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Desorption of dimethylformamide from $Zn_4O(C_8H_4O_4)_3$ framework

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ABSTRACT

Both dimethylformamide (DMF) and diethylformamide (DEF) are important solvents for the synthesis of $Zn_4O(C_8H_4O_4)_3$ framework (MOF-5). It is generally recognized that DMF molecules can be completely displaced by CH_2Cl_2 during the synthesis of MOF-5. Herein, however, it was found that the DMF molecules inside the pores of the MOF-5 framework cannot be displaced by CH_2Cl_2. The desorption of the DMF molecules from the pores, which requires a temperature of 100 °C or above, is the first order with activation energy of 56.38 kJ/mol. In contrast, DEF molecules can be completely displaced by CH_2Cl_2 during the synthesis of MOF-5, because DEF molecules cannot penetrate into the pores of the MOF-5 paste.

1. Introduction

Crystalline metal-organic frameworks (MOFs) are attracting much attention due to their low-density structures, high surface areas, and tunable structures, which have potential applications in hydrogen storage [1–16], CO_2 adsorption [17–23], and catalysis [24–29]. Furthermore, MOFs have exhibited unusual properties of phase transformations [30–36]. Among them, $Zn_4O(C_8H_4O_4)_3$ framework named as MOF-5, which was invented by Yaghi in 1999 [37], is the most studied metal-organic framework due to its ultra-high surface area and inexpensive raw materials [37–41].

Diethylformamide (DEF) and dimethylformamide (DMF) solvents are critical for MOF-5 synthesis, because MOF-5 crystals are produced based on the solvothermal crystallization of a mixture of zinc nitrate and terephthalic acid solution in DEF or DMF [39]. The produced crystals are then subjected to DEF or DMF washing and soaking to remove the by-products and unreacted zinc nitrate [39], and followed by low-boiling point CH_2Cl_2 (40 °C) or $CHCl_3$ (61 °C) washing and soaking to displace the higher-boiling point DEF (176 °C) or DMF (153 °C) in MOF-5 [37–40]. Finally, MOF-5 is vacuumed at a low temperature (usually ambient temperature or 60 °C) to remove CH_2Cl_2 or $CHCl_3$ [37–40]. Generally, it is assumed that CH_2Cl_2 or $CHCl_3$ can displace DEF or DMF completely and thus the solvent remained in MOF-5 after vacuum at room temperature is CH_2Cl_2 or $CHCl_3$. However, in this work, we found that DMF solvent cannot be completely displaced by CH_2Cl_2 washing and soaking during the synthesis, because some of them have been strongly adsorbed inside the pores of MOF-5. Furthermore, to remove such strongly adsorbed DMF, MOF-5 must be treated under vacuum at 100 °C or above.

2. Experimental

2.1. Synthesis of MOF-5

The approach, which was developed by Yaghi and co-workers [39], was employed to synthesize MOF-5 as follows.

Synthesis of MOF-5 in DEF: $Zn(NO_3)_2{\cdot}6H_2O$ (1.8 g, 6.1 mmol) and 1,4-benzenedicarboxylic acid (0.33 g, 2.0 mmol) were dissolved in 50 ml of diethylformamide (DEF) in a 100 ml Pyrex media bottle with a teflon lined lid. The obtained mixture was heated in an oven at 100 °C for 24 h to yield large cube-shaped crystals. The reaction vessel was then removed from the oven and allowed to cool to room temperature and transferred to an argon-filled glove bag. All subsequent manipulations were performed in the glove bag under an argon atmosphere using oven-dried glassware and anhydrous solvents. After the solvent was decanted, the remained solid was washed six times with 50 ml of anhydrous DMF (each time letting the solid soak in DMF for 8 h). Then, the DMF was decanted and the remaining solid was washed six times with 50 ml of anhydrous CH_2Cl_2 (again each time letting the solid soak in CH_2Cl_2 for 8 h). Finally, after the solvent was decanted, MOF-5 sample was vacuumed at room temperature for 24 h to yield $Zn_4O(BDC)_3$ cube-shaped crystals (referred to as MOF-5-E).

Synthesis of MOF-5 in DMF: $Zn(NO_3)_2{\cdot}6H_2O$ (0.45 g, 1.5 mmol) and 1,4-benzenedicarboxylic acid (0.083 g, 0.5 mmol) were dissolved in a solution (consisting of 49 ml DMF and 1 ml H_2O) in a 100 ml Pyrex media bottle with a teflon lined lid. The obtained

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mixture was heated in an oven at 100 °C for 7 h to yield large cube-shaped crystals. The crystals were washed by using DMF and then CH_2Cl_2 with the same procedure described above for MOF-5-E. Finally, the obtained MOF-5 sample was vacuumed at room temperature (referred to as MOF-5-M1), 55 °C (as MOF-5-M2) or 115 °C (as MOF-5-M3) for 24 h to yield $Zn_4O(BDC)_3$ cube-shaped crystals.

2.2. DMF and CH_2Cl_2 soaking treatment of MOF-5-M3

The as-synthesized MOF-5-M3 (0.2 g) was soaked in DMF (50 ml) for 2 h. Then, the DMF solvent was decanted and the obtained white product was vacuumed at room temperature (referred to as MOF-5-M3-a) or 180 °C (referred to as MOF-5-M3-b) for 24 h, respectively. Furthermore, the obtained white product was washed six times with 50 ml anhydrous CH_2Cl_2 (each time letting the solid soak in CH_2Cl_2 for 8 h). After the CH_2Cl_2 solvent was decanted, the white product was vacuumed at room temperature for 24 h (referred to as MOF-5-M3-c).

2.3. Characterization

2.3.1. Temperature-programmed mass spectrum (TPMS)

Temperature-programmed mass spectrum (TPMS) was obtained via the following approach: the sample in a quartz tube reactor was heated from 20 to 620 °C at a rate of 10 °C/min. The liquid and gas products were carried by helium into on-line Hewlett-Packard 5970 Series Mass Selective Detector.

2.3.2. Thermal gravimetric analysis (TGA)

TGA was carried out in nitrogen atmosphere (100 mL/min) at a constant rate of 10 °C/min, using SDT Q600 equipment.

2.3.3. Powder X-ray diffraction (XRD)

X-ray diffraction data was obtained at 1 atm and room temperature by using Scintag XDS2000 Powder Diffractometer at 45 kV, 35 mA for Cu Kα (λ = 1.5406 Å) radiation, with a scan speed of 1 °/min and a step size of 0.03° in 2θ.

2.3.4. Surface area measurement

Surface area was measured with a Micromeritics ASAP 2000 sorptometer using nitrogen adsorption at liquid-nitrogen temperature (77 K). Before nitrogen adsorption measurement, the samples were degassed in situ at 110 °C for 12 h to remove any guest molecule from the sample.

3. Results and discussion

To examine the presence of solvent remained in MOF-5 synthesized with DMF, MOF-5 samples were subjected to thermal gravimetric analysis (TGA). Fig. 1 shows that there are two weight-loss steps for both MOF-5-M1 and MOF-5-M2: the first step corresponding to 13.5% weight loss occurred in the range of 100–210 °C for MOF-5-M1 and 12.5% weight loss in the range of 100–240 °C for MOF-5-M2; the second step beginning at 400 °C with 42.2% and 39.5% weight loss for MOF-5-M1 and MOF-5-M2, respectively. Furthermore, the first step was attributed to the solvent desorption [37–39]. It is generally recognized that CH_2Cl_2 can completely displace DMF from MOF-5 during the synthesis. In other words, it should be assumed that the desorbed solvent (associated with weight loss of 13.5% and 12.5%) is CH_2Cl_2. However, from the temperature-programmed mass spectra (TPMS) of MOF-5-M1 and MOF-5-M2 (Figs. 2 and 3), one can see that the solvent desorption beginning at around 100 °C is due to DMF instead of CH_2Cl_2, indicating the presence of DMF in MOF-5 after displaced by CH_2Cl_2 during the synthesis. In other words, DMF cannot be completely displaced by CH_2Cl_2 washing and soaking due to the strong adsorption of

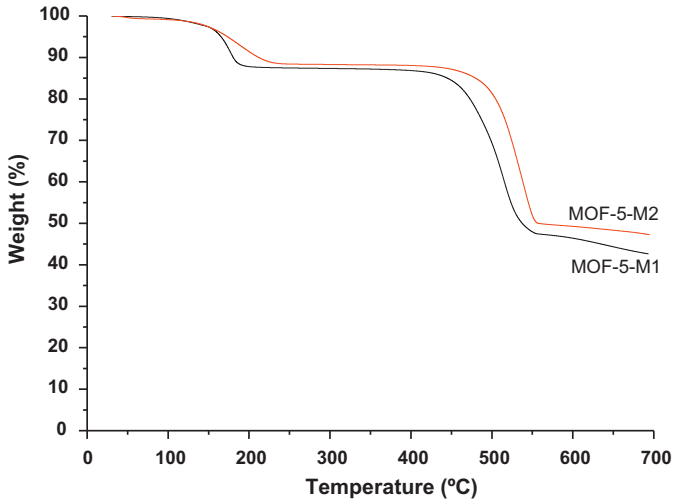

Fig. 1. TG curves of MOF-5-M1 and MOF-5-M2 under nitrogen atmosphere.

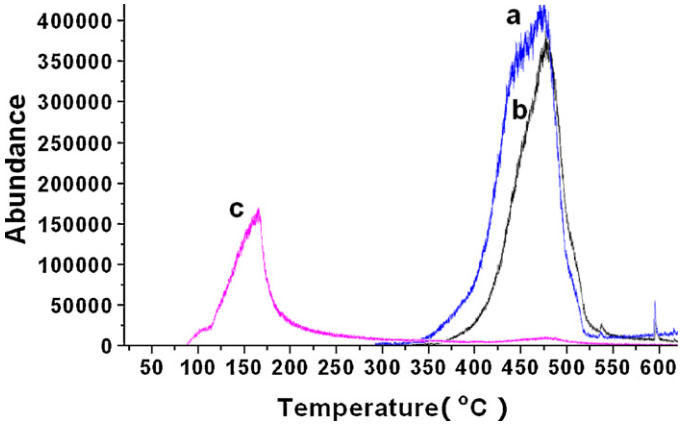

Fig. 2. Temperature-programmed mass spectrum of MOF-5-M1 (a. CO_2, b. benzene and c. DMF).

DMF on MOF-5. Furthermore, if one unit cell of MOF-5 can adsorb one and two DMF molecules, the desorption of the DMF should lead to 8.67 and 15.96% weight loss during the TG measurement, respectively. The weight loss of desorbed DMF from MOF-5-M1 and MOF-5-M2 is 13.5% and 12.5%, respectively, indicating that there should be more than one but less than two DMF molecules adsorbed in one unit cell of MOF-5 (namely, one unit cell of MOF-5-M1 and

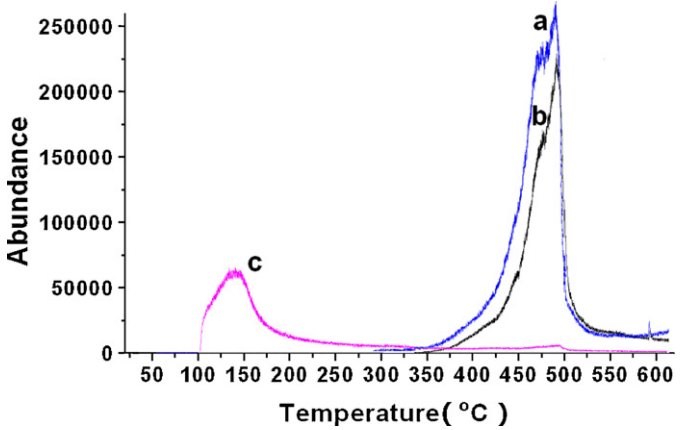

Fig. 3. Temperature-programmed mass spectrum of MOF-5-M2 (a. CO_2, b. benzene and c. DMF).