

New microwave-assisted synthesis of ZIF-8

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A new fast (15 min) microwave-assisted solvothermal synthesis of ZIF-8 with a high specific surface area ($1419 \text{ m}^2 \text{ g}^{-1}$) is proposed, and the molar ratio between zinc salt and linker is optimized.

Metal-organic frameworks (MOFs) are a new growing class of coordination polymers¹ among other porous materials like zeolites, covalent-organic frameworks or polythreaded nets.² The MOFs possess very attractive properties, which have already been exploited in gas storage,³ catalysis,⁴ biomedicine⁵ etc. Zeolitic imidazolate frameworks (ZIFs) form a subclass of MOFs offering particular advantages of both temperature and chemical stability.⁶ The most representative member is ZIF-8, which bears sodalite (SOD) topology and consists of Zn^{2+} and 2-methylimidazolate (HMIIm) linkers in 1:2 stoichiometry.

Many synthetic techniques were proposed to produce ZIF-8.⁷ However, not all of them lead to the material possessing a high specific surface area. The methods of fast synthesis often result in BET specific surface areas of no higher than $1000 \text{ m}^2 \text{ g}^{-1}$.⁸ To obtain a pure ZIF-8 phase with a high specific surface area ($1079 \text{ m}^2 \text{ g}^{-1}$), a reaction mixture with a significant linker excess (a Zn^{2+} :linker molar ratio of 1:70) was employed.⁹ The use of microwave (MW) radiation made it possible to reduce the quantity of linker in excess (Zn^{2+} :linker, 1:20) by a factor of 3.5 again producing ZIF-8 of almost the same specific surface area ($1075 \text{ m}^2 \text{ g}^{-1}$).¹⁰ Here, we describe the fast MW-assisted synthesis with a stoichiometric molar ratio and a double excess of linker leading to ZIF-8 phase materials with high specific surface areas.[†]

The crystal structure of the samples was identified as a ZIF-8 phase by powder XRD,[‡] whose experimental patterns are shown in Figure 1 together with the pattern of a commercial analogue Basolite Z1200 (BASF). Profile analysis in Jana2006 package revealed the single phase with cubic symmetry.[‡] The inset in Figure 1 demonstrates two representative SEM images of ZIF-8₂, showing the same location with different magnification. SEM

[†] The starting materials were $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HMIIm, DMF and triethylamine (TEA) from Sigma-Aldrich, which were used without further purification. All manipulations with reagents were performed in air (under a fume hood). We used the Zn^{2+} :HMIIm:TEA:DMF molar ratios of 1:2:3:289 (hereafter marked as ZIF-8₂) and 1:4:3:289 (ZIF-8₄). The synthesis was started with dissolving zinc nitrate and HMIIm separately in DMF until clear solution; then, TEA was added dropwise to the HMIIm solution with stirring. Both solutions were transferred into a glass liner, capped and placed in a MW oven to be heated at 413 K (140 °C) for 15 min. The resulting milky suspension was allowed to cool down to room temperature. Then, the white precipitate was collected by centrifugation and washed two times with DMF and one time with methanol and then dried at 333 K (60 °C) in a conventional oven.

[‡] The XRD patterns were collected on an ARL X'TRA Powder Diffractometer (Thermo Scientific) using $\text{CuK}\alpha$ radiation. Space group: *I*-43*m* (217), lattice constants: $a = 17.003(3) \text{ \AA}$, cell volume, $4915.4(17) \text{ \AA}^3$, formula units per unit cell, 12. The yield of products was about 45–50% for both samples based on the amount of zinc oxide after calcination at 873 K (600 °C) for 48 h.

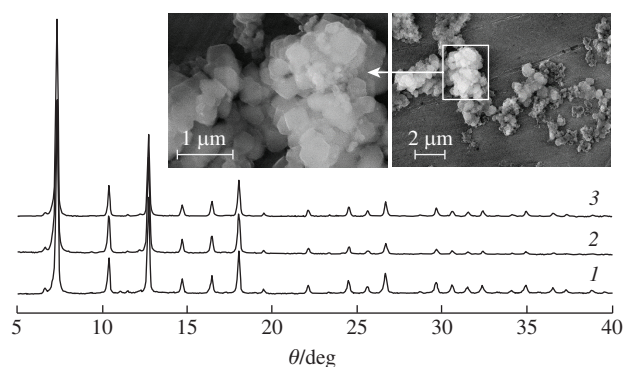


Figure 1 Powder XRD patterns of ZIF-8: (1) commercial analogue Basolite Z1200 (BASF), (2) ZIF-8₂ and (3) ZIF-8₄. Inset: SEM image of ZIF-8₂ with a magnification of the fragment.

images revealed the presence of crystals as hexagonal prisms of about 400 nm.

The collected isotherms of N_2 adsorption/desorption on the samples at 77 K are shown in Figure 2.[§] Specific surface areas were obtained by the BET method: $1419 \text{ m}^2 \text{ g}^{-1}$ for ZIF-8₂ and $1192 \text{ m}^2 \text{ g}^{-1}$ for ZIF-8₄. The average pore widths (4V/A by BET) are 1.78 and 1.63 nm, respectively. The difference in the N_2 uptake can be attributed to the presence of some residual species (e.g., unreacted linker) in the cavities.

The IR spectra of both samples do coincide perfectly as can be seen in Figure 3,[§] extending from the fingerprint region to far-IR. The spectral profile repeats the known one for ZIF-8 (for

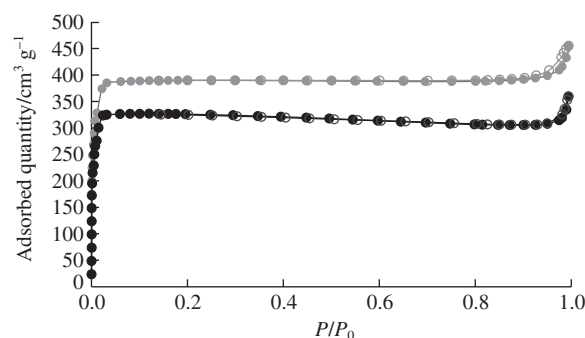


Figure 2 Physisorption of nitrogen at 77 K for ZIF-8: sample ZIF-8₂ (grey) and ZIF-8₄ (black). The adsorption and desorption branches are shown as open and solid circles, respectively.

[§] The isotherms of nitrogen adsorption/desorption were measured on a Micromeritics ASAP 2020 analyzer. Prior to the measurement, the samples were activated at 573 K (300 °C) for 24 h in a dynamic vacuum.

The IR spectra were recorded on a Bruker Vertex 70 spectrometer using a diamond crystal Platinum attenuated total reflectance (ATR) accessory.

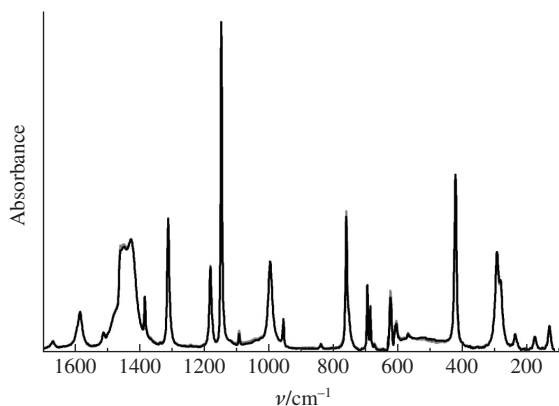


Figure 3 ATR FTIR spectra of ZIF-8_2 (grey) and ZIF-8_4 (black) samples.

example, reported in ref. 11). Briefly, there are the vibrations of imidazole units in the mid-IR region, while Zn–N vibrations are situated in far-IR. The aromatic and aliphatic C–H stretching vibrations, although being present in the spectra, are not reported here to preserve clarity. The peak at 1584 cm^{-1} is assigned to C=N stretch mode. The group of bands at $1550\text{--}1350\text{ cm}^{-1}$ originates from the entire ring stretching. The bands in the spectral region of $1350\text{--}900\text{ cm}^{-1}$ are attributed to the in-plane bending of the ring while those at $800\text{--}500\text{ cm}^{-1}$ belong to the out-of-plane bending.

The proposed synthetic approach could be useful for the preparation of ZIF-8 for applications where the high specific surface area is a key important factor. In this case, a stoichiometric Zn^{2+} :linker ratio would be an optimal choice.

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