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Framework-solvent interactional mechanism and effect of NMP/DMF on solvothermal synthesis of $[Zn_4O(BDC)_3]_8$

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Abstract: In order to explore the effect mechanism of solvent on the synthesis of the metal organic framework materials, the microscopic interaction between solvent and framework and the effects of N,N-dimethyl-formamide (DMF) or N-methyl-2-pyrrolidone (NMP) on solvothermal synthesis of $[Zn_4O(BDC)_3]_8$ were investigated through a combined DFT and experimental study. XRD and SEM showed that the absorbability of NMP in the pore of $[Zn_4O(BDC)_3]_8$ was weaker than that of DMF. The thermal decomposition temperature of $[Zn_4O(BDC)_3]_8$ synthesized in DMF was higher than that in NMP according to TG and FT-IR. In addition, the nitrogen sorption isotherms indicated that NMP improved gas sorption property of $[Zn_4O(BDC)_3]_8$. The COSMO optimized calculations indicated that the total energy of $Zn_4O(BDC)_3$ in NMP was higher than that in DMF, and compared with non-solvent system, the charge of zinc atoms decreased and the charge value was the smallest in NMP. Furthermore, the interaction of DMF, NMP or DEF in $[Zn_4O(BDC)_3]_8$ crystal model was calculated by DFT method. The results suggested that NMP should be easier to be removed from pore of materials than DMF from the point of view of energy state. It can be concluded that NMP was a favorable solvent to synthesize $[Zn_4O(BDC)_3]_8$ and the microscopic mechanism was that the binding force between $Zn_4O(BDC)_3$ and NMP molecule was weaker than DMF.

Key words: solvothermal synthesis; $[Zn_4O(BDC)_3]_8$; N-methyl-2-pyrrolidone; interactional mechanism; COSMO solvation model; density functional method

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1 Introduction

How to select favourable solvent is one of the key questions that should be thought about when any kind of the metal organic framework materials (MOFs) is constructed [1−3]. There are several popular acceptable opinions about the main functions of solvent: deprotonating function on carboxylic acid ligand, promotion of the reactions which are difficult to proceed in aqueous solution due to the ability of solubilizing reactants, obtaining better crystalline materials, being conducive to form the porous structure in frameworks as template. For the purpose to avoid interrupting or participating in synthesized process, the co-ordination trend of solvent should be weaker than that of carboxylic acid ligand. N,N-dimethylformamide(DMF) was the most common solvent and triethylamine (TEA), N,N-diethyl formamide (DEF) and N-methyl-2-pyrrolidone (NMP) were also usually used as solvents [4−6]. Although it was accepted that the solvents not only acted as general solvents but also intervened the self-assembly reaction of MOFs, the mechanism of solvent is not explained clearly until now.

MOF−5 is typical MOFs material reported by LI et al [7] firstly and the hot research topics in this field included porous structure analysis, catalyst supported property and gas adsorption of MOF−5, etc., recently in China [8−10]. In many cases, DMF was the most widely applied solvent. LI and YANG [11] and CHENG et al [12] synthesized MOF−5 in DMF solvent, studied morphology control, and significantly enhanced hydrogen storage in MOF−5 respectively. MOF−5 membranes were synthesized, characterized and

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concentrated on its transport properties in DMF by ZHAO et al [13]. KIM et al [14] synthesized the interpenetrated structure MOF−5 in DMF solvent, and studied the effect of pH on change of structure and property of hydrogen storage.

DEF and NMP were rarely reported using as solvents in synthesizing MOF−5. For instance, MOF−5 was prepared in DEF by ROSI et al [15,16] and SABO et al [17], whose research purposes were to characterize the properties of hydrogen storage [15], infinite secondary building units, forbidden catenation in MOFs [16] and the effect of palladium modified on the specific surface area [17] of MOF−5 respectively. ZHANG and HU [18] investigated the difference of DMF sorption on the $Zn_4O(C_8H_4O_4)_3$ framework synthesized in DMF and DEF. SON et al [19], LU et al [20] and LEE and PARK [21] reported solvent NMP which was selected to synthesize MOF−5. Although the synthesized mechanism of MOFs was also discussed in Refs. [22−25], the reaction mechanism and effect of DMF, NMP and DEF solvents were difficult to make clear because the synthesis processes were self-assemble and usually proceeded in sealed containers, which was the reason why we tried to use experimental and theoretic methods to investigate the solvent effect and reaction mechanism.

In this work, based on the experimental results, the effect of solvent molecules on the framework structure were explored in an unique way for the first time, which was combined with two different angles of views: one was molecule level, using COSMO models to reveal the difference of microscopic properties of structure unit $Zn_4O(BDC)_3$ in different solvents, and another was putting the solvent molecule in the channel of MOF−5 crystal model, simulating the interactions between solvent and framework. Through this study, not only the effects of solvent and the interactional mechanism between solvent and framework were clarified by XRD, SEM, TG, FT-IR, nitrogen sorption isotherms and DFT methods, but also a new combinational research path was provided to understand the self-assemble crystallization process mechanism better.

2 Experimental

2.1 Reagent and equipments

The solvothermal reactions were carried out in Teflon-lined autoclave. All reagents were purchased from commercial sources and used without further purification. $Zn(NO_3)_2{\cdot}6H_2O$ (Analytical regent), terephthalic acid (≥99.0%), N-methyl-2-pyrrolidonewas (Chemical regent), N,N-dimethylformamide (Analytical regent), dichloromethane (Analytical regent) were purchased from Xilong Chemical Co., Ltd., National Chemical Group Co., Ltd., Shanghai Shunqiang Chemical Co., Ltd. and Tianjin Fuyu Fine Chemical Co., Ltd., respectively.

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku 2500 diffractometer equipped with a sealed Cu tube. SEM images were characterized with Nova Nano SEM 230 scanning electron microscope (SEM). IR spectra were determined at room temperature with Nico LET−6700 FT-IR and the thermogravimetric analysis (TG) data were obtained on Thermo TG/FT-IR in nitrogen atmosphere (70 mL/min) at a constant rate of 5 °C/min from 25 to 600 °C. The nitrogen sorption isotherm at 77 K was volumetrically measured up to 10^5 Pa by the auto-sorb 1MP instrument by micro-meritics ASAP2020.

2.2 Solvothermal synthesis

$Zn(NO_3)_2{\cdot}6H_2O$ (1.350 g) and H_2BDC (0.249 g) were dispersed in DMF (49 mL) under ultrasound, then heated at 120 °C for 24 h in a Teflon-lined autoclave. The precipitate was collected by vacuum filtration, washed with DMF, soaked in dichloromethane and dried in vacuum drying oven at 120 °C for 24 h. This precipitate was named as MOF−5_DMF. Using the same approach, replacing DMF with NMP (50 mL), the crystalline precipitate was named as MOF−5_NMP.

Two samples of newly-made precipitate of MOF−5_NMP were soaked in NMP and DMF for 24 h respectively, then soaked in dichloromethane and dried in vacuum drying oven at 120 °C. These two products were named as MOF−5_NMP-N and MOF−5_NMP-D, in which ‘-N’ means -NMP and ‘-D’ means DMF.

3 Results and discussion

3.1 XRD and TEM analysis

Four characteristic peaks at 2θ=6.8°, 9.7°, 13.7° and 15.4° confirmed that the MOF−5 crystalline products (b), (c), (d) and (e) were pure phase by XRD analysis (see Fig. 1). The intensity ratio of the XRD peak at 9.7° to the peak at 6.8° (referred to as the $R1$ value) could predict the adsorption properties of MOF−5 material: the lower the intensity ratio was, the more porous the material was [26−30]. A high $R2$ value (the ratio of the intensity of the peak at 13.8° to that at 6.8°) suggested that it was an interpenetrated structure, especially when the $R1$ value was low [6−8,14]. The $R1$ value of MOF−5_NMP was 0.291 that was closed to the standard value (0.202) and the $R2$ value was lower than $R1$, which meant that the utilization of porous substance of MOF−5_NMP was high and MOF−5_NMP was an ideal non-penetrated MOF−5 material. The $R1$ value (1.224) of MOF−5_DMF was higher than that of MOF−5_standard instead, which implied that MOF−5_DMF had a low surface area and