Research Article

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Study on the structure activity relationship of the crystal MOF-5 synthesis, thermal stability and N₂ adsorption property

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Abstract: The parallel flow drop solvothermal method was utilized to synthesize the crystal of MOF-5 by taking the molar ratio of the metal ions to the organic ligands of 2:1 at 140°C, and the reaction time at 12 hours. Meanwhile, the structure and properties of MOF-5 were characterized by the X-ray diffraction (XRD), scanning electron microscope (SEM), thermogravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR). SEM analysis shown that the crystal morphology of MOF-5 changed from sheet to cubic with increasing reaction temperature and molar ratio of the metal ions to the organic ligands, and its thermal stability was also gradually increased. TGA analysis shown that its thermal stability could live up to 489.36°C. FTIR analysis shown that the terephthalic acid is completely protonated, and the Zn²⁺ and the carboxyl group are formed by the coordination of the multi-tooth bridge in the crystal of MOF-5. Then the structure activity relationship of the crystal MOF-5 synthesis, microstructural, thermal stability and N₂ adsorption property were further studied.

Keywords: Metal-organic frameworks; Parallel flow drop solventthermal method; N₂ adsorption; Thermal stability

1 Introduction

Metal-organic frameworks (MOFs) have been actively investigated for application in, such as, gas adsorption and

storage, chemical sensing, sensors, battery, catalysis, light to electrical energy conversion, membrane, and even drug delivery due to their unsurpassed porosities, well-defined pore structures, high specific surface area, pore volume, designable and flexible structure, and strong physical-chemical stability [1–3]. One of the most widely researched MOFs materials is MOF-5, which has high gas selectivity and capacity [4]. MOF-5, namely [Zn₄O(BDC)₃], is a three-dimensional cubic porous framework with [Zn₄O]⁶⁺ clusters linked together through 1,4-benzenedicarboxylate (BDC²⁻) ligands [5]. Therefore, this specific structure makes MOF-5 large surface area and exceptional pore volume. It has rapidly developed as a hotspot in the crossing fields of energy, chemistry, materials and life science [6]. MOF-5 was mainly synthesized through hydrothermal [7], solvothermal methods [8], microwave-based [9] and sonochemical [10]. Among the methods mentioned above, the solvothermal method is simple and efficient, by which massive product can be formed in one batch. The different synthesis conditions have effect on the crystal growth, crystal structure, crystallite size and morphology of MOF-5. Consequently, regular cubic-shaped and micro-crystallite of MOF-5 could be obtained under certain technological conditions by solvothermal methods. On the other hand, this method was also suitable to explore the synthesis mechanism and reaction process parameters of MOF-5 materials [11, 12]. Therefore, this study used the parallel flow drop solventthermal method to study the relationship between the synthesis and structure, thermal stability and N₂ adsorption properties of MOF-5 crystals.

It is well known that differences conditions in synthesis, filtration, drying, activation, and shaping can easily result in a wide variation in MOF-5 properties such as pore volume, pore size, surface area, and crystallite size. However, in the synthesis process of MOF-5, the bond energy of the coordination bond formed between metal and organic ligands are less than that of covalent bond and metal bond. On the other hand, the framework with a high permeability structure is not enough to support its own quality. After removal of a large number of free solvent molecules

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in the framework, these highly open structures will be obviously distortion or distortion, and the loss of crystallinity. The crystal structure of the crystal MOF-5 will be severely damaged due to the collapse, destroying the crystals structure of the MOF-5 material and cause loss of topological structure into an amorphous powder. For example, Srinivasan [13] studied (R)-[LCu₂(H₂O)₂](dmf)₁₆(H₂O)₁₉ of MOFs material with high porosity framework, and discovered that the volume of solvent in the frame material is about 85% by Platon calculation software, and the theoretical BET specific surface area of the frame material is 4288 m²g⁻¹ by Grand Canonical Monte Carlo simulation. However, the actual measurement of the BET specific surface area is 240 m²g⁻¹. In the process of removal of the solvent molecules, the frame structure is deformed and the bulk of the effective pore volume is lost. The reason is that the frame structure was deformed and the bulk of the effective pore volume was lost in the process of removal of the solvent molecules.

Thermal stability of the crystal MOF-5 is a very important property for practical applications. Nevertheless, most of the thermal stability of the crystal MOF-5 has been reported, which was about 350°C, less than 450°C [14–16]. Thus the difference of the synthesis conditions will directly affect the specific surface area, gas adsorption properties and thermal stability of the crystal MOF-5 [17, 18]. In order to further improve the surface area, gas adsorption properties and thermal stability of the crystal MOF-5, the influence of synthesis conditions on the surface area, gas adsorption properties and thermal stability of the crystal MOF-5 was studied by the new method of the parallel flow drop solvent thermal method. Thereinto, zinc nitrate, terephthalic acid and N,N'-dimethylformamide (DMF) were applied as the zinc source, organic ligands, and organic solvent respectively. Meanwhile, the experiment was conducted to investigate the influence of the reaction time, reaction temperature and the molar ratio of zinc ion to terephthalic acid on the preparation of the crystal MOF-5.

2 Experiment

2.1 Reagents and Instruments

Zinc nitrate, terephthalic acid and N,N'-dimethylformamide (DMF) were chemically pure. The instruments utilized for the analysis and characterization included JSM-6700F type SEM, IFS-type 66v/s infrared spectrometer, laser particle analyzer, X'Pert PRO-type X-ray power diffractometer,

DSC200F3-type differential scanning calorimetry (DSC), ASAP2020M rapid specific surface area and pore analyzer and so on.

2.2 Preparation of the Crystal MOF-5

The crystal MOF-5 was synthesized using the parallel flow drop solvothermal method by taking zinc nitrate, terephthalic acid and DMF as the zinc source, organic ligands, and organic solvent respectively. Firstly, Zn(NO₃)₂·6H₂O (5.95 g, 0.02 mol) dissolved in distilled water as solution A. H₂BDC (9.97 g, 0.06 mol) dissolved in DMF as solution B. A certain amount of DMF solution placed in a stainless-steel reactor lined with polytetrafluoroethylene (PTFE) as the base fluid. Then, the solution A and B dripped into the bottom liquid, which has heated to a certain temperature and stirred vigorously. The molar concentration and pH of solution A and solution B is known at this time. The drop acceleration of solution A and solution B were adjusted according to different the molar ratio and pH in this process. The synthesis conditions involved 120°C with stirring for 1 hour. Then, the MOF-5 samples were reacted at 140°C in a programmable oven for 12 hours, before being cooled to room temperature naturally. After the reaction, the mixture was filtered. The filter cake was aged for 4 hours using 20 mL of acetone, and then refined and washed by DMF for 3 times before being dried at 110°C for 12 hours. Finally, the white powder of the crystal MOF-5 was obtained. The advantage of this method was that it could ensure the reactants have a high degree of supersaturation by controlling the speed of the solution. In addition, the reaction temperature, reaction time and pH were easy to control. Because of the higher degree of supersaturation of the solution, the nucleation rate was faster than the growth rate, and the small grain size and large specific surface area of MOF-5 were obtained.

3 Results and Discussion

The experiment was conducted to investigate the influence law of the reaction time, reaction temperature and the molar ratio of zinc ion to terephthalic acid on the preparation of the crystal MOF-5. The parallel flow drop solvothermal method was utilized to synthesize the crystal of MOF-5 by taking the molar ratio of the metal ions to the organic ligands of 2:1 at 140°C, the reaction time at 12 hours, the drop acceleration of zinc nitrate at 50 mL·min⁻¹, and the drop acceleration of terephthalic acid at 40 mL·min⁻¹, drying

temperature at 110°C. This is the optimum technical conditions.

3.1 XRD Analysis of the Crystal MOF-5

Figure 1 shown the XRD patterns of the crystal MOF-5 under the optimum technical conditions. As shown in the Figure 1, the strong peaks at 6.8°C, 9.6°C, 13.8°C, 19.8°C and 29.8°C in the XRD pattern of the crystal MOF-5 show the characteristic diffraction peak of the crystal MOF-5. The seven characteristic peaks basically coincided with those of the standard XRD spectra of the crystal MOF-5 with no interference peak being found. The results are consistent with the results of Yang Ming's [19]. The diffraction peak of XRD diffraction contrast synthesis of MOF-5 materials under different temperature was found, the MOF-5 materials were synthesized at different temperatures of 120°C to 160°C, but the diffraction peak intensity weakened, and appeared in 19.8° had left acromion, probably due to a small amount of bond breaking MOF-5 material drying or synthesis process, caused lattice distortion [20]. The results shown that the synthesis temperature is 140°C better. Therefore, it was inferred that this crystal with high crystallinity belonged to the crystal MOF-5. The average particle size of the crystal MOF-5 is 8.7 μm (It was analyzed by Scherrer Equation). The average particle size of the crystal MOF-5 is 10.3 μm (It was analyzed by laser particle analyzer). The particle size of the crystal MOF-5 is 5-10 μm (It was analyzed by SEM). Obviously, the results of the analysis of the three different methods are basically consistent.

Figure 1: XRD of the crystal MOF-5.

3.2 FTIR Analysis of the Crystal MOF-5

As demonstrated in the FTIR of the crystal MOF-5 in Figure 2, the strong peaks at the point 3500-3200 cm^{-1} was caused by the O-H of adsorbed water. There are two strong absorption peaks in about 1384 cm^{-1} and 1657 cm^{-1} , which belong to the stretching vibration peaks of $-\text{C}=\text{O}$ in $-\text{COO}-\text{Zn}^{2+}$. They are $-\text{C}=\text{O}$ asymmetric stretching vibration peaks (ν_{as}) and symmetric stretching vibration peaks (ν_s), respectively. Compared with the infrared spectra of ligand terephthalic acid at 1660 cm^{-1} , the stretching vibration peaks of $-\text{C}=\text{O}$ have obvious red shift. This is due to ligand $-\text{COO}-$ in the H_2BDC and Zn^{2+} ion coordination form $-\text{COO}-\text{Zn}^{2+}$, making the carbonyl on the electron distribution is relatively uniform, the electron cloud density decreased. The electron averaging leads to a certain degree of red shift of the carbonyl stretching vibration peak to a certain extent, while the double bond property is not obvious, the typical $\nu_{\text{C}=\text{O}}$ can not be seen, but ν_{as} and ν_s are replaced by them, and the two peaks are between them. The peak width ($\Delta\nu$) is 273 cm^{-1} , less than 300 cm^{-1} , which proves that the terephthalic acid is completely protonated, and the Zn^{2+} and the carboxyl group are formed by the coordination of the multi-tooth bridge with MOF-5 [21]. Infrared spectra of different synthesis temperature, 120°C and 160°C for the synthesis of MOF-5 peak is 140°C when the peak weakened, the peak shape becomes wide, and there are defects, showed that a small amount of bond rupture, resulting in reduced stability. Therefore, the optimum synthesis temperature is 140°.

Figure 2: FTIR of the crystal MOF-5.

3.3 TGA Analysis of the Crystal MOF-5

Using a molar ratio of the metal ions to the ligands of 2:1 at 140°C, and the reaction time at 12 hours, thermal stability of MOF-5 was studied by TGA in Figure 3. The TGA shows the weight loss from 74.94°C to 282.33°C that is attributed to solvent mass loss. The second stage, within the temperature range of 282.33–489.36°C with an estimated mass loss of 16.5% is attributed to the release of DMF in MOF-5, it is guest organic molecule. However, dramatic mass losses, indicating the collapse of the frame-works, were observed at 489.36°C, and 515.46°C. After decomposition, the residual amount was 40.57% (the theoretical quantity is 42.43%), which was close to the theoretical decomposition residue. This shown that the maximum temperature for the crystal MOF-5 to remain stable was 489.36°C, and the purity was high.

Figure 3: TGA of the crystal MOF-5.

3.4 Effects of Molar Ratio of the Metal Ions to the Ligands on the Stability of the Crystal MOF-5

Figure 4 shows the SEM images of the crystal MOF-5 prepared by the parallel flow drop solvothermal method. The comparison of images illustrates that the differences in synthesis conditions greatly influence the morphology of the material. As shown in the SEM of the crystal MOF-5 in Figure 4a, when the molar ratio of the metal ions to the ligands was 1:2, the crystal MOF-5 were sheet-shaped with dimensions of approximately 1 to 6 μm. As shown in the

Figure 4: SEM of the crystal MOF-5.

SEM of the crystal MOF-5 in Figure 4b, when the molar ratio of the metal ions to the ligands was 1:1, the crystal MOF-5 were prismatic-shaped with dimensions of approximately 5 to 10 μm . As shown in the SEM of the crystal MOF-5 in Figure 4c, when the molar ratio of the metal ions to the ligands was 2:1, the crystal MOF-5 were cubic-shaped with dimensions of approximately 4 to 8 μm . With the increase of zinc nitrate and terephthalic acid molar ratio, crystal morphology from sheet to cubic changes, particle size from no rules to rule changes. This indicated that high the molar ratio of the metal ions to the ligands may urge MOF-5 into self-confining, resulting in regular cubic morphology and large crystallite size. The results are consistent with the results of David Durette's [22]. Therefore, the optimum molar ratio of metal ions to ligands was set to 2:1.

3.5 Effects of Reaction Temperature on the Stability of the Crystal MOF-5

As shown effect of reaction temperature on the stability of the crystal MOF-5 in Figure 5. The thermal stability of MOF-5 crystals formed by the molar ratio of metal ions to the ligands and the reaction temperature were different, which show that the thermal stability increased with the increased of the molar ratio of the metal ions to the ligands. The thermal stability of the crystal MOF-5 was increased at first and then decreased with the rising of reaction temperature. The organic ligands can adopt different conformation and coordination mode under different reaction temperature. In the lower reaction temperature, the single tooth type of the acid was coordinated, and the crystal mor-

phology tended to be low. However, at the higher temperature, the coordination of the metal and organic ligands was promoted by the multi tooth form. This promoted the dissolution of metal and organic ligands and the coordination reaction activity, and the crystal structure became complete structure of cube or hexahedron [23]. This indicates that the coordination ability of the acid is enhanced with the increase of the reaction temperature. It helps to increase the dimension and stability of the crystal MOF-5 frame structure [24]. Therefore, the optimum reaction temperature in these experiments was set to 140°C, and the thermal decomposition temperature of the crystal MOF-5 was 489.36°C.

3.6 Effects of Reaction Temperature on the N_2 Adsorption Property of the Crystal MOF-5

As shown in Figure 6 and Table 1, all the samples show a reversible type I isotherm with a steep initial increase at low pressures and saturation at higher pressures, being characteristic of the microporous material with high amounts of N_2 adsorption. The sample prepared at the lower reaction temperature has the smallest Langmuir specific surface areas of 583.6 m^2g^{-1} . The low Langmuir specific surface areas of the crystal MOF-5 of this work may be due to the low dimensional. The sample prepared at the higher reaction temperature has the largest Langmuir specific surface areas of 927.8 m^2g^{-1} . The large Langmuir specific surface areas of the crystal MOF-5 of this work may be due to the multidimensional. The results show that the dimen-

Figure 5: Effect of reaction temperature on the stability of the crystal MOF-5.

Figure 6: Effect of reaction temperature on the Nitrogen adsorption isotherms of the crystal MOF-5.

Table 1: Effect of reaction temperature on the textural properties of the crystal MOF-5.

reaction temperature of MOF-5 /°C	BET surface area /m ² g ⁻¹	Langmuir surface area /m ² g ⁻¹	micropore volume /cm ³ g ⁻¹
120	638.4	924.1	0.32
140	734.9	927.8	0.36
160	685.7	901.8	0.34

sionality of the MOFs increased when the reaction temperature was raised, which can be explained that the gas adsorption property of MOF microcrystals can vary according to crystal morphology or exposed surfaces. Therefore, the decrease of crystal size induces the increase in the crystal surface area and leads to the large amount of N₂ adsorption in the relative high-pressure region, which has important potential application in gas adsorption and storage. The result also suggests that a high reaction temperature may benefit to form multidimensional frameworks with large voids.

4 Conclusion

This paper outlined the influence of reaction temperature on the stability of the crystal MOF-5. It can be seen that the reaction temperature has remarkable influence on the stability of the crystal MOF-5. It is also clear that the stability of the crystal MOF-5 can differ greatly by changing reaction temperature as well as other reaction conditions.

- 1) Zinc nitrate, terephthalic acid and DMF were applied as the zinc source, organic ligands, and organic solvent respectively in the research. Meanwhile, the parallel flow drop solvent thermal method was utilized to synthesize the crystal of the crystal MOF-5 by taking molar ratio of the metal ions to the ligands being 2:1, the reaction temperature at 140°C, the reaction time being 12 hours, and drying temperature at 110°C.
- 2) Infrared spectrum analysis shown that the terephthalic acid is completely protonated, and the Zn²⁺ and the carboxyl group are formed by the coordination of the multi-tooth bridge with the crystal MOF-5. XRD analysis shown that this crystal with high crystallinity belonged to the crystal MOF-5. Other analysis shown that the specific BET surface area is about

734.9 m²g⁻¹, the thermal decomposition temperature is 489.36°C.

- 3) SEM analysis shown that increases with increasing reaction temperature and molar ratio of Zn(NO₃)₂/H₂BDC, crystal morphology from sheet to cubic changes. The coordination form of the crystal MOF-5 is changed from single tooth type to multi tooth type, and thermal stability is also gradually increased.

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