

PHASE-TRANSITION FUNCTION OF MINERALIZER IN THE SYNTHESIS OF POROUS CHROMIUM-BENZENEDICARBOXYLATES

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The aim of this paper is to investigate the influence of the mineralizers chlorine ion (Cl⁻) and fluorine ion (F⁻) on the structure formation of porous chromium-benzenedicarboxylates (Cr-BDCs). It was proved that Cl⁻ plays a role as mineralizer which is similar to F⁻ that can increase the crystallinity of MIL-101. In contrast, the MIL-101 phase cannot be transformed into the MIL-53 phase without mineralizer. The phase-transition occurs only after the addition of the mineralizer (Cl⁻ or F⁻) to the system. The results suggest that the mineralizer is the key component affecting the phase-transition of Cr-BDCs.

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1. Introduction

Metal-organic frameworks (MOFs) are a class of porous crystalline materials constructed from metal ions or metallic clusters combining with organic bridging ligands [1-3]. Due to the high surface area, ordered porous structure and adjustable chemical functionality, they have attracted increasing academic and industrial attentions in hydrogen storage [4], catalysis [5] and gas separation [6], sensing [7], and drug delivery [8].

Different structured MOFs, e.g. cobalt succinate phases, cobalt pyridine-3,4- dicarboxylate phases, cadmium camphorate phases, manganese oxybis(benzoate) phases and manganese trimellitates [9], can be synthesized from the same metal ions and organic ligands. What they have in common is that the different phases can be thermodynamically controlled by temperature. Chromium-benzenedicarboxylates (Cr-BDCs) such as MIL-101 (Cr₃O(F/OH)(H₂O)₂[C₆H₄(CO₂)₂]) (MIL stands for Material of Institute Lavoisier) [10] and MIL-53 (Cr(OH)[C₆H₄(CO₂)₂].nH₂O) [11], both can be synthesized from chromium ion and terephthalic acid. MIL-101 has super high Langmuir surface area, wide pore size and large cell volume. MIL-53 solids exhibited an original breathing phenomenon upon hydration-dehydration. Both the three-dimensional materials are widely used in gas storage, gas separation and catalysis [12-17]. MIL-101 is kinetically favorable while MIL-53 is thermodynamically favorable in the synthesis process. The MIL-101 phase can be transformed into MIL-53 phase in certain conditions. Nevertheless it is barely reported the key factor affecting the phase transition of Cr-BDCs between MIL-101 and MIL-53. Khan reported that water concentration, acidity and synthesis time can cause a phase transition of Cr-BDCs [18, 19]. However, the effect of chlorine ion (Cl⁻) existed in reactant mixture was ignored. Cl⁻ is in the halogen cluster and may show the function similar to fluorine ion (F⁻), which was used as mineralizer in the synthesis of crystalline materials [20].

In this paper the function of Cl⁻ and F⁻ on the phase transition of Cr-BDCs was investigated at different crystallization time by comparing with traditional synthesis method.

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2. Experimental sections

2.1. Chemicals and equipments

Terephthalic acid (H_2BDC) was purchased from ACROC ORGANICS. Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), chromium chloride ($CrCl_3 \cdot 6H_2O$), sodium hydroxide ($NaOH$), hydrochloric acid (HCl), hydrofluoric acid (HF) were purchased from Sinopharm Chemical Reagen Co. Ltd. All of the chemicals were analytical purity and used without further purification. The deionized water is homemade.

Powder XRD patterns were collected by Dm/Xa-2400 with $CuK\alpha$ radiation ($\lambda = 1.5418$, 40 kV, 100 mA) from 0.6 to 30° at a rate of $4^\circ/\text{min}$. SEM images were taken using a Nova Nano SEM 450.

2.3. Synthesis

MIL-101 was synthesized using chromium salt ($Cr(NO_3)_3 \cdot 9H_2O$ or $CrCl_3 \cdot 6H_2O$, 0.2 M), H_2BDC (0.2 M), mineralizer (HF or HCl , 0.02 M) and deionized water (80 ml). $NaOH$ was used to adjust the pH value of the reactant solution in some samples. The mixture in a 110 ml Teflon-lined autoclave was hydrothermally treated at $220^\circ C$ for 24 h or at $150^\circ C$ for 240 h in a drying oven. After cooling to room temperature, the suspension in the autoclave was precipitated by centrifugation. The precipitate was then washed with deionized water and dried at $100^\circ C$ for 8 h. The product was named as MIL-101(X)-Y or MIL-53(X)-Y (X = anion of chromium salt, Y = mineralizer).

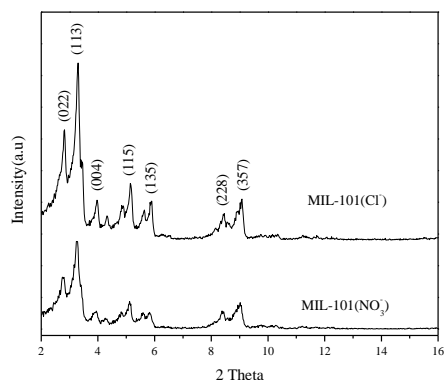


Fig.1. XRD patterns of MIL-101 synthesized at $220^\circ C$ for 24 h using different chromium salts: $Cr(NO_3)_3 \cdot 9H_2O$ and $CrCl_3 \cdot 6H_2O$.

3. Results and discussion

Fig.1 shows the XRD patterns of MIL-101 (CSD number: 415697) synthesized from $Cr(NO_3)_3 \cdot 9H_2O$ - H_2BDC - H_2O and $CrCl_3 \cdot 6H_2O$ - H_2BDC - H_2O . Intensities of the diffraction peaks of MIL-101(Cl^-) are stronger than those of MIL-101(NO_3^-), indicating that the crystallinity of MIL-101(Cl^-) is higher than that of MIL-101(NO_3^-). It can be explained that the Cl^- caused an increase in crystal growth rate, and the same phenomenon by using F^- was also reported [10].

It can be seen in Fig.2 the SEM images of MIL-101(NO_3^-) (Fig.2a) and MIL-101(Cl^-) (Fig.2b) are both octahedral morphology. MIL-101(Cl^-) presents more well-defined shape and uniform distribution of particles size.

In order to further confirm the function of Cl^- , $Cr(NO_3)_3$ - H_2BDC - H_2O - HCl was chosen to investigate their influences on the formation of MIL-101 by comparing with the synthesis systems of $Cr(NO_3)_3$ - H_2BDC - H_2O - HF , $CrCl_3$ - H_2BDC - H_2O - $NaOH$ and $Cr(NO_3)_3$ - H_2BDC - H_2O . XRD patterns in Fig.3 show that the structure of MIL-101 obtained from four synthesis systems are different with each other despite the pH values (shown in Table 1). Both Cl^- and F^- ions have significantly increased the crystallinity of MIL-101, which confirms that Cl^- plays a role as mineralizer which is similar to F^- in the formation of MIL-101 structure synthesized from $Cr(NO_3)_3$ - H_2BDC - H_2O .

Fig.4 shows the XRD patterns of Cr-BDCs synthesized at 150 °C for 240 h. The MIL-53 (CCDC number: 181154) structure was obtained by using HF or HCl as mineralizer. In order to eliminate the possible effect of H^+ , synthesis systems of $CrCl_3-H_2BDC-H_2O-NaOH$ and $Cr(NO_3)_3-H_2BDC-H_2O$ were also investigated for comparison. It is found that MIL-53 phase was also obtained from $CrCl_3-H_2BDC-H_2O-NaOH$ system. However, MIL-101 phase was not found synthesized from $Cr(NO_3)_3-H_2BDC-H_2O$ under the same synthesis condition. The SEM image (Fig.2c) shows the typical MIL-53 morphology, which is same as the literature [18]. As shown in Table 1, both MIL-53 and MIL-101 can be synthesized at pH=1.4-3.5, which indicates that pH value is not a decisive factor for the phase transition. The only difference is the existence of F and Cl. Obviously, the two ions is the main factor causing the phase transition of Cr-BDCs.

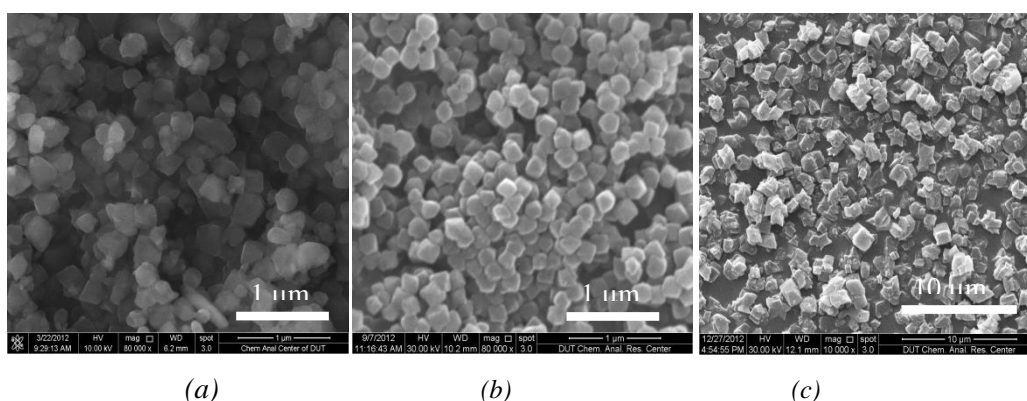


Fig. 2. SEM images of typical Cr-BDCs: (a) MIL-101(NO_3^-) synthesized at 220 °C for 24 h; (b) MIL-101(Cl⁻) at 220 °C for 24 h; (c) MIL-53(Cl⁻)-NaOH at 150 °C for 240 h.

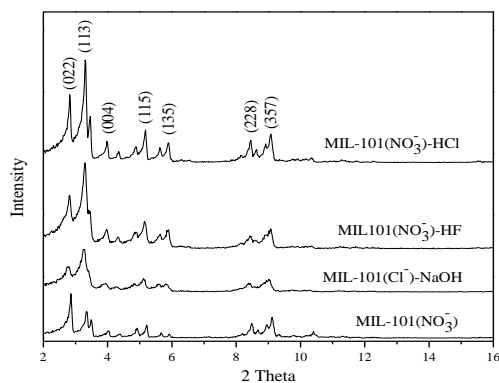


Fig. 3 XRD patterns of Cr-BDCs obtained at 220 °C for 24 h using different synthesis compositions.

Table 1. Products of different reactant compositions synthesized at different condition.

Compositions	Synthesis condition		
	pH	220 °C, 24 h	150 °C, 240 h
$Cr(NO_3)_3-H_2BDC-H_2O$	2.5	MIL-101	MIL-101
$Cr(NO_3)_3-H_2BDC-H_2O-HF$	2.9	MIL-101	MIL-53
$Cr(NO_3)_3-H_2BDC-H_2O-HCl$	1.4	MIL-101	MIL-53
$CrCl_3-H_2BDC-H_2O-NaOH$	3.5	MIL-101	MIL-53

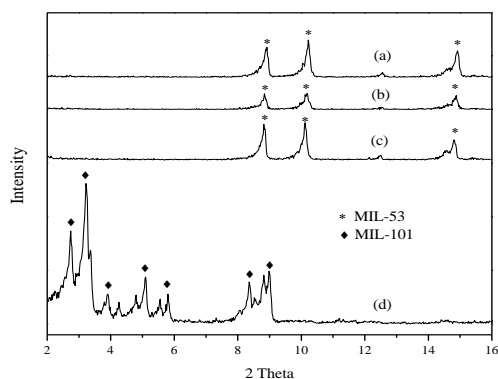


Fig. 4. XRD patterns of Cr-BDCs synthesized at 150 °C for 240 h using different synthesis compositions: (a) MIL-53(NO_3^-)-HF (b) MIL-53(NO_3^-)-HCl (c) MIL-53(Cl)-NaOH (d) MIL-101(NO_3^-).

4. Conclusions

In this study we investigated the influence of Cl^- and F^- on the framework structure and morphology of porous chromium-benzenedicarboxylates, MIL-101 and MIL-53. Cl^- was proved to play a role as mineralizer which is similar to F^- in the formation of MIL-101 synthesized from $\text{Cr}(\text{NO}_3)_3\text{-H}_2\text{BDC-H}_2\text{O}$. It is also observed that Cr-BDC crystallized for 240 h forms only MIL-101 structure without mineralizer. However, it can be transformed into MIL-53 if there is a mineralizer (F^- or Cl^-) in the synthesis solution. Therefore, it can be safely concluded that the mineralizer is the key factor causing phase transition of Cr-BDCs. The mechanism of the mineralization regarding the phase transition of the Cr-BDCs is under investigation.

Acknowledgements

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