



Highly efficient mechanochemical synthesis of an indium based metal-organic framework with excellent water stability



Yongwei Chen^a, Jing Xiao^a, Daofei Lv^a, Tiezhen Huang^a, Feng Xu^a, Xuejiao Sun^{b,*}, Hongxia Xi^a, Qibin Xia^{a,*}, Zhong Li^a

^a School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

^b School of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, China

ARTICLE INFO

Keywords:

Metal-organic framework
Mechanochemical synthesis
Water stability
CO₂/CH₄
CO₂/N₂
Adsorption and separation

ABSTRACT

Mechanochemical synthesis, induced by mechanical grinding, is demonstrated to be rapid and efficient for metal-organic frameworks (MOFs) synthesis. For this purpose, a mechanochemical synthesis route was proposed for the first time for preparation of water stable indium metal-organic frameworks **InOF-1**. The effects of preparation conditions such as the addition of solvents and grinding time were discussed, and the **InOF-1** synthesized through optimized condition was used to investigate its selective CO₂ adsorption. Results showed that using liquid-assisted grinding for 20 min with CH₃CN (0.4 mL) could lead to highly crystalline and porous **InOF-1** with a Brunauer-Emmett-Teller (BET) surface area of 707 m²/g. The addition of a small amount of solvent into the system could dramatically improve the crystallinity and porosity of **InOF-1**. More importantly, the synthesized product with the highest specific surface area retained its crystallinity and porosity after being soaked in water for 12 h. Its CO₂ adsorption capacity reached as high as 4.03 mmol/g at 273 K and 100 kPa, and CO₂/CH₄ and CO₂/N₂ adsorption selectivities were up to 7.5 and 45, respectively. The superior performance of the mechanochemically synthesized **InOF-1** makes it a potential candidate for CO₂ adsorption and separation.

1. Introduction

Over 85% of our current global energy demand (Liu et al., 2012) is satisfied by the combustion of fossil fuels (McDonald et al., 2012) with unavoidable vast CO₂ emission to the atmosphere. The globally averaged CO₂ concentration in air continues to rise, which surpassed 400 ppm in 2013 (Kumar et al., 2015), provoking the undesirable greenhouse effect. Currently, substantial research effort has been made on reducing CO₂ emission, where the technology of carbon capture provides an efficient way (Chu, 2009) for the selective removal of CO₂ from flue gas in power plants (Mason et al., 2015; Wang et al., 2016). Among various technologies, adsorption is advantageous due to its high efficiency and low operating cost (Kizzie et al., 2011). Traditional adsorbents such as zeolites and activated carbons have been extensively studied for CO₂ capture (Diaz et al., 2008; Drage et al., 2009; Jimenez et al., 2012; Palomino et al., 2012). To further enhance the efficiency of CO₂ capture, the development of new adsorbents with superior CO₂ adsorption capacity and selectivity is desirable.

MOFs are a class of crystalline porous materials that have recently attracted intensive attention for CO₂ capture and separation (Keskin

et al., 2010; Wang et al., 2014; Zhang et al., 2011, 2014; Zhou et al., 2016) with the advantages of extremely high surface areas and pore volumes (Furukawa et al., 2010), tunability of pore sizes (Lu et al., 2016) and modularity of properties (Deng et al., 2010; Hu et al., 2014), as well as flexibility for chemical functionalization by modifying the metal clusters or organic ligands (Bae et al., 2011; Burd et al., 2012; Jasuja et al., 2014; Liu et al., 2011; Nguyen et al., 2014; Nugent et al., 2013; Qu et al., 2016; Tan et al., 2015; L.J. Wang et al., 2014; Zhang et al., 2013). MOFs are generally synthesized by traditional hydrothermal or solvothermal method, which requires long reaction time and the involvement of a large amount of organic solvent (Bowmaker, 2013; James et al., 2012; Julien et al., 2016; Užarević et al., 2016). Thus, it is crucial to develop a more efficient and environmentally friendly methodology for MOFs synthesis.

In recent years, mechanochemical method has been demonstrated to synthesize some MOFs (Beldon et al., 2010; Julien et al., 2016; Klimakow et al., 2010; Užarević et al., 2016; Yuan et al., 2010). For example, James et al. (Pichon et al., 2006; Prochowicz et al., 2015; Yuan et al., 2010) successfully synthesized Cu(INA)₂ (INA = isonicotinate), MOF-5 and Cu-BTC by mechanochemical method. Recently,

* Corresponding authors.

E-mail addresses: sun061302125@163.com (X. Sun), qbxia@scut.edu.cn (Q. Xia).

Friščić and coworkers (Beldon et al., 2010; Julien et al., 2016; Užarević et al., 2016) prepared ZIF-8, MOF-74 and UiO-66 by the implementation of mechanochemical synthesis. Mechanochemical method for the preparation of MOFs can not only dramatically reduce reaction time from several days to a couple of minutes, but also avoid the use of a large amount of solvent. However, it should be noted that in the case of MOF-74 and Cu-BTC, the framework structures would decompose under humid conditions or exposure to water solution (Burtch et al., 2014; Jiao et al., 2015; Zuluaga et al., 2016). Though ZIF-8 and UiO-66 are water stable MOFs (Kim et al., 2012; Verploegh et al., 2015), their usage for CO₂ capture is limited due to the low CO₂ adsorption capacity and selectivity (Cao et al., 2015; McEwen et al., 2013). Hence, it is necessary to develop the facile mechanochemical method to prepare MOFs with not only high CO₂ adsorption capacity and selectivity but also excellent water stability.

Indium based **InOF-1** with excellent water stability and superior CO₂ adsorption ability was synthesized by Qian et al. (2012) using a traditional solvothermal method. Up to now, the mechanochemical synthesis of indium based MOFs has not been reported yet. Herein, the rapid mechanochemical synthesis of **InOF-1** was investigated and the synthesized material was studied for CO₂ capture. A liquid-assisted grinding (LAG) mechanochemical method was applied to rapid synthesis of **InOF-1**. The influence of synthesis parameters such as addition of solvents and grinding time on the structure and porosity of **InOF-1** was discussed and reported here. Overall, the superior performance of **InOF-1** indicated that it can be a potential MOFs adsorbent for CO₂ capture.

2. Experimental

2.1. Materials

Indium acetate hexahydrate [In(OAc)₃·6H₂O, 99.99%] and organic ligand 3,3',5,5'-biphenyltetracarboxylic acid (H₄bptc, C₁₆H₁₀O₈, 98%) were obtained from Beijing HWRK Chem Co. Ltd. (China). Etanol (EtOH, 99%), N,N-dimethylformamide (DMF, 99%) and acetone (99%) were got from Guangdong Guanghua Sci-Tech Co. Ltd. (China). Acetonitrile (CH₃CN, 99%) was purchased from Shanghai Kunling chemical reagent Co. Ltd. (China).

2.2. Synthesis of [In₂(OH)₂(BPTC)]·6H₂O (**InOF-1**)

The **InOF-1** samples were prepared in a QM-3C ball mill via a fast room-temperature solvent-assisted mechanochemical synthesis. Firstly, In(OAc)₃·6H₂O (1.752 g) and H₄bptc (0.495 g) were filled in a stainless steel milling jar containing three 10 mm diameter stainless steel balls. Secondly, several solvents (H₂O, DMF, CH₃CN, CH₃CN/DMF) were respectively added into well-mixed precursor materials. After that, the mixtures were ground for the required time at 40 Hz based on our previous experience (Li et al., 2016). Then, the products were washed with H₂O/EtOH (1:1, v/v) and acetone. Finally, the products were dried at 423 K under vacuum overnight. Table 1 summarizes the preparation conditions of **InOF-1** samples.

2.3. Characterization

Powder X-ray diffraction (PXRD) experiments were conducted on a Bruker D8 Advance X-ray diffractometer operating at 40 kV and 40 mA, using Cu-K_α radiation with a scan speed of 2°/min and a step size of 0.02° in 2θ. Scanning electron microscope (SEM) was performed on a Hitachi SU-70 instrument, which was performed on a sample powder previously dried and sputter-coated with a thin layer of gold. Thermogravimetric analysis (TGA) of the sample was carried out on a Netzsch STA 449F3 instrument heating from 303 to 873 K in nitrogen atmosphere at a rate of 10 K/min. N₂ isotherms were measured at 77 K on a Micromeritics ASAP 2460 instrument equipped with commercial

Table 1
Preparation conditions of **InOF-1** samples.

Sample	Solvent used	Amount of solvent (mL)	Grinding time (min)
A	–	–	20
B	H ₂ O	0.2	20
C	DMF/CH ₃ CN (1:1 v/v)	0.2	20
D	DMF	0.2	20
E	CH ₃ CN	0.2	20
F	CH ₃ CN	0.4	20
G	CH ₃ CN	0.6	20
H	CH ₃ CN	0.8	20
I	CH ₃ CN	0.4	10
J	CH ₃ CN	0.4	30
K	CH ₃ CN	0.4	40
L	CH ₃ CN	0.4	60

software for calculation and analysis. The pore textural properties were estimated using BET equation and the pore size distribution was calculated using density functional theory (DFT) method.

2.4. Water stability experiment

The sample was placed in a 20 mL vial with 15 mL deionized water to sit statically at room temperature for 12 h. The resulting product was isolated by centrifugation and washed with acetone followed by drying at 423 K. Then, the samples were analyzed using PXRD, surface area measurements and porosimetry analyzer.

2.5. Adsorption experiments

CO₂, CH₄ and N₂ adsorption experiments were performed on a 3Flex Surface Characterization Analyzer (Micromeritics, American) at 273, 288 and 298 K. Prior to measurement, 60–80 mg samples were degassed at 423 K for 8 h. The gas adsorption isotherm was obtained under pressure ranging from 0 to 100 kPa. Ultrahigh purity grade CO₂ (99.99%), CH₄ (99.99%) and N₂ (99.99%), were used for all adsorption measurements.

3. Results and discussion

3.1. Formation of **InOF-1**

3.1.1. Effect of solvent

Fig. 1 shows the PXRD patterns of the samples. The A–H samples

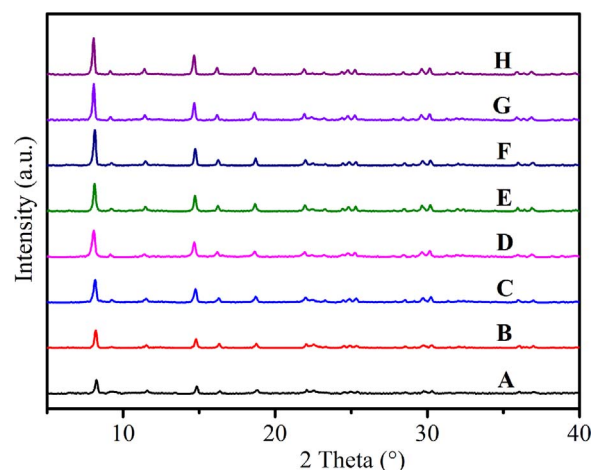


Fig. 1. PXRD patterns of **InOF-1** samples prepared for 20 min grinding with different types and amounts of solvents.

Download English Version:

<https://daneshyari.com/en/article/6467889>

Download Persian Version:

<https://daneshyari.com/article/6467889>

[Daneshyari.com](https://daneshyari.com)