Materials Characterization 136 (2018) 407–416

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

Structural transition from two-dimensional ZIF-L to three-dimensional ZIF-8 nanoparticles in aqueous room temperature synthesis with improved CO_2 adsorption

Imran Ullah Khan[a,b,c], Mohd Hafiz Dzarfan Othman[a,*], A.F. Ismail[a], N. Ismail[a], Juhana Jaafar[a], Haslenda Hashim[a], Mukhlis A. Rahman[a], Asim Jilani[a,d]

[a] Advanced Membrane Technology Research Centre (AMTEC), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[b] School of Chemical and Material Engineering (SCME), National University of Science and Technology (NUST), H-12 Islamabad, Pakistan
[c] Process System Engineering Centre (PROSPECT), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[d] Center of Nanotechnology, King Abdul-Aziz University, 21589 Jeddah, Saudi Arabia

ARTICLE INFO

Keywords:
Rapid synthesis
Particle size
Molar ratio
Transition
Basicity
Desorption

ABSTRACT

A new micron-sized leaf- two-dimensional (2D) structured zeolitic imidazolate framework (ZIF-L) and nano-sized ZIF-8 were successfully synthesised in aqueous basic solution at room temperature with the same molar ratio of reagents (Zn^{+2}/Hmim = 8). Both ZIFs have attracted tremendous research interest due to their wide applications including absorption, separation, and catalysis. This phase and morphology change could be tailored by changing the concentration of base-type additive triethylamine (TEA). Also, this morphology change from 2D (ZIF-L) to three-dimensional (3D) (ZIF-8) was observed by X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA), attenuated total reflectance infrared (ATR-IR) spectroscopy analysis, and surface area and pore textural properties using micromeritics gas adsorption analyser. The total amount of basic sites and carbon dioxide (CO_2) desorption capacity were also calculated using CO_2 temperature-programmed desorption (CO_2-TPD) technique. Furthermore, TEA/total mole ratio of 0.0006 was proved as transition loading between two phases. Also, the particle and crystal size of samples decreased with increasing TEA/total mole ratio. The smallest ZIF-L and ZIF-8 particles obtained were 1.6 μm and 177 nm, respectively that showed excellent thermal stability. The basicity and uptakes of CO_2 improved proportionally with TEA and followed this order: ZIF-8 > ZIF-L. This study provides some new insights into zeolitic imidazolate framework by controlling crystal growth and morphology.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are a new subclass of metal-organic frameworks (MOFs) and emerge as a new family of molecular sieves and porous structure. The highly diversified structures, tunable pore sizes, and versatile functionalities inspired many researchers to explore its different industrial applications such as CO_2 adsorption [1], catalysis [2], membrane fabrication for gas separation [3], and gas storage [4,5]. Common metal sites used for synthesis of ZIFs are Zn^{+2} and Co^{+2} and there are many types of imidazole-type linkers like imidazole (IM), 1-methylimidazole (mIM), 2-methylimidazole (Hmim), 1-ethylimidazole (eIM), and 2-nitroimidazole (nIM). The combination of different metal sites and imidazole ligands would result in different structures and properties of ZIFs [6]. Solvothermal method and microwave-assisted are the most versatile approaches and to the best of our knowledge, most types of MOFs can be synthesised through these methods [6,7,8]. Despite the maturity of the process, both approaches suffer from high energy requirement while utilising expensive organic solvent in highly diluted manner [9,10]. Contradictory, aqueous system synthesis is reported to provide economical, rapid, nano-sized, and higher yield of formation compared to solvothermal and microwave-assisted synthesis [9,11]. Up to date, only limited types of MOFs have been successfully synthesised in aqueous solution because most organic ligands are insoluble in water [12,13].

Among the MOFs, ZIF-L and ZIF-8 have been documented to be well compatible with aqueous system synthesis. Nonetheless, MOFs are well-developed porous compounds but ZIFs are still in their infancy, such as crystal growth and pore structure. Recently, many researchers have synthesised and characterised various types of ZIFs particles [2–4,13–32]. Liquid-phase diffusion in methanol process is used for the

---

* Corresponding author.
E-mail address: hafiz@petroleum.utm.my (M.H.D. Othman).

https://doi.org/10.1016/j.matchar.2018.01.003
Received 20 October 2017; Received in revised form 30 December 2017; Accepted 1 January 2018

production of ZIFs crystals [28,29] but it takes many days to produce it. Zhang et al. [33] identified that Co/Hmim molar ratio played an important and crucial role in the synthesis of ZIF-L-Co with leaf-like structure. They also concluded that lower concentration of reactants gave larger particle size and vice versa. Pan et al. [34] replaced the organic solvent with water during the synthesis of ZIF-8 at room temperature and the resultant ZIF-8 nanoparticles showed excellent thermal stability. However, the requirement of the high molar ratio of zinc salt and organic ligand (1:70) makes this process costly and hazardous. Despite the different approaches that have been used for tuning the crystal shape and morphology of ZIFs, far less effort has been employed to the economical, friendly, and fast synthesis of ZIFs for CO_2 adsorption.

ZIF-L and ZIF-8 have many similarities that provides a unique opportunity to investigate their crystal growth during the synthesis such as both have the same reagents, i.e., zinc salt and Hmim [22,31]. Also, similar CO_2 adsorption capacity makes them promising materials for purification of natural gas [4]. A 2D ZIF-L is made up of the same building blocks as ZIF-8 [28] and have been widely used in various separation processes as an adsorbent to remove hazardous wastes such as dyes, aromatics, arsenic, and heavy metals [35], gas detachment, heterogeneous catalysis, drug delivery, and sensors [36].

The objective of this work is to investigate the effect of base type additive (TEA) on the morphology of ZIFs and CO_2 adsorption performance. Besides, critical loading of TEA that was used for intermediate structure between ZIF-L and ZIF-8 was identified during the synthesis process. Also, its influence on their CO_2 adsorption capacity would be reported and discussed here. The temperature programmed desorption (TPD) is the best technique to calculate basicity and CO_2 adsorption/desorption behaviour of porous materials [37]. To the best of our knowledge, the presented CO_2-TPD results for ZIF-L and ZIF-8 are the first experimental evidence of basicity calculations.

2. Experimental Section

2.1. Materials

The materials used to synthesise ZIF-L were zinc nitrate hexahydrate (Zn $(NO_3)_2 \cdot 6H_2O$, 99% purity), an organic linker, 2-methylimidazole (Hmim, 99% purity), and base-type additive triethylamine (TEA, 99.5% purity) to change its structure. All chemicals were purchased from Sigma-Aldrich and used without any further purification.

2.2. Synthesis of ZIF-L and ZIF-8

The synthesis of ZIF-L was described in literature [1,28] while some changes were done in this work to enhance the yield, decrease the chemical usage and improved desorption capacity. Briefly, the key synthesis parameters were the ratio of Hmim/zinc ion molar ratio (e.g., 8) and TEA/total mole ratio of the reactants. Approximately 2.95 g (1.98 mmol) of Zn $(NO_3)_2 \cdot 6H_2O$ and 6.5 g (15.83 mmol) of Hmim were dissolved in 200 mL of deionised water. Various amounts of TEA were added to Hmim solution as the deprotonation agent as shown in Table 1. Then, the aqueous solution of Zn $(NO_3)_2 \cdot 6H_2O$ was added into the aqueous solution of Hmim with stirring. The mixture was stirred at room temperature at various time intervals. The product was obtained by repeated centrifugation (10,000 rpm for 10 min), washed by deionised water to remove residual chemicals, and then dried in an oven at 60 °C for 12 h. The products ZIF-L (A0, A1, A2, and A3) were obtained at TEA/total mole ratios of 0, 0.0002, 0.0003, and 0.0005, respectively. Also, A4 and A5 represented transition stage. Meanwhile, ZIF-8 samples (A6 and A7) were also obtained when the TEA/total mole ratios of the reactants were increased up to 0.001 and 0.002, respectively. The yield of the products was measured using Eq. (1) and reported in Table 1.

Table 1
Different TEA/total mole ratio, yield and time for the synthesis of ZIL-L and ZIF-8.

Sample	TEA/total mole ratio	TEA volume (mL)	Duration of synthesis (min)	Yield (%)	Product
A0	0	0	240 [23]	90	ZIF-L
A1	0.0002	0.5	60	80	ZIF-L
A2	0.0003	1	60	90	ZIF-L
A3	0.0005	1.5	60	90	ZIF-L
A4	0.0006	2	60	80	Transition phase
A5	0.0009	3	60	80	Transition phase
A6	0.001	4	60	80	ZIF-8
A7	0.002	5	60	90	ZIF-8

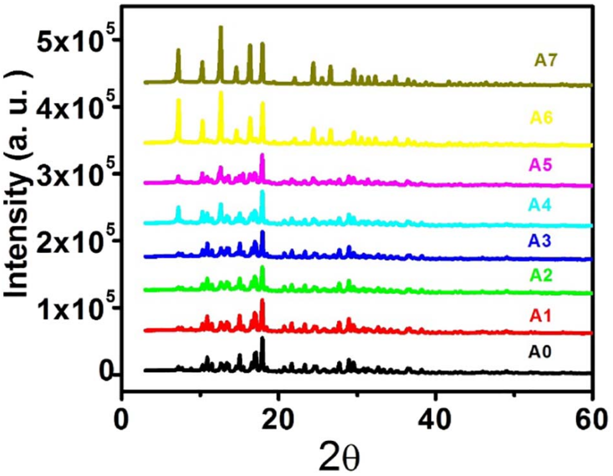

Fig. 1. XRD pattern of the synthesised samples with different TEA/total mole ratios: A0 (0), A1 (0.0002), A2 (0.0003), A3 (0.0005), A4 (0.0006), A5 (0.0009), A6 (0.001), and A7 (0.002).

$$\text{Yield}\ (\%) = \frac{\text{ZIF} - \text{L or ZIF} - 8\ (\text{obtained})}{\text{ZIF} - \text{L or ZIF} - 8(\text{theoretical})} \times 100 \tag{1}$$

2.3. Characterization

2.3.1. Physicochemical Analysis

The field emission scanning electron microscopy (FESEM) images were taken using a Hitachi SU 8020 microscope. The X-ray diffraction (XRD) analysis was performed on a Rigaku smart lab diffractometer using CuKα radiation at 40 KV and 30 mA in the 2θ range of 3°–100°. The attenuated total reflectance infrared (ATR−IR) spectroscopy analysis was performed using IRTracer-100 (Single Reflection Diamond for Spectrum Two, Shimadzu) to observe the functional groups of the synthesised ZIF-8 samples. The thermogravimetric analysis (TGA, Q 500, TA Instrument, USA) was used to check the thermal stability of the synthesised samples at different TEA loadings. TGA recorded the weight changes of the sample when heated from 30 to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The flow rate of N_2 was used up to 40 mL/min. The specific BET surface area, pores textural properties of the synthesised samples, and nitrogen adsorption-desorption isotherms were measured using Micromeritics gas adsorption analyser ASAP 2010 instrument equipped with a commercial software for calculation and analysis.

2.3.2. CO_2 Temperature Programmed Desorption (CO_2-TPD)

CO_2 temperature-programmed desorption tests were conducted to determine the total amount of basic sites on the surface of the ZIF-L and ZIF-8 samples. Experiments were carried out on Auto Chem II 2920