Preparation of Novel MOF with Multipolar Pore and Adsorption Properties of VOCs

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Abstract. MOF-5 crystals were prepared by solvothermal synthesis, and characterized by electron microscopy (SEM), X-ray powder diffraction (XRD), and specific surface area (BET). The adsorption of formaldehyde, acetone, glycerol and toluene were studied. The effects of reaction solvent ratio, adsorption time and synthesis temperature on adsorption were investigated. The results show that the reaction solvent ratio is 2.6, the crystal particles have good integrity, the cracking phenomenon and aggregation phenomenon are less, the size is more uniform, highly crystalline, the specific surface area and pore volume are larger, and the pore size distribution is more concentrated. The adsorption time is 48 h, the synthesis temperature is 95°C. Under high temperature conditions, MOF-5 has a high-dimensional skeleton crystal structure with higher specific surface area and pore volume. MOF-5 has the best adsorption effect on toluene.

1. Introduction
Nowadays, air pollution has become a global problem, and volatile organic compounds (VOCs) are an important part of air pollution [1]. VOCs pose great harm to the environment and human health [2], because most VOCs are toxic, carcinogenic, and can cause photochemical smog, ozone consumption, etc. [3-4]. At present, methods for treating VOCs mainly include absorption, incineration, catalytic oxidation and thermal oxidation, etc. Among them, the most widely used method is the absorption. The commonly used adsorbents include activated carbon and zeolite molecular sieves, but these two adsorbents are easily blocked and have poor adsorption effects on organic macromolecules [5-6].

The new porous nanomaterials, Metal Organic Frameworks (MOFs), have a wide range of applications in the fields of catalysis, adsorption, separation and storage gases due to their structural tunability and diversity. Representative of the MOF-5 materials, the pore size and specific surface area exceeds that of conventional molecular sieves. In this study, MOF-5 crystals were prepared by solvothermal synthesis method, and their adsorption effects on VOCs were investigated to provide reference for the search for adsorbents of high quality VOCs.
2. The experimental process
Weigh Zn(NO$_3$)$_2$·6H$_2$O and H$_2$BDC (terephthalic acid) in different solvent ratios, dissolve in N,N-dimethylformamide (DMF) with vigorous stirring, add 2.2 mL after dissolving Ethylamine solution, then a white precipitate was formed, placed in a constant temperature water bath, heated and stirred for 30 min, filtered, and washed with DMF (N, N-dimethylformamide), then dried at 373 K for 5 hours, finally prepared MOF-5 Crystal. The adsorption capacity (mg/g) of MOC-5 is used as absorbent to absorb VOCs as shown in formula (1):

$$\eta = \frac{M_2 - M_1}{M_1} \times 1000$$

(1)

Where: $M_1$ is the mass of the sample before adsorption and $M_2$ is the mass of the sample after adsorption.

3. Experimental results and discussion
3.1. Effect of different reaction solvent ratios of metal ions and organic ligands
The effect of different reaction solvent ratios on adsorption of toluene is shown in Figure 1. It can be seen from Figure 1 that the molar ratio of Zn(NO$_3$)$_2$·6H$_2$O to H$_2$BDC (terephthalic acid) has a great influence on the synthesis of MOF-5 crystal, and the molar ratio of Zn(NO$_3$)$_2$·6H$_2$O to H$_2$BDC is relatively low. When the adsorption capacity is low, the skeleton structure formed is not stable enough, but as the molar ratio increases, the adsorption capacity increases gradually, which is more conducive to the synthesis of MOF-5 crystals with developed pore structure. In this experiment, the adsorption effect was the highest when the reaction solvent ratio was 2.6:1, and the adsorption effect was the lowest when the solvent ratio was 2.0:1. In summary, the optimum molar ratio of Zn(NO$_3$)$_2$·6H$_2$O to H$_2$BDC required to synthesize high quality MOF-5 crystals is 2.6.

![Figure 1. Adsorption capacity of toluene with different reaction solvents](image)

3.1.1. XRD of MOF-5 with different reaction solvent ratios. The XRD pattern of MOF-5 for different reaction solvent ratios is shown in Figure 2, the position and intensity of the diffraction peaks of the reaction solvent ratios of 2.0 and 2.6 are substantially the same, and the main peak positions of the MOF-5 crystals having a reaction solvent ratio of 2.0 are $\theta =8.09$, $\theta =8.70$, $\theta =12.24$, $\theta =14.78$, $\theta =15.63$, $\theta =16.39$, $\theta =17.60$, Among them, $\theta =12.24$, $\theta =14.78$ are two weak diffraction peaks, and other diffraction peaks are typical diffraction peaks of MOF-5 crystal, and the intensity of diffraction peak is large, which indicates that the crystallinity of this material is high and the reaction solvent is high. The MOF-5 crystal with a ratio of 2.0 should be a MOF-5 crystal with a high degree of crystallinity. The diffraction peak position and
The intensity of the XRD pattern of the MOF-5 crystal sample having a reaction solvent ratio of 2.6 were also consistent with the crystal plane diffraction peak position of the MOF-5 crystal.

Figure 2. XRD spectrum of crystals synthesized at different reaction solvent molar ratios

3.1.2. SEM of MOF-5 with different reaction solvent ratio. The SEM of the different reaction solvent ratios of MOF-5 is shown in Figure 3. It can be seen from Figure 3 that when the reaction solvent ratio of Zn(NO$_3$)$_2$·6H$_2$O/H$_2$BDC is 2, the crystal geometry is an irregular block structure, and the crystals are roughened. With the increase of Zn(NO$_3$)$_2$·6H$_2$O, the growth trend of crystals changes. When the molar ratio of Zn(NO$_3$)$_2$·6H$_2$O/H$_2$BDC reaches 2.6, the crystal particles have good integrity, rupture and aggregation. Less, the size is more uniform, which indicates that the molar ratio of Zn$^{2+}$ to H$_2$BDC is optimal in the 2.6 synthesized MOF-5 crystals.

Figure 3. SEM image of MOF-5 crystals with different reaction solvent ratios

3.1.3. BET of MOF-5 with different reaction solvent ratio. The BET data of MOF-5 for different reaction solvent ratios are shown in Table 1. It can be seen from Table 1 that as the molar ratio increases, the specific surface area of the sample gradually increases, the pore volume gradually increases, and the pore diameter gradually decreases. The molar ratio in Zn(NO$_3$)$_2$·6H$_2$O/H$_2$BDC When the ratio is 2.0, the specific surface area is 10.7 m$^2$/g, indicating that the pore structure is not developed. When the molar ratio of Zn(NO$_3$)$_2$·6H$_2$O/H$_2$BDC is 2.6, the specific surface area is 58.4 m$^2$/g. Large specific surface area
and pore volume, and pore size distribution are also concentrated. It is indicated that in the reaction solution with a relatively low molar ratio, the ligand will coordinate in a monodentate form, and the skeleton structure is unstable, forming a crystal of a low-dimensional structure. It is not conducive to the formation of MOF-5 crystals with developed pore structure.

| Sample | Specific surface area | Average pore volume | Average aperture |
|--------|-----------------------|---------------------|------------------|
| 2.0    | 10.7                  | 0.018               | 49.2             |
| 2.2    | 31.1                  | 0.051               | 19.3             |
| 2.4    | 35.0                  | 0.109               | 24.0             |
| 2.6    | 58.4                  | 0.148               | 8.77             |
| 2.8    | 27.6                  | 0.031               | 28.7             |

3.2. Effect of adsorption time on adsorption capacity of MOF-5 crystal

The effect of different adsorption time on the adsorption of toluene on MOF-5 crystal is shown in Figure 4. It can be seen from Figure 4 that the adsorption capacity of toluene in MOF-5 crystal increases sharply with the increase of adsorption time, and then the trend tends to level off, indicating that the crystal material skeleton remains in the time (48 h) of the reaction of the experiment. In the state of growth, the pore volume and specific surface area increase greatly with the increase of reaction time until saturation, which indicates that toluene has high and rapid adsorption performance in MOF-5 crystal material, and then the adsorption rate gradually decreases. The adsorption gradually reaches saturation, and its adsorption capacity does not change. Taken together, the best time for adsorption is 48h.

3.3. Effect of Synthesis Temperature on Adsorption Capacity of MOF-5 Crystal

The temperature of the reaction synthesis is the first factor to be considered in each reaction condition. If the reaction temperature is too low, the reaction kinetics cannot be met, and the metal ion and the ligand cannot be coordinated; if the reaction temperature is too high, the formation may be destroyed. The skeletal structure of the material, in addition, the coordination ability of the ligand is different at different temperatures, and this difference may result in different skeleton structures of the finally obtained MOFs. MOF-5 crystals of different synthesis temperatures were prepared at a reaction solvent molar ratio of 2.6.

The effect of different synthesis temperatures on the adsorption of toluene is shown in Figure 5. It can be seen from Figure 5 that the adsorption effect increases with the increase of the synthesis temperature, and the adsorption effect of MOF-5 prepared at 95 °C is the best. The reason for this may be that under low temperature conditions, BDC mostly has a single-dental coordination, and the crystal
morphology exists in a low-dimensional form. Under high temperature conditions, BDC is coordinated in a multi-tooth shape, and the crystal morphology exists in a high-dimensional form. It can be seen that the reaction temperature has a great influence on the skeleton structure of MOFs. The metal ions and organic ligands are easy to generate the crystal structure of the high-dimensional skeleton by entropy-driven phase transformation under high temperature conditions. Therefore, the samples obtained at high temperature are lower than those obtained at low temperature. Has a higher specific surface area and pore volume.

![Figure 5. Adsorption capacity of toluene at different reaction temperatures](image)

3.4. Adsorption capacity of MOF-5 materials for different adsorbates
At a reaction solvent molar ratio of 2.6 and a synthesis temperature of 95 °C, MOF-5 adsorbs formaldehyde, acetone, glycerol, and toluene, respectively. The adsorption effect of MOF-5 on different adsorbates is as follows. It can be seen from Figure 6 that the adsorption of toluene by MOF-5 crystal is the best at any adsorption time, followed by acetone, formaldehyde and glycerol. The adsorption of adsorbate by MOF-5 was the highest in 12~24h, and the adsorption rate decreased gradually after 36h until the adsorption was saturated.

![Figure 6. MOF-5 adsorption capacity of different organic substances](image)
4. Conclusion
The ratio of different reaction solvents of genus ions to organic ligands was 2.6, the adsorption time was 48 h, and the synthesis temperature was 95 °C. The adsorption effect of MOF-5 crystals on VOCs was the best. At this time, the MOF-5 crystal particles have good integrity, less rupture and aggregation, larger uniformity, high crystallinity, high-dimensional skeleton crystal structure, large specific surface area and pore volume, and pore size distribution. More concentrated. MOF-5 has the largest adsorption capacity for toluene, the maximum adsorption capacity can reach 780.5 mg, and the adsorption capacity for glycerol is the smallest. The characterization results of XRD, BET and SEM are consistent with the conclusions.

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