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Improved synthesis and hydrogen storage of a microporous metal–organic framework material

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ABSTRACT

A microporous metal–organic framework MOF-5 [$Zn_4O(BDC)_3$, BDC = 1,4-benzenedicarboxylic] was synthesized with and without H_2O_2 by improved methods based on the previous studies. The obtained materials were characterized by X-ray diffraction, scanning electron microscopy and nitrogen adsorption, and their hydrogen storage capacities were measured. The synthesis experiments showed that H_2O_2 favored the growth of high quality sample, large pore volume and high specific surface area. The measurements of hydrogen storage indicated that the sample with higher specific surface area and large pore volume showed better hydrogen storage behavior than other samples. It was suggested that specific surface area and pore volume influenced the capacity of hydrogen storage for MOF-5 material.

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1. Introduction

A new class of nanoporous material, so called metal–organic frameworks (MOFs) which possess a very low density, high surface area and large porous volume are receiving growing attention. The design and synthesis of porous metal–organic frameworks with nanometer scale periodicity has tremendously expanded, and the member of MOFs is becoming larger and larger and the structure is becoming richer and richer by assembling the metal ions and organic ligands. Meanwhile, because this kind of material shows potential behavior in areas [1–7] including catalysis, separation, sorption and many other fields, more and more researcher groups devote themselves to exploiting novel compositions and architectures in view of practical applications.

A series of MOF-*n* materials was produced by Eddaoudi et al. [8]. One typical member of MOF-*n* family, MOF-5, was a zeolite-like material formed by $[Zn_4O]^{6+}$ groups joined to an octahedral array of $[O_2C–C_6H_4–CO_2]_2$ (1,4-benzendicarboxylate, BDC) groups, space group (Fm-3m) with $a = 25.6690(3)$ Å, $V = 16{,}913.2(3)$ Å and $Z = 8$. For hydrogen storage of MOF-5, the first report indicated that MOF-5 showed high hydrogen storage capacities, 4.5 wt% at 77 K and 0.8 bar, and 1 wt% at room temperature and pressure of 20 bar [9]. In the late researches, this group observed that maximum uptakes hydrogen of MOF-5 can reach 1.32 wt% at 1 bar and 77 K [10]. However Panella and Hirscher [11] announced hydrogen storage value of 1.6 wt% for MOF-5 at pressures above 10 bar, but the adsorption capacity of MOF-5 was very low at room temperature, less than 0.2 wt% at pressures up to 67 bar.

With reference to previous reports about hydrogen storage of MOF-5, our interest was to improve synthesis of a high quality MOF-5 material to increase the hydrogen storage capacity, and discuss the effect factors on hydrogen storage capacity of MOF-5. In this paper, the synthesis conditions of MOF-5 were investigated. The typical samples were characterized with XRD, SEM and N_2 adsorption. The hydrogen storage capacity of MOF-5 was measured at 77 K.

2. Experimental

2.1. Raw materials

$Zn(NO_3)_2 \cdot 6H_2O$, 1,4-benzenedicarboxylic acid(H_2BDC), N-N-dimethylformamide (DMF), triethylamine(TEA) and H_2O_2 (30%) were of A.R. Grade reagent from commercial sources and used without further purification.

2.2. Synthesis

Based on the synthesis condition of the literature [12], the synthesis method was improved in this paper. The typical synthetic procedure was as follows: $Zn(NO_3)_2 \cdot 6H_2O$ and H_2BDC were dissolved in DMF under room temperature and atmospheric condition, and then the mixture solution was placed in a large beaker. TEA was placed in a small beaker and this was placed in the centre of the large beaker. The large beaker was sealed and placed in static

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condition at room temperature. Finally the white products were collected by centrifugation and washed with DMF, then dried at 373 K. The same synthesis was repeated by adding a small amount of H_2O_2 to DMF solution containing H_2BDC and $Zn(NO_3)_2 \cdot 6H_2O$, and TEA was slowly diffused to the mixture solution. The ratio of materials was taken by mol ratio in all synthesis experiments.

2.3. Characterization

The crystallinity of the samples were determined from X-ray powder diffraction patterns collected on a Rigaku D/max-2500 diffractometer with Cu Kα1 radiation (λ = 1.5406 Å) and operated at 40 kV and 100 mA. The relative crystal crystallinity was calculated by comparing the diffraction intensities of the four major peaks at 2θ = 6.8°, 9.6°, 13.7° and 15.4°.

The crystal morphologies were observed on a JSM-6700F scanning electron microscope.

N_2 adsorption data were measured on an ASAP 2000 M gas adsorption apparatus at liquid nitrogen temperature.

2.4. Hydrogen storage measurements

Hydrogen storage measurements were performed using volumetric setup that had been previously tested for hydrogen storage of metal alloy. All samples were heated up to 523 K under vacuum until the sample mass equilibration and no guest molecules was evacuated before making hydrogen storage measurement at 77 K.

3. Results and discussion

3.1. Synthesis conditions

According to the literature [11], adding H_2O_2 may improve the quality of MOF-5. In this paper, the effect of H_2O_2 on synthesizing MOF-5 was investigated (Table 1) and synthesis conditions were optimized. It was found that the relative crystallinity of MOF-5 increased by adding appropriate amount of H_2O_2 and that the sample with the ratio H_2O_2/H_2BDC = 1.03/1 had the highest relative crystallinity. TEA was essential in the synthesis of MOF-5 materials. Its effect on prepared MOF-5 was studied at $Zn(NO_3)_2 \cdot 6H_2O/H_2BDC$ = 2/1, H_2O_2/H_2BDC = 1.03/1, DMF/H_2BDC = 21/1. MOF-5 with H_2O_2 had the highest relative crystallinity when TEA/H_2BDC = 7.91/1 from the results of Table 2.

Table 1
Effects of H_2O_2 on MOF-5 synthesis.

Sample	H_2O_2/H_2BDC	Phase	Relative crystallinity (%)
1	0	MOF-5	73
2	0.68/1	MOF-5	84
3	1.03/1	MOF-5	100
4	1.37/1	MOF-5	68

Table 2
Effects of TEA on MOF-5 synthesis with H_2O_2.

Sample	TEA/H_2BDC	Phase	Relative crystallinity (%)
1	0	Amorphous	–
2	4.94/1	MOF-5	85
3	7.91/1	MOF-5	100
4	10.87/1	MOF-5	69

3.2. XRD of samples

The XRD patterns of MOF-5 were showed in Fig. 1. The sample in Fig. 1a was from the system without H_2O_2 and the sample in Fig. 1b was from the system with H_2O_2. The peak positions and relative intensities of synthesized samples were similar with reported XRD patterns of MOF-5 [11]. The data showed the synthesized samples with and without H_2O_2 were MOF-5. Comparing Fig. 1a and b, the peak intensities in Fig. 1b were higher than those in Fig. 1a. So MOF-5 from the system with H_2O_2 had higher relative crystallinity than the sample from the system without H_2O_2.

3.3. Morphology of samples

The morphologies of the typical samples were observed with SEM method. As shown in Fig. 2, the samples synthesized with and without H_2O_2 were also irregular particles. The sample with H_2O_2 (Fig. 2b) was obviously larger than that of sample without H_2O_2 (Fig. 2a) at the same magnification scale.

3.4. Nitrogen adsorption measures

The pore properties were analyzed based on the nitrogen adsorption isotherms at 77 K (Fig. 3). The MOF-5 sample with addition of H_2O_2 had higher BET surface area and larger pore volume than the sample without addition H_2O_2, the corresponding data were shown in Table 3. This suggested that introduction of H_2O_2 could increase the surface area and pore volume of sample.

3.5. Hydrogen storage experiments

The organic guests contained in MOF-5 sample would occupy a majority of void areas of framework. Generally, organic guest may

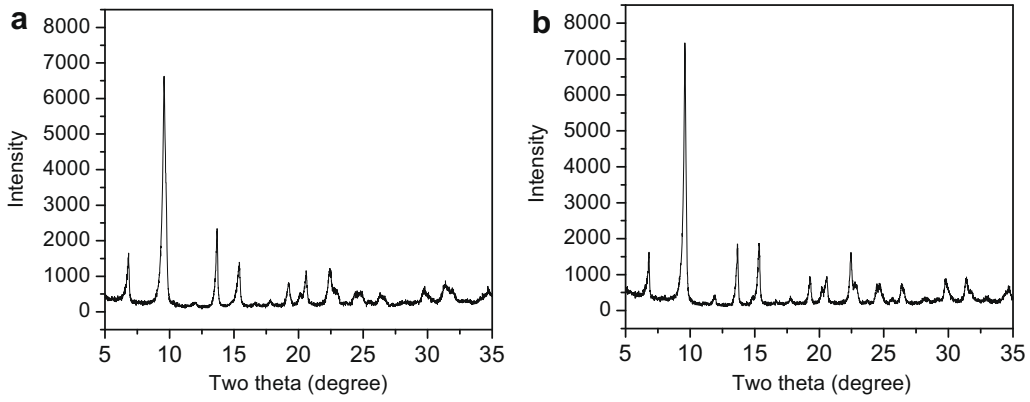

Fig. 1. XRD patterns of MOF-5 samples: (a) without addition of H_2O_2 and (b) with addition of H_2O_2.

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