Electronic Supplementary Information

Experimental investigation on the water stability of amino-modified indium metal–organic framework

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Regents

Terephthalic acid (H_2BDC), 2-aminoterephthalic acid ($BDC\text{-}NH_2$) and indium nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$) were obtained from Alfa Aesar China Co., Ltd. (Tianjin, China). N'N-dimethylformamide (DMF) and methanol were supplied by Guangzhou Chemicals Co. Ltd. (Guangzhou, China). All reagents were analytical grade and used without further purification.

Synthesis

Preparation of MIL-68(In) and MIL-68(In)-NH_2

MIL-68(In) was synthesized through a solvothermal method reported by Ferey's group[1]. The mixture of $In(NO_3)_3 \bullet xH_2O$ (1.05 mmol), H_2BDC (1.20 mmol) and DMF (5.00 mL) was placed in a 25 mL Teflon liner. After stirred for 30 min, the liner was sealed in a stainless steel autoclave and heated at 100℃ for 48 h. After natural cooling, white powder was collected and washed with DMF. Then, the product was filtered and dried under vacuum at 100℃ for 12h. The resulting sample was then kept in a desiccator.

MIL-68(In)-NH_2 was prepared solvothermally using reported method[2]. Typically, $In(NO_3)_3 \bullet xH_2O$ (3.84 mmol) and $BDC\text{-}NH_2$ (1.29 mmol) were mixed with DMF (12.4 mL) in a 25 mL Teflon liner. After stirred for 30 min, the liner was sealed in a stainless steel autoclave and heated at

125℃ for 5 h. After natural cooling, light yellow powder was collected, washed with DMF and immersed in fresh methanol for three days. The methanol was changed once a day. Finally, the sample was filtered and dried under vacuum at 100℃ for 12h. The resulting sample was then kept in a desiccator.

Characterization

Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Cu Kα radiation. N_2 adsorption-desorption isotherms of the samples at 77 K were measured with a Micromeritics ASAP 2020 instrument. The BET surface areas can be obtained by analyzing the N_2 adsorption-desorption isotherms. Scanning electron microscope (SEM) was performed on a MERLIN Compact instrument.

Evaluation of water stability of MIL-68(In)-NH_2

1. The effect of water molecule on the MIL-68(In)-NH_2 synthesis

$In(NO_3)_3 \cdot xH_2O$ (3.84mmol) and BDC-NH_2 (1.29mmol) were mixed with DMF (12.4mL) until complete dissolution of the solids. Then, 12.9% and 18.2% water (by mass) were separately added in the precursor solutions. The resulting mixtures were subsequently stirred followed by the same synthesis procedure as for MIL-68(In)-NH_2. The structure and

morphology evolutions of the resulting products were monitored by XRD, SEM and BET, respectively.

2. Tolerance study of the MIL-68(In)-NH_2 and MIL-68(In) crystal in acidic solutions

The acid-tolerance of MIL-68(In)-NH_2 and MIL-68(In) was tested in acidic solutions at different pH. The solution pH was adjusted to 1, 2, 3 and 5 with 0.1M and 1M HCl, respectively. The MIL-68(In)-NH_2 and MIL-68(In) samples were immersed in acidic solutions for 2 h at a MIL-68(In)-NH_2 or MIL-68(In)/solution weight ratio of 0.04:100. The samples were collected and then subjected to XRD and BET analysis.

3. Hydrothermal tests for MIL-68(In)-NH_2 and MIL-68(In)

The hydrothermal tests for the MIL-68(In)-NH_2 and MIL-68(In) crystals were performed in hot water (80 °C) for 24 h. The crystal concentration ($W_{MOF}/(W_{MOF}+W_{water})$) was 0.060 wt%. Following hydrothermal test, the samples were collected and then analyzed by XRD, BET and SEM, respectively.

4. Comparative study of stability of MIL-68(In)-NH_2 and MIL-68(In) after exposure to water

A given amount of MIL-68(In)-NH_2 and MIL-68(In) powders was separately immersed in room-temperature water at a MOF/solution weight ratio of 0.04:100. The samples were collected at different durations and then analyzed by XRD and BET, respectively.

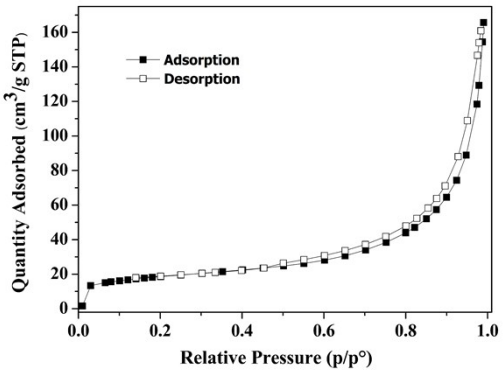

Fig. S1 N_2 adsorption-desorption isotherm of the MIL-68(In)-NH_2 sample after hydrothermal test in 80℃water for 12 h.

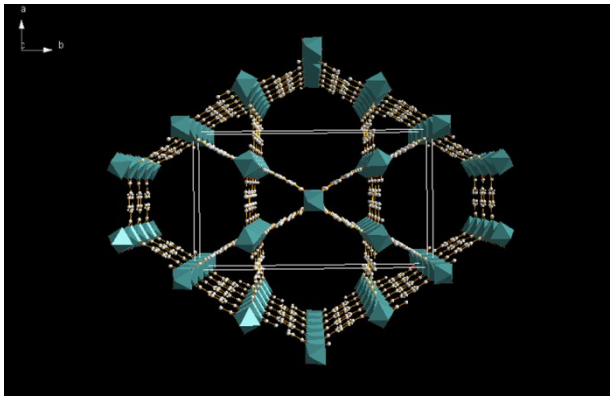

Fig. S2 The structure of MIL-68(In).

Reference:

1 C. Volkringer, M. Meddouri, T. Loiseau, N. Guillou, J. Marrot, G. Ferey, M. Haouas, F. Taulelle, N. Audebrand and M. Latroche, *Inorg. Chem.,* 2008, **47**, 11892-11901.

2 R. Liang, L. Shen, F. Jing, W. Wu, N. Qin, R. Lin and L. Wu, *Appl Catal B-Environ.,* 2015, **162**, 245-251.