



Water–alkane interface promotes the formation of metal–organic frameworks



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ABSTRACT

To develop facile, rapid and low-energy route for metal–organic framework (MOF) formation is of great importance. Here a water–alkane interface strategy was proposed for the MOF formation at room temperature. The content and molecular structure of alkane phase were found to have remarkable effect on regulating the porosity properties of MOFs. For example, the MOF synthesized in 1:1 (v/v) water/*n*-hexane mixture has the largest BET surface area (1474.1 m²/g) and total pore volume (0.7030 cm³/g). The mechanism was discussed from the competitive adsorption of water and alkane in the micropores of MOF building blocks during formation process.

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1. Introduction

In recent years, metal–organic frameworks (MOFs) have attracted much attention due to their structural topologies and potential applications in adsorption, catalysis, drug delivery, etc [1,2]. The solvothermal method is widely adopted for synthesizing MOFs [3–5]. The usually used solvents are organic solvents such as *N,N*-dimethyl-formamide (DMF), dimethyl sulphoxide (DMSO), tetrahydrofuran (THF). In most cases, a reaction time up to dozens of hours and high temperatures (>100 °C) are needed [3–8]. To accelerate the MOF formation, microwave [9], ultrasonication [10], solvent mixtures (e.g. ethanol/water mixture [11–13]), surfactant-directed routes [14,15], and CO₂-expanded liquids [16] have been proposed. Although the surfactant-directed route is efficient in promoting the MOF formation at room temperature, it suffers from economic, environmental, and separation problems. To develop facile, surfactant-free and low-energy route for MOF formation is of great importance.

On the other hand, it is well known that a major drawback to the practical application of MOFs is the poor hydrostability

[17,18], which is critical to storage and durability when MOFs are exposed to a moist atmosphere. For example, the skeleton of Cu₃(BTC)₂ (BTC = 1,3,5-benzenetricarboxylate), which is one of the most extensively explored MOFs [19–21], displays ruinously collapse after immersion in water at room temperature for 4 h [22]. Diverse kinds of methods have been proposed to enhance the hydrostability of MOFs [17,23,24], including modification of organic linker and/or metal center [25,26], synthesis of MOF nanocomposites [27,28], plasma enhanced chemical vapor deposition of perfluoroalkanes [22], etc. Generally, water is absolutely avoided in the preparation of the water-sensitive MOFs.

In light of the above considerations, here we report a water–alkane interface method for the rapid and simple synthesis of Cu₃(BTC)₂ at room temperature. By utilizing water/alkane mixture, Cu₃(BTC)₂ can form in 2 h just by stirring at room temperature. This method involves no surfactant and the product can be easily separated from the solvent system. Moreover, it was found that the content and molecular structure of alkane have a profound effect on the porosity properties of the MOFs. The possible mechanism was discussed from the competitive adsorption of water and alkane in the micropores of MOF building blocks during formation process.

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2. Experimental section

2.1. Materials

Copper (II) perchlorate hexahydrate ($\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, purity 98%), 1,3,5-benzenetricarboxylic acid (H_3BTC , purity 98%), n-octane (purity 98%), n-decane (purity 98.5%), n-dodecane (purity 99%), n-tetradecane (purity 98%), 1-chlorohexane (purity 95%), and 1-bromohexane (purity 99%) were purchased from J&K Scientific Corporation. n-Hexane (purity 99%), isooctane (purity 99.5%) and double distilled water were provided by Beijing Chemical Reagent Company. All these materials were used without further purification.

2.2. Synthesis of MOFs

In a typical reaction, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.3 mmol) and H_3BTC (0.2 mmol) were dissolved in water/alkane mixture, then appropriate triethylamine was added into the system for deprotonation. The mixtures were stirred at room temperature for 2 h. The products were obtained by washing with ethanol and water and drying at 80 °C under vacuum for 24 h.

2.3. Characterization of MOFs

The products were characterized by X-ray diffraction (XRD) (Model D/MAX 2500, Rigaku) with $\text{Cu K}\alpha$ radiation at a scanning rate of 5°min^{-1} . The porosity properties were gained from N_2 adsorption–desorption isotherms using a Micromeritics ASAP 2020M system. The FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer and the samples were prepared by the KBr pellet method. The thermogravimetric (TG) measurement was carried out using Pyris 1 TGA with N_2 flow of 10 mL/min. The morphologies of the as-synthesized MOFs were characterized by scanning electron microscope (SEM, HITACHI S-4800).

2.4. Hydrostability of MOFs

The MOF (0.1 g) was put in a closed vial containing 5 mL of water, then the mixture was stirred at room temperature for different time. The MOF after water treatment was characterized by XRD.

3. Results and discussion

First of all, we tried the synthesis of $\text{Cu}_3(\text{BTC})_2$ in pure water at room temperature, using $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and H_3BTC as MOF precursors. The XRD patterns of the samples synthesized at reaction time of 2 and 12 h (patterns b and c in Fig. 1) are definitely different from that of the simulated HKUST-1 (pattern a in Fig. 1), suggesting that the $\text{Cu}_3(\text{BTC})_2$ cannot form at such experimental conditions. It has been well recognized that the coordination bonds of $\text{Cu}_3(\text{BTC})_2$ can be attacked by water molecules, leading to the breakage of coordination bonds and subsequent damage of frameworks [17,23,24]. The XRD patterns of the samples synthesized in water/n-hexane mixtures with different n-hexane volume ratios are shown as patterns d–g in Fig. 1. The reaction time was 2 h. The peak positions and relative intensities agree well with those of the simulated HKUST-1, indicating that $\text{Cu}_3(\text{BTC})_2$ can form in a short time with the aid of alkane. FT-IR spectra (Fig. S1) reveal that the carboxylate groups of H_3BTC were coordinated to Cu (II) ions. TG analysis shows that the MOF can keep stable up to 300 °C (Fig. S2).

The porosity properties of $\text{Cu}_3(\text{BTC})_2$ synthesized in water/n-hexane mixtures were determined by N_2 adsorption–desorption method. All samples present typical type-I mode without obvious

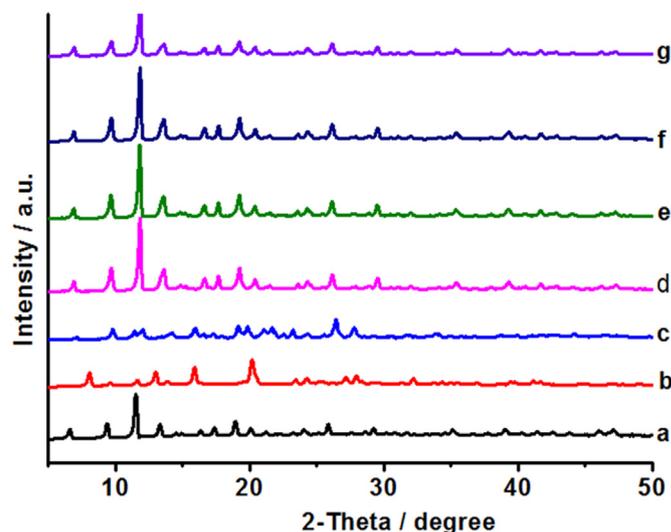


Fig. 1. The simulated XRD pattern of HKUST-1 (a). The XRD patterns of the samples synthesized in pure water at reaction time of 2 h (b) and 12 h (c). XRD patterns of $\text{Cu}_3(\text{BTC})_2$ synthesized in water/n-hexane mixtures with oil:water volume ratio of 1:9 (d), 2:8 (e), 3:7 (f), and 5:5 (g) at reaction time of 2 h.

hysteresis loops (Fig. 2A). The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) and total pore volume (V_{t}) of the MOFs synthesized are shown in Fig. 2B. Interestingly, both BET surface area and pore volume increase with the increasing alkane content. As

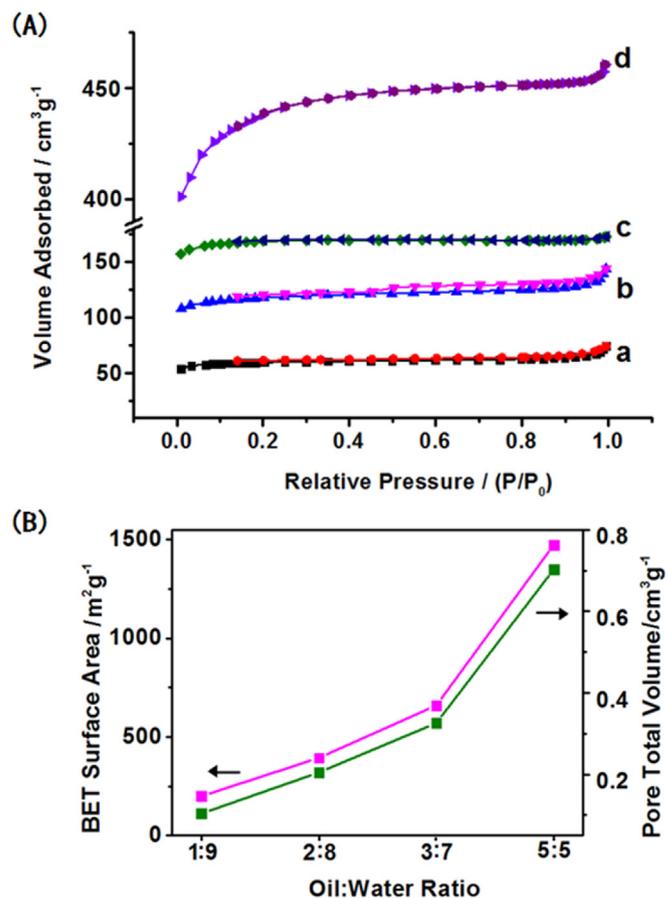


Fig. 2. A: N_2 adsorption–desorption isotherms of the MOFs synthesized in water/n-hexane mixtures with oil:water volume ratio of 1:9 (a), 2:8 (b), 3:7 (c), and 5:5 (d). B: Dependence of BET surface area and total pore volume of $\text{Cu}_3(\text{BTC})_2$ on oil:water volume ratio.

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