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# Acid-assisted hydrothermal synthesis and adsorption properties of high-specific-surface metal–organic frameworks

Yuanhui Ma, Jing Lin *, Yanming Xue, Jie Li, Yang Huang, Chengchun Tang *

*School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China*

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ABSTRACT

In this work, we report on the controlled growth of trivalent metal–organic frameworks, MIL-53(Al), via an acid-assisted hydrothermal method. We demonstrated that some coordination modulation such as hydrochloric acid and acetic acid, could offer hydrogen ions or extra charge as well as competitive organic linkers during the hydrothermal synthesis, which was beneficial for improving crystal quality, controlling crystal morphology and increasing surface areas of the metal–organic frameworks. In addition, the use of additive acids also enhanced the product yields and thermal stability of the frameworks. The synthesized high-specific-surface MIL-53(Al) displayed strong $CO_2$-adsorption capacity, indicating their potential applications as valuable adsorbent for low-concentration $CO_2$ capture.

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## 1. Introduction

The synthesis of metal–organic frameworks (MOFs) has been attached much attention due to their properties such as huge porosity, regular cavities, dynamic flexibility and possible applications [1–3] including gas adsorption, storage, separation, sensors, analysis, luminescence, magnetism and drug delivery. One of the typical MOFs, $Al(OH)(O_2C–C_6H_4–CO_2)$, denoted as MIL-53, has been reported by Férey group [4]. The framework is built up of infinite trans chains of corner-sharing $AlO_4(OH)_2$ octahedron. MIL-53(Al) exhibits high surface area of 1140 $m^2/g$ and large internal volume. The key factor of the successful MOFs synthesis is based on the proper design. Some parameters such as pH or additives are not only responsible for the phase formation but also present a way to improve the crystal quality, morphology, yields as well as adsorption properties of the MOF products.

We report on the controlled growth of trivalent metal–organic frameworks, MIL-53(Al), via an acid-assisted hydrothermal method. Two kinds of novel MIL-53(Al) frameworks, denoted as $MIL\text{-}53(Al)_{HCl}$ and $MIL\text{-}53(Al)_{HAc}$, were synthesized with the assistance of hydrochloric acid (HCl) and acetic acid (HAc) during the hydrothermal treating process, respectively. The use of coordination modulation such as HCl and HAc could enhance the product yields and thermal stability of the metal–organic frameworks. Besides, the use of additive acids also improved the crystal quality and increased the surface areas of the frameworks. The product synthesized with the addition of HCl showed much higher $CO_2$-adsorption capacities at relative low pressure than the product synthesized without acid assist.

## 2. Experimental

All chemicals were of regent-grade quality and obtained from commercial sources. 1.66 g terephthalic acid (Tianjin university kewei corporation), 1.00 g $AlCl_3$ (Tianjin guangfu fine chemical research institute) and 0.5 ml HCl (Tianjin university kewei corporation) were dissolved in 70 ml *N,N*-dimethylformamide (DMF, Tianjin guangfu fine chemical research institute) with magnetic stirring. When it became transparent, the solvent was transferred into a Telfon-lined stainless steel bomb and heated under an autogenous pressure to 190 °C for 72 h. After cooling down to room temperature, the solid was filtered off and washed with DMF. Then the product was dried at 50 °C in the vacuum drying oven for one days to obtain the sample $MIL\text{-}53_{as}(Al)_{HCl}$. With the aim of removing disordered terephthalic acid molecules and DMF molecules which were trapped inside framework's tunnels, the as-prepared $MIL\text{-}53_{as}(Al)_{HCl}$ was post-treated at 300 °C for 1 h in air, leading to a nanoporous open-framework material $MIL\text{-}53_{ht}(Al)_{HCl}$. When the 0.5 ml HCl was replaced by 2 ml HAc (Tianjin bodi chemical corporation limited), $MIL\text{-}53_{as}(Al)_{HAc}$ and $MIL\text{-}53_{ht}(Al)_{HAc}$ were produced. In the same condition, we obtained $MIL\text{-}53_{as}(Al)$ and $MIL\text{-}53_{ht}(Al)$ without introducing any acid. The $CO_2$-adsorption isotherms of the MIL-53(Al) series were measured using the automatic gas sorption analyzer AutoSorb iQ at 0 °C after samples were degassed for 3 h at 200 °C under vacuum.

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* Corresponding authors. Tel.: +86 22 60202660; fax: +86 22 60202660.
*E-mail addresses:* dr.linjing@gmail.com (J. Lin), tangcc@hebut.edu.cn (C. Tang).

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The structure and morphology of the samples were examined using X-ray powder diffraction (XRD, BRUKER D8 FOCUS) and field emission scanning electron microscopy (SEM, HITACHI S-4800). Thermogravimetry (TG) and differential thermal analysis (DTA) were measured on a SDT Q-600 thermal analyzer from room temperature to 700 °C at a heating rate of 10 °C/min under argon flow. The nitrogen physisorption isotherms were measured at 77 K on an automatic gas sorption analyzer AutoSorb iQ.

## 3. Results and discussion

After the acid-assisted hydrothermal treating process, we obtained two kinds of white products: MIL-53(Al)$_{HCl}$ and MIL-53(Al)$_{HAc}$. The yield of MIL-53(Al)$_{HCl}$ is 69.3 wt% (1.10 g) based on the Al salt and the MIL-53(Al)$_{HAc}$ is 76.0 wt% (1.20 g). These values are much higher than that of pure MIL-53(Al) sample prepared without the addition of acids (50.7 wt%, 0.80 g). This indicates that the use of acid during the synthesis process could effectively improve the yield of the MIL-53(Al) products.

The structure and morphology of the different products were studied. Fig. 1(a) shows the XRD patterns of MIL-53$_{as}$(Al)$_{HAc}$ and MIL-53$_{as}$(Al)$_{HCl}$ prepared with the addition of HCl and HAc, respectively. The peak intensities of MIL-53$_{as}$(Al)$_{HAc}$ and MIL-53$_{as}$(Al)$_{HCl}$ are much higher than that of MIL-53$_{as}$(Al), indicating that the introducing of acid into the synthesis process could effectively improve the crystallinity of the frameworks.

The morphologies of the MIL-53(Al) crystals are shown in Fig. 1 (b)–(d). Well-crystallized cocoon-like hierarchical structure and numerous clusters of uniform rods are observed. Fig. 1(b) shows that the aggregative micro-rods are assembled into a cocoon-like structure in MIL-53(Al). However, the introduction of HCl strongly destroyed the original morphology of MIL-53$_{as}$(Al), as displayed in Fig. 1(c) and (d) shows that the synthesized MIL-53$_{as}$(Al)$_{HAc}$ has a well-dispersed nanorod structure with an average diameter of 0.2 μm. The introduction of HAc not only destroyed the original morphology of MIL-53(Al), but also led to a new well-dispersed nanorod structure. Therefore, it can be concluded that morphologies of the products are strongly influenced by the addition of different acids. The crystallization of metal–organic frameworks is an equilibrium reaction between an inorganic metal salt and organic acid [5]. In our work, they are expressed as:

$$[AlCl_3]+[H_2BDC]+3[OH^-]=[Al(OH)(BDC)]+3[Cl^-]+2[H_2O];$$

$$[AlCl_4-]+[H_2BDC]+3[OH^-]=[Al(OH)(BDC)]+4[Cl^-]+2[H_2O];$$

The reactions can be easily driven in acidic condition according to product yields and intensity of XRD patterns. The addition of inorganic acid could lead to the hydrolysis of DMF and the result might act as a donor to offer hydroxyl ions for the synthesis of MIL-53(Al) [4]. When HCl was used as the addition, the hydrolysis rate of DMF could be accelerated. Meanwhile, the anion [Cl$^-$] might cause $AlCl_3$ to transform into [$AlCl_4^-$] or something else that had kinetic and thermodynamic advantages as well as balanced the positive charge of the framework [6]. Therefore the use of HCl had positive effects on crystal quality and yield of the product. However, the HCl environment was not favorable for the crystal morphology in the way. Contrast to the HCl, the introduction of HAc was beneficial to the crystal morphology, product yield, as well as the porosity of the framework. As shown in Fig. 1(d), a well-dispersed nanorod structure was obtained due to the effect of the additive HAc. The HAc had similar effect as the HCl by offering hydrion which could accelerate hydrolysis rate of DMF. When HAc was used as the addition, the hydrolysis of DMF could also be accelerated and offer hydroxyl ions for the synthesis of the framework [4]. So the use of HAc was beneficial for the synthesis of MIL-53(Al) and led to higher product yields. In addition, the use of HAc could accelerate the nucleation rate and decelerate crystal growth rate. Meanwhile the HAc could compete with the organic linker in order to coordinate with the metal ions and disturb or inhibit crystal growth in some directions during nucleation and crystal growth, so the HAc facilitated the formation of well-dispersed nanorods with high crystallinity [7,8].

Pore textural properties of the metal–organic frameworks were calculated from the nitrogen adsorption and desorption isotherms at 77 K. All samples were outgassed at 200 °C for 3 h under vacuum. Fig. 2(a) illustrates the nitrogen adsorption/desorption isotherm of the MIL-53(Al)$_{HCl}$. According to the IUPAC nomenclature

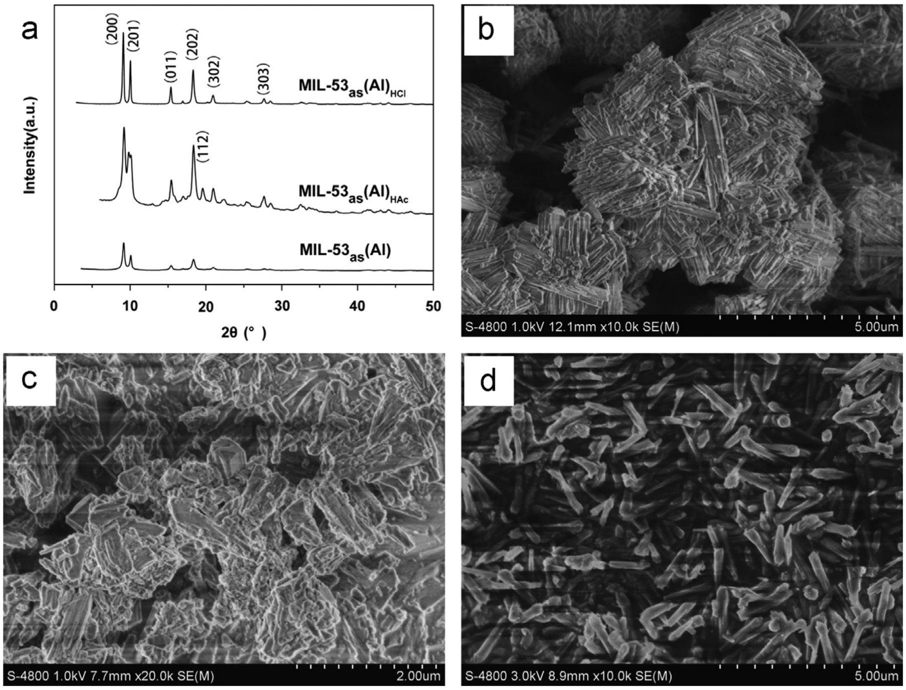

**Fig. 1.** (a) XRD patterns of MIL-53$_{as}$(Al), MIL-53$_{as}$(Al)$_{HAc}$ and MIL-53$_{as}$(Al)$_{HCl}$. (b)–(d) SEM images of MIL-53(Al), MIL-53(Al)$_{HCl}$ and MIL-53(Al)$_{HAc}$, respectively.

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