

Microwave Synthesis of a Porous Metal-Organic Framework, Zinc Terephthalate MOF-5

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Organic-inorganic porous hybrid materials are currently of great interest and importance for the novel coordination structure, relatively facile preparation, special properties and potential practical applications.^{1,2} Recent studies have been focused on the design and synthesis of porous materials which possess a very low density, high surface area and specific functionality. Among these materials, metal organic frameworks (MOFs), originally coined and intensively studied by Yaghi *et al.* are crystalline and well-defined structures, consisting of metal ions or oxo-bridged metal clusters linked by organic carboxylates.^{2a-c} In particular, a series of MOF-5s have open metal frameworks with high Langmuir surface areas (1000-4500 m²/g) and thermal stability.^{2b,3} These porous "organic" zeolites are mimicking the frame and properties of the zeolite, and thus many potential industrial applications arise from the promising properties of these high-surface materials. The structural architecture of MOFs can be extended to the real zeolite frameworks by Ferey *et al.* who showed the MTN type structure from chromium oxo cluster ion and terephthalate, very recently.⁴ In general, MOFs can be synthesized by a slow diffusion method - diffusion of amine into a solution containing metal salt and organic carboxylic acid - for weeks or a solvothermal reaction technique for hours.² Recent literature, however, revealed that it is not easy to prepare MOF-5 with a high surface area by both methods.⁵ Resulting MOF nanocrystalline materials^{5a} and space group *Fm-3m* like MOF-5 materials^{5b} had Langmuir surface areas of 727 and 572 m²/g, respectively, but these figures are far below the reported value of 2900 m²/g by Yaghi.^{2a} Furthermore, both groups noticed that their MOFs slowly tend to decompose in moisture and acid, thus this instability may limit their practical applications.

On the other hand, a microwave irradiation method has been studied in the syntheses of not only organic molecules⁶ but also inorganic materials.⁷⁻¹¹ More recently, microwave-assisted synthesis of inorganic materials requiring several days for their crystallization has attracted much attention. This technique provides synthesis methods of porous materials with saving the reaction time within a few minutes⁸ and offering phase selectivity⁹ and facile morphology control.¹⁰ Very recently, some of us recently reported that microwave technique can be well applied to the rapid synthesis as well

as phase selective crystallization of porous hybrid solids including MIL-77, MIL-100 and MIL-101.¹¹

Here we describe the first result on the microwave synthesis of MOF-5, Zn₄(O)(BDC)₃·guest molecules (BDC = 1,4-benzenedicarboxylate) with a high surface area, as named MW MOF-5 (Microwave MOF-5). MW MOF-5 was synthesized in *N,N'*-diethylformamide (DEF) using microwave irradiation. Equimolar amount of H₂BDC (1.57 mg, 0.60 × 10⁻² mmol) and zinc nitrate tetrahydrate (1.50 mg, 0.60 × 10⁻² mmol) in a DEF (0.6 mL) were placed in a 10 mL tube. The tube was sealed with a rubber septum and placed in a microwave oven (Discover, CEM, maximum power of 300 W). The resulting mixture was heated at 95 °C, held for 9 min and then cooled to room temperature. The colorless crystalline materials (2.10 mg, 27% yield) were obtained by centrifuging, washing with *N,N'*-dimethylformamide (DMF, 3 × 5 mL) and drying briefly in the air.

The morphology of MW MOF-5 was studied by scanning electron microscopy (SEM) after gold deposition. The SEM image shows three dimensional cube-like microcrystals with the length of 2-4 μm as illustrated in Figure 1. Its morphology was consistent with the previous result which was obtained from slow diffusion with addition of H₂O₂, even though SEM image of MOF-5 produced by H₂O₂ is not clear.^{5a}

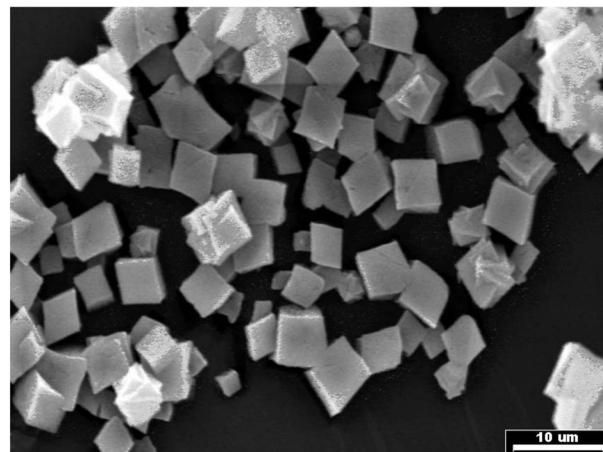


Figure 1. The SEM image of MW MOF-5 obtained from microwave irradiation at 95 °C for 9 min.

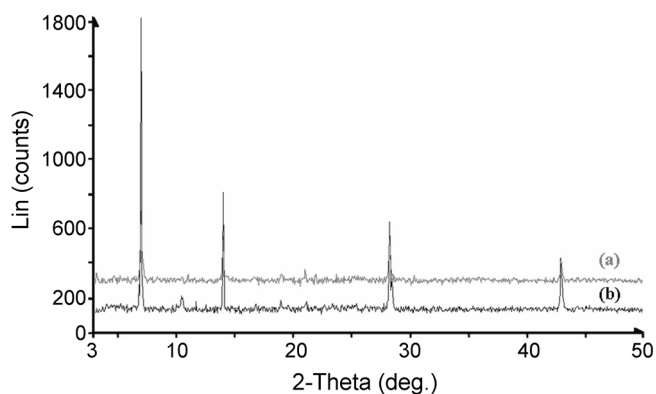


Figure 2. XRD patterns of MOF-5 prepared by the hydrothermal reaction (a) and microwave irradiation (b).

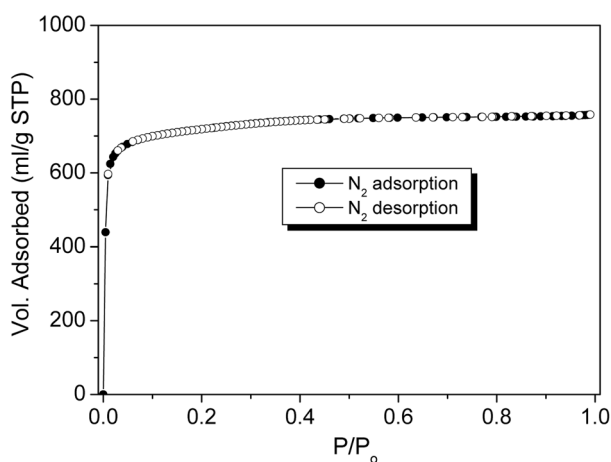


Figure 3. Adsorption-desorption isotherms of nitrogen over MW MOF-5 after evacuation at 200 °C for 3 h.

Figure 2 shows the XRD pattern of as-synthesized MW MOF-5 under microwave irradiation. The XRD pattern of the sample obtained from microwave irradiation was well matched with that of as-prepared MOF-5 by hydrothermal reaction as well. MW MOF-5 is also characterized by the vibrational stretching frequencies of C-O of BDC and DEF that are 1605 and 1648 cm^{-1} using a FT-IR (Perkin-Elmer System 2000, KBr pellet, 4000-400 cm^{-1}), respectively, which values are consistent with those of MOFs.^{2a-c}

Thermal behavior of the as-prepared MW MOF-5 was investigated using thermogravimetric analysis (TGA). The TGA profile reveals two weight changes around 200 and 475 °C. The first gentle slope of weight loss (*ca.* 36%) between 100 and 200 °C attributes to the solvated molecules that are the mixture of non-volatile DEF (bp 176 °C) and water (calcd 40%). The second major loss of *ca.* 39% accounts for the framework decomposition of organic carboxylates (calcd 38%). Overall thermal stability is similar to the previous result.^{2a}

To confirm the permanent porosity, we obtained the N_2 adsorption isotherm of MW MOF-5 using a gas sorption analyzer (Micromeritics, ASAP 2000) after careful evacu-

ation at 200 °C. The N_2 adsorption isotherm reveals a typical type-I behavior, as plotted in Figure 3. Fitting the BET and Langmuir equations to the resulting isotherm N_2 gives estimated surface areas of $S_{\text{BET}} = 2869 \text{ m}^2/\text{g}$ and $S_{\text{Lang}} = 3060 \text{ m}^2/\text{g}$, respectively, which are close to the reported value of 2900 m^2/g by Yaghi.^{2a} Extrapolation of t-plot yields an available micropore volume of 0.94 cm^3/g .

In summary, we have first shown that MW MOF-5 is synthesized efficiently within several minutes and its physicochemical and textural properties are very similar to those synthesized by conventional hydrothermal heating. Thus mass production of MW MOF-5 can possibly be applied to practical applications. Current work is focused on investigating the role of concentration, molar ratio of metal and ligand, temperature and time on the synthesis of MW MOF-5.

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