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Preparation of metal organic frameworks MIL-101 (Cr) with acetic acid as mineralizer

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Abstract. Pure metal organic frameworks MIL-101(Cr) was directly prepared without any purification treatment using acetic acid as mineralizer. The physical structure and morphology of the material were studied by means of powder X-ray diffraction(XRD), thermogravimetric(TG), scanning electron microscope(SEM) and N2 adsorption-desorption and compared with conventional MIL-101(Cr) which synthesized with hydrofluoric acid as mineralizer. The results demonstrate that the specific surface area and pore volume of the MIL-101(Cr) synthesized with acetic acid as mineralizer are superior to hydrofluoric acid as mineralizer. The MIL-101(Cr) sample synthesized with acetic acid as mineralizer is stable above 450°C, higher than the MIL-101(Cr) synthesized with hydrofluoric acid as mineralizer.

1. Introduction
Carbon dioxide is the main component of greenhouse gas[1]. The potential way to reduce its emissions is to improve the efficiency of energy use and increase the use of low carbon energy. At the same time, the capture and separation of the emitted CO₂ is also an important means to achieve CO₂ emission reduction[2]. The existing methods of CO₂ capture are mainly include membrane separation method[3], supergravity separation method[4], adsorbent adsorption separation method and so on[5-7], and CO₂ adsorbents mainly include activated carbon adsorbent, molecular sieve, hydrotalcite, functionalized mesoporous silica and metal organic framework material (MOFs)[8,9]. Metal organic framework material (MOFs) has been widely concerned with its superior physical and chemical properties, such as high specific surface area, adjustable pore size and multi-functional structure[10,11], which have good application prospects in gas storage[12], separation[13], industrial catalytic[14] and removal of environmental pollutants[15]. MIL-101(Cr) is a three-dimensional chromium terephthalate-based porous material with the empirical formula [Cr₃(O)ₓ(bdc)y(H₂O)₂]·nH₂O(bdc=benzene-1,4-dicarboxylate, X=(OH or F). It possesses the framework of augmented MTN zeolite topology.

Most of the existing methods of preparation of MIL-101(Cr) use hydrofluoric acid (HF) as mineralizer. The specific surface area of the prepared material is generally not higher than that of 3200m²·g⁻¹. This is because the incompletely reacted terephthalic acid (H₂BDC) remains in the MIL-101 channel without activation after synthesis, resulting in a decrease in the specific surface area and pore volume of MIL-101. In order to remove excess H₂BDC in the cell, the material must be washed repeatedly with the hot solution of ammonium fluoride, N,N'-dimethylformamide (DMF) and ethanol, so this complicated purification process is not conducive to prepare MIL-101. Zhao and co-workers think that reducing the pH value of the reaction solution is not conducive to the dissolution of terephthalic acid and the formation of chromium triad[16], while Jun, JW and co-workers suggest that
the formation of chromium trimer in the synthesis of MIL-101 is more important than the dissolution of terephthalic acid, and the proper reduction of pH in the reaction solution is beneficial to the formation of chromium tripolymer [17]. Zhao et al. [16] proposed the preparation of MIL-101 using nitric acid (HNO₃) as a mineralizer. This method can increase the yield of MIL-101 by 80%, and the specific surface area of the obtained sample can reach 3100 m²·g⁻¹. Compared with MIL-101 prepared with HF as a mineralizer, HNO₃ as a strong acid not only enhances the corrosion of reactive metal elements, but also harms the human body. In this study metal organic frameworks MIL-101(Cr)-A was directly prepared without any purification treatment using acetic acid as mineralizer and the physical structure and morphology of the material were compared with conventional MIL-101(Cr) which synthesized with hydrofluoric acid as mineralizer.

2. Experimental section

2.1. Experimental section

2.1.1. Materials. Chromium (III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, 99%), terephthalic acid (H₂BDC, 99%), N,N’-dimethylformamide (DMF, 99.5+%), hydrofluoric acid (HF, 40% v/v), ethanol (EtOH, 99.7+%), acetic acid and ammonium fluoride. All chemicals were of analytical reagent (AR) grade and used as obtained from commercial sources without further purification. Deionized water (DI) was used for the reaction and washing solvent.

2.1.2. Synthesis of MIL-101(Cr). MIL-101(Cr) was synthesized according to a published procedure [18] by scaling up approximately three times. First, 12g of Cr(NO₃)₃·9H₂O, 5g of H₂BDC, 6mL of HF were mixed in 130mL of DI water and stirred for 15 min. Next, the solution was transferred into an autoclave which was tightly sealed and heated at 493K for 20 h and cooled afterwards slowly to room temperature at a rate of 298K/h over 8 h.

After synthesis, a detailed treatment was applied to remove the unreacted reactants and solvents. The resultant slurry was placed in centrifugal tubes and the supernatant solution was removed after centrifugation, after the supernatant solution was centrifuged again, the resulting precipitate was put together and washed 3 times with DMF (100mL each time). The solid was isolated by centrifugation and soaked in 100°C ethanol for 20 h and washed 5 times with hot DI water (120 mL each time at 60°C). After the final isolation, the wet solid was dried at 150°C for 8 h in a vacuum oven.

2.1.3. Synthesis of MIL-101(Cr)-A. MIL-101(Cr)-A was prepared using acetic acid as a mineralizer. 6.4g of Cr(NO₃)₃·9H₂O and 2.64g of terephthalic acid were dissolved in 18mL of acetic acid and 62 mL of deionized water was added. After stirring for 30 minutes, the solution was transferred to an autoclave and reacted at 220°C for 20h. After cooling to room temperature, the product was centrifuged and the supernatant was removed. After centrifugation, the product was soaked in ethanol for 2 hours. After cooling, centrifugation, washing and drying, the resulting solid was placed in a vacuum drying oven and dried at 150°C for 2 hours to obtain MIL-101(Cr)-A.

2.2. Samples characterization

XRD patterns of the prepared materials were identified by the power X-ray diffraction (PXRD) using Cu Kα radiation in a range of 2θ from 5° to 65° at a scan speed of 8°/min.

Structure and morphology of the crystals were determined by SEM with high magnification and high resolution.

The BET surface areas (S_BET) and pore volumes (V_pore) of materials were studied by nitrogen adsorption/desorption isotherms, at 77K on a V-sorb 2800p.

Thermal stability of samples were measured under a nitrogen atmosphere (20 mL/min flow rate) at a heating rate of 5°C/min from 50° to 650° using a METTLER TGA/DSC2 1600LF instrument.
3. Results and discussion

3.1. Powder X-ray diffraction patterns

The powder X-ray diffraction patterns of the MIL-101(Cr) and MIL-101(Cr)-A sorbents are demonstrated in Figure 1. It ought to be noted that the PXRD patterns of MIL-101(Cr) mainly shows the characteristic peaks of the two phases, which are the characteristic diffraction peaks of MIL-101(Cr) between 2θ=5°-10° and the characteristic diffraction peaks of terephthalic acid between 2θ=17°-35°, respectively. We can also found that the PXRD patterns of MIL-101(Cr)-A has the same characteristic diffraction peaks, this means that we synthesized MIL-101(Cr) successfully using acetic acid as mineralizer.

![Figure 1. PXRD patterns of the MIL-101(Cr) and MIL-101(Cr)-A.](image)

3.2. Nitrogen adsorption-desorption isotherms

In order to examine textural characteristics of the MIL-101(Cr) and MIL-101(Cr)-A, nitrogen adsorption-desorption isotherms on two samples were determined at 77K(Figure 2). It was observed that N\textsubscript{2} adsorption isotherms of the MIL-101(Cr) and MIL-101(Cr)-A were reversible and did not exhibit any hysteresis loop due to desorption process. The major adsorption of N\textsubscript{2} in the adsorption isotherms occurred at low relative pressure (P/P\textsubscript{0}=0.08). It was reported that the MIL-101(Cr) has two types of microporous cages, hence, a secondary adsorption step in the range of 0.1< P/P\textsubscript{0}<0.2 arose by these two types of microporous windows. The specific surface area and pore volume of each sample were calculated from nitrogen adsorption-desorption isotherms and the results are shown in Table 1. The values of S\textsubscript{BET} and V\textsubscript{Pore} of MIL-101(Cr)-A are higher than MIL-101(Cr), which indicates that acetic acid increased porosity of material.

![Figure 2. N\textsubscript{2} adsorption-desorption isotherms on the MIL-101(Cr) and MIL-101(Cr)-A.](image)
3.3. Thermal analysis
Figure 3 demonstrates the derivative thermogravimetric curves for evaluating the thermal stability of the prepared MIL species. The DTG curve of MIL-101(Cr) indicates the peaks below 100 °C attributed to desorption of physically adsorbed water and keep stable between 100-350 °C, then, the sharp peak occurring at about 350 °C is assigned to the removal of OH/F groups and the collapse of the structure of MIL-101(Cr). The MIL-101(Cr) sample synthesized with acetic acid as mineralizer is stable above 450 °C, higher than the MIL-101(Cr). In other words, the introduction of mounts of acetic acid can change thermal stability of the MIL.

3.4. The SEM images
The structure and morphology of the crystals were determined by the SEM images are provided in Figure 4(a),(b). Figure 4(a) (at the left-hand side) exhibits the compactness of the MIL-101(Cr), which consists of mounts of octahedral crystals. The structure and morphology of the MIL-101(Cr)-A is showed in Figure 4(b), it was concluded that acetic acid did not destroy the structure of the MIL and the presence of acetic acid in the process of structure formation might have higher cohesive force affecting the framework structure.
4. Conclusion
In this research, MIL-101(Cr) was directly prepared without any purification treatment using acetic acid as mineralizer. Compared with traditional MIL-101(Cr), MIL-101(Cr)-A is stable above 450 °C, higher than the MIL-101(Cr), the values of $S_{BET}$ and $V_{pore}$ of MIL-101(Cr)-A are higher than MIL-101(Cr), which indicates that acetic acid increased porosity of material. So MIL-101 can be synthesized successfully using acetic acid as mineralizer.

References
[1] Yamasaki A 2003 An overview of CO2 mitigation options for global warming: Emphasizing CO2 sequestration options Journal of Chemical Engineering of Japan 36(4) 361-75
[2] D’Alessandro D, Smit B, Long J 2010 Carbon dioxide capture: Prospects for new materials Angewandte Chemie-International Edition 49(35) 6058-82
[3] Cao Y Y, Yang E C, Wang W J 2015 Carbon dioxide membrane separation technology Specialty Petrochemicals 32(1) 53-60
[4] Huang W L, Zhang B L, Liu H B, et al. 2017 Removal of CO2 from associated gas in offshore oilfield by high gravity method Modern Chemical Industry 113-16
[5] Palomino M, Corma A, Rey F, et al. 2010 New insights on CO2–methane separation using LTA zeolites with different Si/Al ratios and a first comparison with MOFs Langmuir 26(3) 1910-17
[6] Goetz V, Pupier O, Guillot A 2006 Carbon dioxide-methane mixture adsorption on activated carbon Adsorption-journal of the International Adsorption Society 12(1) 55-63
[7] Konstas K, Taylor J W, Thornton A W, et al. 2012 Lithiated porous aromatic frameworks with exceptional metal storage capacity Angewandte Chemie 51(27) 6639-42
[8] Férey G, Mellot-draznieks C, Serre C, et al. 2005 A chromium terephthalate-based solid with unusually large pore volumes and surface area Science 309(5743) 2040-42
[9] Zhu Q L, Xu Q 2014 Metal-organic framework composites Chemical Society Reviews 43(16) 5468-512
[10] Farha O K, Hupp J T 2010 Rational design, synthesis, purification, and activation of metal-organic framework materials Accounts of Chemical Research 43(8) 1166-75
[11] Tanabe K K, Cohen S M 2016 Postsynthetic modification of metal-organic frameworks—a progress report Chemical Society Reviews 47(15) 1315-29
[12] Wu H, Gong Q, Olson D H, et al. 2012 Commensurate adsorption of hydrocarbons and alcohols in microporous metal organic frameworks Chemical Reviews 112(2) 836-68
[13] Zheng B, Liu H, Wang Z, et al. 2013 Porous NbO-type metal–organic framework with inserted acylamide groups exhibiting highly selective CO2 capture Crystengcomm 15(18) 3517-20
[14] Herbst A, Khutia A, Janiak C 2012 Bronsted instead of Lewis acidity in functionalized MIL-101(Cr) MOFs for efficient heterogeneous (nano-MOF) catalysis in the condensation reaction of aldehydes with alcohols Inorganic Chemistry 53(14) 7319
[15] Li X J, He C F, Huang B, et al. 2016 Progress in removal of environmental pollutants by metal organic frameworks Chemical Society Industry and Engineering Progress 35(2) 586-94
[16] Zhao T, Jeremias F, Boldog I, et al. 2015 High-yield, fluoride-free and large-scale synthesis of MIL-101(Cr) Dalton Transactions 44(38) 16791
[17] Khan A A, Jun J W, Jhung S H 2010 Effect of water concentration and acidity on the synthesis of porous chromium benzenedicarboxylates European Journal of Inorganic Chemistry 2010(7) 1043-1048
[18] Hong D, Hwang Y K, Serre C, et al. 2010 Porous chromium terephthalate MIL-101 with coordinatively unsaturated ed sites: surface functionalization, encapsulation, sorption and catalysis Advanced Functional Materials 19(10) 1537-52.