

Microwave Assisted Synthesis of Cr-doped UiO-66 with Enhanced Water Adsorption Capacity

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ABSTRACT

The metal-organic framework UiO-66 is a promising water vapor adsorbent in the application of adsorption heat pumps due to its good stability and hydrophilicity. In this paper, we prepared some pure and Cr-doped UiO-66 samples by the traditional solvothermal method and microwave-assisted solvent synthesis method, respectively. And we characterized these samples by XRD、FTIR、BET, etc. The results show that the micropore volume and BET specific surface area of UiO-66 synthesized by the microwave-assisted method is much higher than those synthesized by the conventional solvothermal method. In particular, MW-1.5Cr-UiO-66 synthesized by microwave method has the highest BET specific surface area (1524m²/g) and water uptake (0.59g/g), which is 105.4% and 47.5% higher than UiO-66 synthesized by solvothermal method, respectively. This is more conducive to the application of UiO-66 in the field of adsorption heat pumps.

Keywords: Adsorption heat pumps; Porous materials; metal-organic framework (MOF); UiO-66

1. INTRODUCTION

The adsorption heat pump is a kind of thermochemical energy storage system which uses the adsorption/desorption process to achieve energy utilization[1]. It can effectively improve the grade of energy and will not produce toxic and harmful substances. So it is an effective way to solve the problem of insufficient energy supply. Suitable adsorbent-adsorbate working pairs are important to improve the performance of the adsorption heat pump[2]. Metal-

organic frameworks (MOFs) are considered to be promising adsorbents for adsorption heat pumps due to their high specific surface area, large pore volume, and adjustable structure[3, 4].

Due to its good water stability, UiO-66 which is composed of Zr₆O₄(OH)₄ clusters and 1, 4-benzoate (BDC) ligands[5] may be a promising adsorbent for the adsorption heat pump. However, the water adsorption capacity (0.36g/g)[6] of UiO-66 still needs to be improved. Some previous studies[7, 8] have shown that the doping of foreign metals is an effective way to improve the adsorption properties of MOFs. For example, Mn-doped UiO-66 (797.18m²/g) prepared by Zhao et al.[7] has a higher specific surface area than pure UiO-66 (582.34 m²/g). Zhou et al.[8] found that the doping of magnesium not only makes MIL-101 (Cr) have a higher surface area but also creates new and strong adsorption sites for CO₂. Therefore, the CO₂ adsorption capacity of MIL-101 (Cr) is significantly improved.

In this paper, we prepared some Cr-doped UiO-66 and investigated their structural properties and water vapor adsorption properties. Considering that the microwave-assisted hydrothermal method can greatly shorten the reaction time and reduce energy consumption[9] compared with the traditional hydrothermal methods. We prepared Cr-doped UiO-66 samples by microwave-assisted hydrothermal method.

2. PAPER STRUCTURE

2.1 Materials and methods

The reagents required for experiments: 1, 4-benzene dicarboxylic acid (H₂BDC, 99%), N, N-dimethylformamide

(DMF), hydrochloric acid (HCl, 37%), chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%), zirconium chloride (ZrCl_4 , 99%), glacial acetic acid and methanol. All chemicals are purchased commercially.

In a conventional synthesis process, 0.476g H_2BDC , 0.668g ZrCl_4 , and a certain amount of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0g, 0.574g, 1.147g, 1.721g) were dissolved in 45ml DMF. Then, 5ml of glacial acetic acid and 1.5ml of HCl were added to this solution and continuously stirred for 1h by a magnetic stirrer. The mixed solution was transferred to a 100ml microwave reactor and maintained at 120°C for 2 hours. The precipitates were centrifuged at 4000r/min and washed three times with DMF and methanol respectively. Then, the products were dried at 80°C for 6h. Finally, the samples were heated at 250°C for 2h. According to the molar ratio of Cr to Zr, these samples were named MW-UiO-66, MW-0.5Cr-UiO-66, MW-1Cr-UiO-66, and MW-1.5Cr-UiO-66.

P-UiO-66 was synthesized by the following process[10]: 2.69g H_2BDC , 1.89g ZrCl_4 were dissolved in 48.7ml DMF. Then, 1.43ml HCl was added to this solution and continuously stirred for 1h by a magnetic stirrer. The mixed solution was transferred to a 100ml Teflon sealed tank and maintained at 120°C for 24 hours. The washing and drying process is the same as that of the microwave method. This sample was named P-UiO-66.

The crystal structure of the samples was characterized by an X-ray diffractometer (XRD, Rigaku D/max2500X). The $\text{Cu K}\alpha$ ray ($\lambda = 1.54056 \text{ \AA}$) (40 kV, 200 mA) was used as the X-ray source, and the selected 2θ scanning range was $5^\circ - 50^\circ$ with a step of 0.01° . The infrared spectrums of the samples in the range of $400-2200\text{cm}^{-1}$ were measured by a LambdaFTIR-7600 Fourier transform

infrared spectrometer. The nitrogen sorption isotherms and the isotherms of water adsorption were measured using vapor adsorption and a specific surface aperture analyzer (Beishide BSD-PMV) at 77K. Before the tests, the samples were activated under vacuum at 150°C for 6h.

2.2 XRD and FTIR

The XRD patterns are shown in Fig. 1(a). The XRD pattern of UiO-66 has three dominating peaks at 7.4° , 8.5° , and 25.8° , corresponding to (111), (200), and (600) crystal planes, respectively[11]. The characteristic peaks of the Cr-doped UiO-66 samples match well with unmodified UiO-66, indicating that the doping of Cr did not change the crystal structure of UiO-66. As shown in Fig.1(b), the infrared spectrums of Cr-doped UiO-66 samples were similar to pure UiO-66[5, 12], and no extra absorption peak was observed. This indicates that we have successfully prepared UiO-66 samples with good crystallinity.

2.3 Porosity

As shown in Figure 2 (a), the nitrogen isotherms of all samples are typical type I sorption isotherms, which means all samples have a typical microporous structure. The pore size distributions obtained by H-K model analysis are presented in Figure 2(b). Combined with Table 1, the micropore volume (V_{Micro}) and BET specific surface (S_{BET}) area of UiO-66 synthesized by the microwave-assisted method are much higher than those synthesized by the conventional solvothermal method. The BET specific surface area ($1272\text{m}^2/\text{g}$) and micropore volume ($0.53\text{cm}^3/\text{g}$) of MW-UiO-66 is 71.7% and 39.5% higher than UiO-66 synthesized by the solvothermal

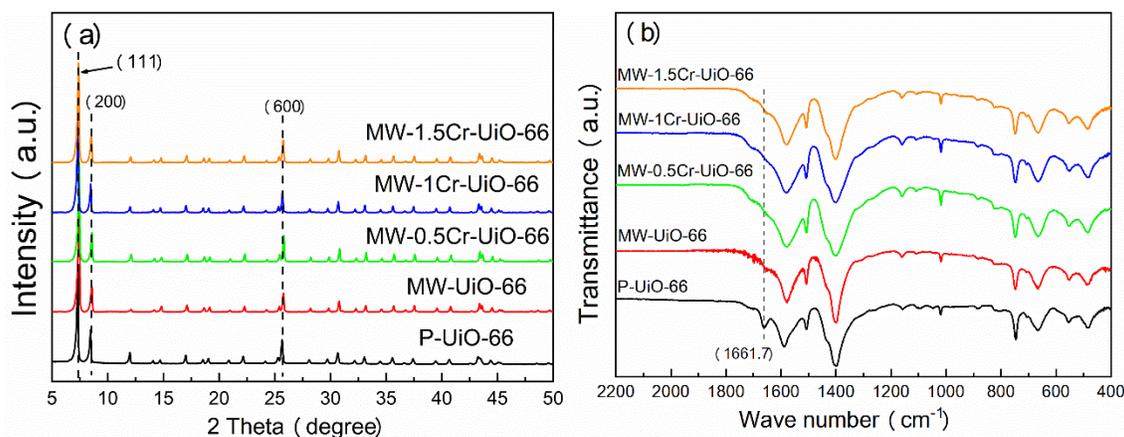


Figure 1. (a) XRD patterns and (b) FTIR curves of P-UiO-66, MW-UiO-66 and Cr-doped UiO-66 samples.

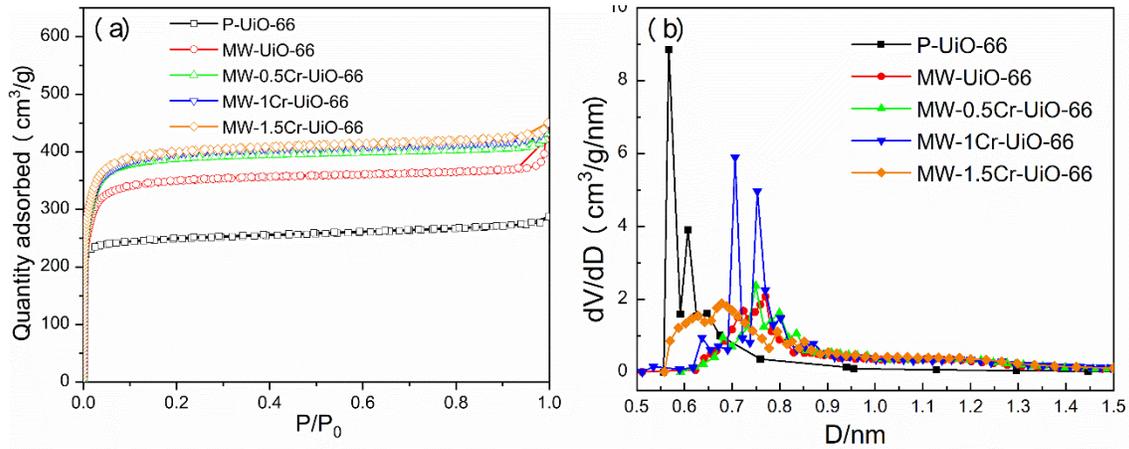


Fig. 2. (a) Nitrogen sorption isotherms and (b) pore size distributions of P-UiO-66, MW-UiO-66 and Cr-doped UiO-66 samples

method, respectively. At the same time, Cr-doped UiO-66 has a higher specific surface area and pore volume than MW-UiO-66, the BET-specific surface area of 1.5Cr-UiO-66 (1524 m²/g) is 19.8% higher than the unmodified MW-UiO-66 (1272 m²/g). This is beneficial to improve the water adsorption capacity.

Table 1. Pore structure and water uptake parameters of P-UiO-66, MW-UiO-66, and Cr-doped UiO-66 samples

Sample	S_{BET} (m ² /g)	V_{Micro} (cm ³ /g)	Adsorbed water at P/P ₀ = 0.3 (g/g)	Adsorbed water at P/P ₀ = 0.9 (g/g)
P-UiO-66	741	0.38	0.12	0.40
MW-UiO-66	1272	0.53	0.15	0.54
MW-0.5Cr-UiO-66	1454	0.59	0.17	0.57
MW-1Cr-UiO-66	1422	0.60	0.17	0.58
MW-1.5Cr-UiO-66	1524	0.61	0.18	0.59

2.4 Adsorption properties

As shown in Fig.3, the sorption isotherms of all samples show similar "S" adsorption curves. The water vapor uptake of the samples is close to saturation at P/P₀=0.5. It is noteworthy that the water adsorption capacity of all UiO-66 samples prepared by the microwave-assisted method is much higher than that of UiO-66 (0.40g/g) prepared by the conventional solvothermal method. With the doping of Cr, the saturated water vapor adsorption capacity of the

samples increased gradually from 0.54g/g (UiO-66) to 0.59g/g (1.5Cr-UiO-66). Results should be clear and

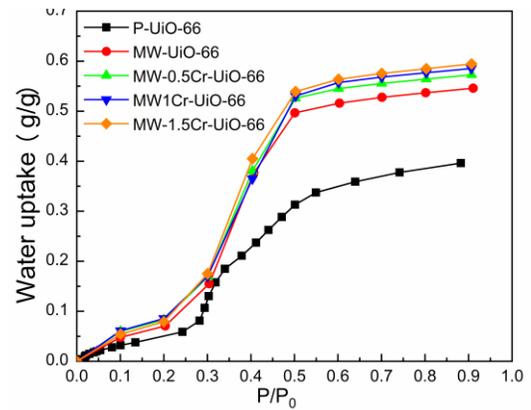


Fig. 3. Water adsorption isotherms of P-UiO-66, MW-UiO-66 and Cr-doped UiO-66 samples

concise.

The water vapor adsorption mechanism of porous materials mainly depends on the pore size distribution. According to the studies of Jerome et al.[3], when the pore diameter of the material is smaller than the critical size DC (DC = 2.0nm for water), the water clusters will be formed in the material instead of capillary condensation. So it is a water clusters adsorption process for UiO-66 due to the micropore size 0.5-1.0nm, which is only slightly larger than the effective diameter of the water molecule (0.28nm). Narrow pores are not conducive to the diffusion and adsorption of water molecules in UiO-66, which results in a lower increase of saturated water vapor adsorption capacity (8.9%) for MW-1.5Cr-UiO-66. However, compared with the water uptake of UiO-66 (0.36g/g), [6, 13] the water vapor adsorption capacity of MW-1.5Cr-UiO-66 is relatively high, which is more

conductive to the application of UiO-66 in the field of the adsorption heat pump.

3. CONCLUSION

In this paper, a series of UiO-66 samples were prepared by the traditional solvothermal method and microwave-assisted solvent synthesis method, respectively. It was found that the doping of Cr can improve the specific surface area and water vapor adsorption capacity of UiO-66. MW-1.5Cr-UiO-66 has the highest BET specific surface area (1524m²/g) and water vapor adsorption capacity (0.59g/g). The doping of Cr can change the pore size distribution and improve the specific surface area and pore volume of UiO-66, which is beneficial to enhance the water adsorption capacity. These results can provide a kind of thinking and reference for the application of UiO-66 material in the field of the adsorption heat pump.

ACKNOWLEDGEMENT

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