 60 minute sample when integrating the area under the peak at 2y = 4.31 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 a 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. Fig. S1 (ESI†) illustrates the PXRD pattern of a sample which was mixed with all ZIF-11 components for only two minutes before microwave heating. This sample shows excellent crystallinity and RHO topology. Fig. S2 (ESI†) is a representative SEM image of this sample.

Fig. 2 illustrates the 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 mm and 4.14 1.85 mm, respectively. Fig. S3 (ESI†) shows the size distributions of these samples. The relatively small crystal size of the microwave synthesized ZIF-11 crystals can be associated with the high nucleation rate provided by the microwave heating. It is known that microwaves lead to a high dissolution of reactants at very short times, promoting the formation of an increased 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.

Fig. 3 shows the nitrogen adsorption–desorption isotherms of 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^{-1} and 745 m^2 g^{-1} for the samples synthesized for 15 min and 60 minutes, 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 60 minutes sample might 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.

Fig. S4 (ESI†) shows the FTIR spectra of ZIF-11 synthesized via a microwave assisted approach 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 CQC bending around 730 cm^{-1}, C–H bending around 1450 cm^{-1}, CQC 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.

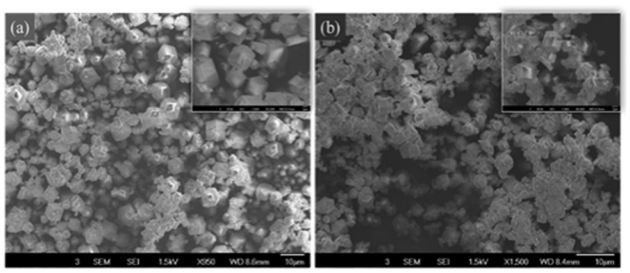

Fig. 2 Representative SEM images of ZIF-11 crystals synthesized via a microwave assisted approach with heating times: (a) 15 min and (b) 60 minutes. Inset scale bars are 1 mm.

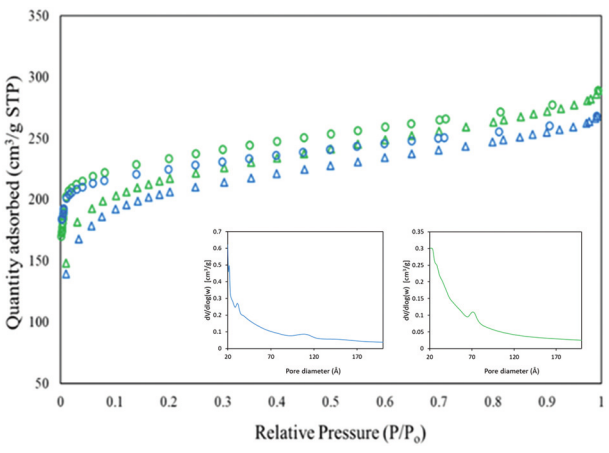

Fig. 3 Nitrogen adsorption (triangles)–desorption (circles) isotherms at 77 K of ZIF-11 crystals synthesized via a microwave assisted approach: (blue) 15 minutes and (green) 60 minutes. Insets indicate the pore size distributions.

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

Synthesis approach	Synthesis time and temp.	Crystal size (mm) N_2 surface area (m^2 g^{-1})	Ref.
Solvothermal	4 days, 100 1C	Not reported 1676 m^2 g^{-1} (simulation)	1
Centrifugation	1–30 min, 18 1C	B0.04–16.61	8
Room temp.	Stirring 3 h, 23 1C	B2–8	9
Room temp.	Stirring 3 h, 23 1C	Not reported (97 m^2 g^{-1})	10
Room temp.	Stirring 3 h, 23 1C	B1–6	11
Room temp.	Stirring 4 h, 23 1C	B0.5–4.5	12
Room temp.	Stirring 2 h, 23 1C	B 0.5–2.5	13
Room temp.	Stirring 3 h, 23 1C	B1–3	14
Room temp.	Stand for 4 h, stirred 2 h, 4 h	22, 36	15
Sono-crystallization	6–12 h, 60 1C	B1–5	16
Refluxed	100 1C	Not reported	17
Refluxed	6–96 h, 60 1C, 100 1C	B2–4.5	18
Microwave	15 & 60 min, 100 1C	B2–7 (745 m^2 g^{-1})	This work

Fig. S5 (ESI†) shows the TGA profile of ZIF-11 synthesized via a microwave assisted approach for 15 minutes. ZIF-11 is stable up to B520 1C. 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 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.

Conclusions

In summary, a prototypical zeolitic imidazolate framework denoted as ZIF-11 was prepared via microwave heating. The rapid and localized heating provided by microwaves led to the formation of regular ZIF-11 crystals with narrow size distribution. ZIF-11 crystals in the size range of B5 mm and 3 mm 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^{-1} 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 of the successful synthesis of ZIF-11 crystals via a microwave assisted approach.

Conflicts of interest

There are no conflicts to declare.

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