



# Rapid synthesis of metal-organic frameworks MIL-53(Cr)

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## ABSTRACT

MIL-53(Cr) is a well-known and important metal-organic framework material. However, the long synthesis time of MIL-53(Cr) restricts its applications. Herein, we report a facile method to kinetically modulate the crystallization route and decrease the synthesis time of 72 to only 8 h by simply increasing the usage of HF.

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## 1. Introduction

The MIL-53 is one of the best representatives of Metal-organic frameworks (MOFs) with large “breathing” effects [1–8], which are of great interest for their applications in adsorption, drug release, electrochemistry and photocatalysis [9–14]. MIL-53(Cr) is the first three-dimensional nanoporous chromium(III)-based solid, which is transformed from another well-known MOFs, MIL-101 (Cr), when the synthesis time is prolonged from 8 h to 3 days [15,16]. The long synthesis time restricts its applications. Herein, we report a facile, rapid and inexpensive method to synthesize MIL-53(Cr) through the traditional hydrothermal synthesis, which modulates the crystallization route and decreases the reaction time of 72 to only 8 h with high phase purity.

## 2. Experimental

### 2.1. Sample preparation

In a typical synthesis, chromium(III) nitrate  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1.6 g, 4.0 mmol (Aladdin, 99%)), 1,4-benzene dicarboxylic acid BDC (0.67 g, 4.0 mmol (Aladdin 99%)) and hydrofluoric acid ((Haohua, 40%), varied from 4.0 to 9.6 mmol) was added in 20 ml  $\text{H}_2\text{O}$  (1.1 mol). The composition of the reaction mixture is 1.0Cr:1.0BDC:1.0~2.4HF:284 $\text{H}_2\text{O}$ . The mixture is ultrasonically treated

for 30 min and transferred to a hydrothermal autoclave, which is then put into an oven at 220 °C for a specific time. After natural cooling, the solid product was recovered by filtration, washed with ethanol, and dried at 100 °C for 2 h.

### 2.2. Characterizations

Powder X-ray diffraction data were collected at room temperature on a Rigaku Miniflex600 diffractometer using  $\text{CuK}\alpha$  radiation. Scanning electron microscope (SEM) images were acquired using a FEI Quanta250FEG microscope. Infrared (IR) spectra were obtained using a Rayleigh WQF-510 FTIR spectrometer.  $^{19}\text{F}$  MAS NMR was acquired on a Bruker AVANCE III 600 spectrometer, using a 3.2 mm probe with a 45° pulse width of 1  $\mu\text{s}$  and a 20 s recycle delay at a spinning rate of 22 kHz. The chemical shifts were referenced to  $\text{Na}_3\text{AlF}_6$  of –191 ppm.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of products obtained with different content of HF added in the reaction mixture and different hydrothermal time. By comparing them with previous XRD patterns in literatures [16], it can be found that MIL-101 of a cubic cell and  $Fd-3m$  space group is the main product after hydrothermal treatment of 8 h when the content of HF is 1.0. When we increase the hydrothermal time to 72 h, the MIL-53 of an orthorhombic cell and  $Pnma$  space group become the main phase although some MIL-101 is still remained, which means a phase transformation occurs [15]. However, when the content of HF is increased to 2.4, pure

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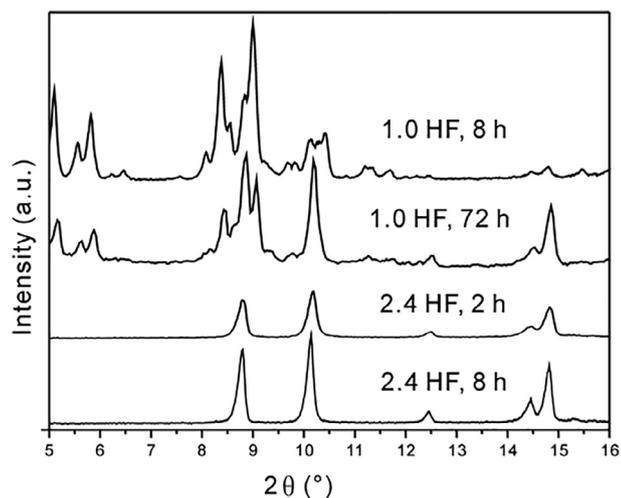


Fig. 1. XRD patterns of products obtained with different content of HF added in the reaction mixture (1.0Cr:1.0BDC:xHF) and different hydrothermal time.

MIL-53 phase is obtained after hydrothermal treatment of only 8 h. The SEM images are shown in Fig. 2. When the content of HF is 1.0 and hydrothermal time is 8 h, the crystal particle of the product is octahedral, this is in accordance with the typical morphology of MIL-101 [17–20]. In contrary, when the hydrothermal time increased to 72 h or the content of HF increased to 2.4, the octahedral morphology disappears and a lamellar morphology is mainly observed. This is in accordance with the morphology of MIL-53 [13,14,21].

The frameworks of MIL-101(Cr) is made of trimeric chromium building unit linked by BDC, while the frameworks of MIL-53(Cr) is made of chromium octahedra monomer also linked by BDC. We can see that MIL-101(Cr) and MIL-53(Cr) can be obtained from the same reaction mixture but different hydrothermal time. MIL-101 is kinetically preferred and MIL-53 is thermodynamically preferred when the content of HF is 1.0. When the content of HF is

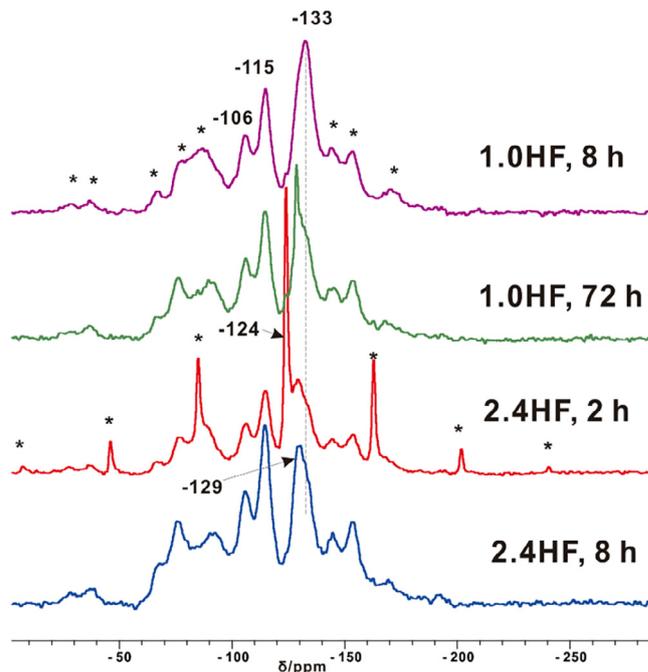


Fig. 3.  $^{19}\text{F}$  MAS NMR spectra of products obtained with different content of HF added in the reaction mixture (1.0Cr:1.0BDC:xHF) and different hydrothermal time. Asterisks denote spinning sidebands.

increased to 2.4, we set the hydrothermal time as a very short time of 2 h. In such a short reaction time, the production is predominated by unreacted white BDC powder. However, we can still find from the XRD pattern (Fig. 1) that only some MIL-53 phase is formed, and not any diffraction peak of MIL-101 can be observed. The SEM image also shows a lamellar morphology of MIL-53 (Fig. 2c). The  $^{19}\text{F}$  MAS NMR spectra of the samples with different content of HF and different hydrothermal time are shown in Fig. 3. For all the samples, the peaks at  $-106$  and  $-115$  ppm

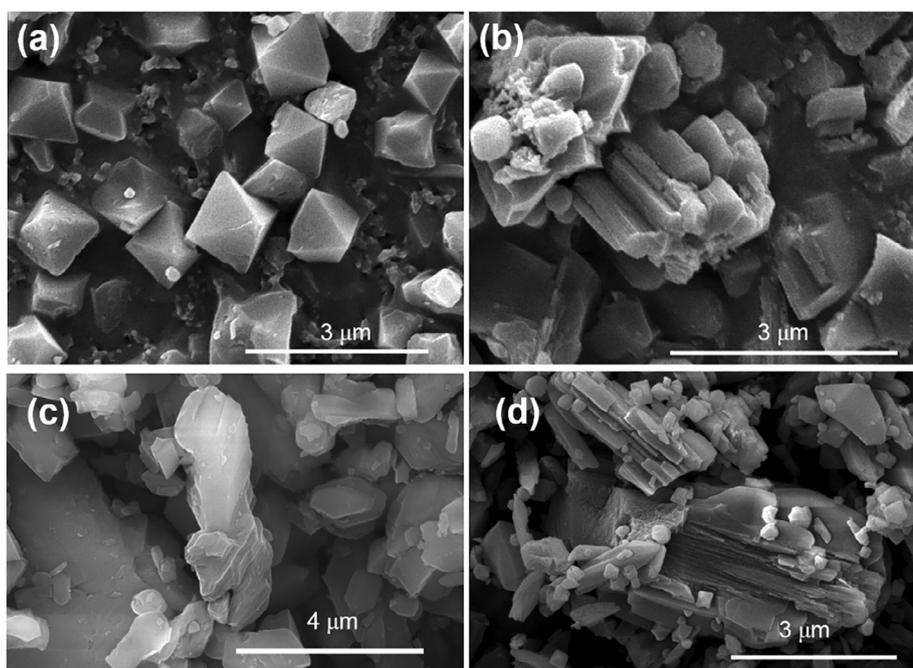
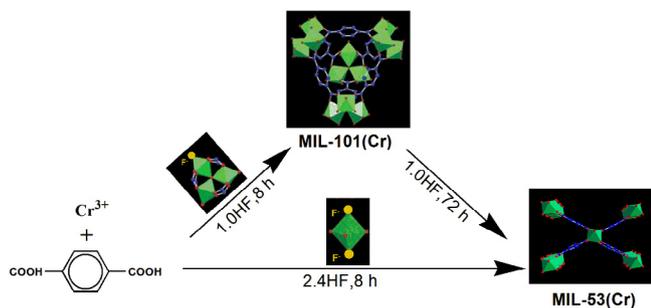


Fig. 2. SEM images of the products obtained with different content of HF added in the reaction mixture (1.0Cr:1.0BDC:xHF) and different hydrothermal time. (a) 1.0 HF, 8 h. (b) 1.0 HF, 72 h. (c) 2.4 HF, 2 h and (d) 2.4 HF, 8 h.



**Scheme 1.** (a) Schematic illustration of the different crystallization route for different content of HF added in the hydrothermal synthesis of MIL-53(Cr).

originate from the bi- and monofluoroarene of the BDC unit in the MOFs product, indicating that some added HF reacts to the BDC. In the spectrum of the product of 1.0HF and 8 h hydrothermal time, the peak at 133 ppm can be ascribed to the fluorine connected to the trimeric chromium building unit of the MIL-101 phase. When the hydrothermal time increased to 72 h or the content of HF increased to 2.4, the peak at -129 ppm arises, which can be assigned to the fluorine connected to the chromium octahedra monomer of the MIL-53 phase. When the content of HF is 2.4 and hydrothermal time is 2 h, another peak at -124 ppm ascribed to the residual fluorine anion appears, indicating the HF participates in the crystallization process. The peak at -129 ppm indicates the product is MIL-53 phase, which consists with the XRD results. HF is a well-known mineralizer. Increasing the content of HF benefits the chromium octahedra monomer and accelerates the forming of MIL-53 crystal nucleus. As a result, the synthesis route is changed kinetically. The MIL-53 is directly formed rather than transforming from MIL-101 (Scheme 1), and thus the synthetic time is dramatically decreased [21,22].

#### 4. Conclusion

MIL-53(Cr) is a well-known and important MOFs material. The long synthesis time of at least 72 h restricts its applications. Herein, we simply adjusted the content of mineralizer, HF, in the hydrothermal synthesis and kinetically changed the crystallization route. Increasing the added HF is beneficial for the forming of MIL-53(Cr) crystal nucleus. As a result, the MIL-53(Cr) is directly formed rather than transforming from MIL-101 phase, and thus the synthetic time is dramatically decreased from 72 to only 8 h, which provides a facile, rapid and inexpensive method to rapidly synthesize MIL-53(Cr) with high phase purity.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.126519>.

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