



Processing of thermally stable 3D hierarchical ZIF-8@ZnO structures and their CO₂ adsorption studies



Minju Thomas^{a,b}, Balagopal N. Nair^{c,d,**}, G.M. Anilkumar^c, A. Peer Mohamed^a,
K.G.K. Warriar^a, U.S. Hareesh^{a,b,*}

^a Material Science and Technology Division, National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram 695019, India

^b Academy of Scientific and Innovative Research (AcSIR), New Delhi, India

^c R&D Center, Noritake Co., Limited, 300 Higashiyama, Miyoshi, Aichi 470-0293, Japan

^d Nanochemistry Research Institute, Department of Chemistry, Curtin University, GPO Box U1987, Perth WA6845, Australia

ARTICLE INFO

Article history:

Received 14 October 2015

Received in revised form 7 January 2016

Accepted 31 January 2016

Available online 3 February 2016

Keywords:

Zeoliticimidazolate framework-8

Carbondioxide adsorption

Solvothermal reaction

ABSTRACT

Core-shell hybrid structures of ZnO-Zeolitic Imidazolate Framework-8 (ZIF@ZnO) were obtained by the solvothermal treatment of ZnO hierarchical structures having an average cluster size of $\sim 3 \mu\text{m}$ and surface area of $\sim 19 \text{m}^2/\text{g}$. The surface area and pore volume of these supported structures could be tailored as a function of reaction time and temperature. Solvothermal treatment of ZnO structures in the presence of imidazole at 95 °C for 24 h induced extremely large surface area of $733 \text{m}^2/\text{g}$ for the ZIF@ZnO samples. Samples thus obtained demonstrated a CO₂ adsorption capacity of 0.34 mmol/g at 25 °C compared to the value of 0.052 mmol/g measured for the ZnO structures. More significantly, the ZnO core helped the ZIF-8 surface fractal assemblies to significantly improve the thermal stability and retain their near spherical shapes allowing better handling in any practical adsorption application. The results validate that surface conversion of ZnO microstructures to ZIF-8 could be an efficient pathway towards the development of ZIF based supported adsorbents for CO₂ separation.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Zeoliticimidazolate frameworks (ZIF) are topological isomorphs of zeolites by virtue of the similarity in the metal-imidazole-metal angle of 145° with that of Si-O-Si angle [1,2]. ZIFs also possess extremely good chemical and thermal stability [3–6] coupled with high surface area values. These desirable attributes of ZIF have recently attracted widespread interest and hence are being explored for a variety of applications ranging from molecular separation to catalysis [7–10]. One of the major applications of ZIF-8 is the separation of carbon dioxide (CO₂) from flue gas streams to reduce carbon dioxide emissions to the atmosphere. Although, several materials are being investigated for this purpose [11–15] ZIFs, a typical member of Metal Organic Framework (MOF) family

is considered as a candidate material for low temperature separation applications [16,17].

Conventional methods of ZIF-8 synthesis employ solvothermal treatment of metallic zinc precursors in the presence of imidazole [3,18,19]. In addition, solvent free techniques like mechanochemical synthesis [20–22] were also employed for ZIF preparation. More recently, the use of metal oxides and hydroxides in place of metal salts enabled the formation of ZIF-8 as a surface layer of few nanometers thickness [23]. Alternatively, melting of low melting point ligands during the physical mixing with oxides/hydroxides present as salt offer solvent free method of ZIF-8 synthesis [24].

Functional materials consisting of ZIF-8 based hetero-structures are anticipated to impart significant advantages by virtue of the synergistic effects [25,26]. Incorporation of carbon nanotubes (CNT) into ZIF-8 was shown to improve the pore characteristics and the nanocomposites thus obtained showed enhanced carbon dioxide (CO₂) adsorption characteristics [27]. Fe₃O₄@ZIF-8 magnetic core-shell microspheres demonstrated enhanced catalytic activity for the Knoevenagel condensation reaction of ethyl cyanoacetate and benzaldehyde [28]. The insitu growth of ZIF on polyurethane fibers, derived by electrospinning, was reported for fabricating air purifying clothes by virtue of their high surface area and CO₂ capture [29]. Synthesis of highly stable

* Corresponding author at: Material Science and Technology Division, National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram 695019, India. Fax: +91 471 2491712.

** Corresponding author at: R&D Center, Noritake Co., Limited, 300 Higashiyama, Miyoshi, Aichi 470-0293, Japan. Fax: +81 561 344997.

E-mail addresses: bnair@n.noritake.co.jp (B.N. Nair), hareesh@niist.res.in (U.S. Hareesh).

ZIF-8 membrane on a macroporous alumina tube resulted in the development of a good molecular sieve of H_2 over CO_2 and CH_4 [30]. Although several reports on processing of ZIF based adsorbents have been published [31], the major issue that has limited the practical viability of ZIF is the absence of strategies that develop supported ZIF adsorbents. In fact, this concern is also highlighted in recent reviews on the applications of MOFs and ZIFs necessitating the development of supported structures for wide spread practical applications in the field of adsorption, catalysis and membrane based separation [32,33]. This is particularly important considering the fact that compaction processing of MOFs to monoliths often resulted in considerable reduction of surface area and loss of crystal structure [34]. It is therefore desirable to transform surface layers of self-supported aggregates of ZnO to ZIF enabling the development of asymmetric structures with controlled porosity on the transformed layer. The properties of membranes and adsorbents could be further improved by having a surface fractal structure with superior interface area between the solid surface and gas molecules.

The present work therefore explores the feasibility of converting porous aggregates of ZnO with relatively poor surface area into 3D hierarchical structures of extremely high surface area. Such ZIF@ZnO core shell structures are then demonstrated to show enhanced CO_2 adsorption characteristics compared to the precursor ZnO structures, while retaining the near spherical shape and uniform particle size characteristics. Improved thermal stability of the hybrid structures compared to pure ZIF-8 was another added advantage. It is shown that, the process route reported in this paper allows the development of stable and supported adsorbents of ZIF-8@ZnO.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Sodium hydroxide (97%, Merck, India), Zinc nitrate hexahydrate (96% Merck, India), 2-methyl imidazole (Sigma Aldrich, India), Methanol (Merck, India) were the chemicals used.

2.1.2. Synthesis of ZnO hierarchical structures

Aqueous solutions of Sodium hydroxide and Zinc nitrate hexahydrate (96%, Merck, India) in the molar ratio of 25:1 were mixed under constant magnetic stirring for two hours at room temperature. The suspension thus formed was further refluxed at $100^\circ C$ for one hour. The formed precipitate was filtered, washed five times with distilled water and dried in an air oven at $70^\circ C$.

2.1.3. ZIF-8/ZnO (ZIF@ZnO) hybrid structures

1 g of as prepared ZnO aggregates was dispersed in 30 mL methanol (Merck India). A solution of 2 g 2-methylimidazole (Sigma-Aldrich, India) in 220 mL methanol (1:2 ratio) was added to the ZnO dispersion and the mixture was subjected to solvothermal treatment in a Teflon vessel for 24 h at $65^\circ C$ (sample denoted as ZIF@ZnO65). The precipitate was further washed three times with methanol and dried in a vacuum oven at $40^\circ C$ for 24 h. The influence of reaction time on the structure of ZIF@ZnO formed was evaluated at various synthesis durations of 6, 12, 24, 48 and 96 h at the synthesis temperature of $65^\circ C$. The temperature dependence of the formation of ZIF-8 was examined by varying the synthesis temperature from $65^\circ C$ to $75^\circ C$ and $95^\circ C$ (samples denoted as ZIF@ZnO65, ZIF@ZnO75, and ZIF@ZnO95 respectively). The synthesis duration was fixed as 24 h in all the above three cases. For comparison of porous structure, we have also prepared unsupported ZIF-8 as reported elsewhere [18]. For this, a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (2.933 g) in 200 mL methanol was mixed with a

solution of 2-methylimidazole (HmIm) (6.489 g) in 200 mL of methanol under stirring at room temperature. After 1 h the formed particles were collected and washed with methanol and dried in a vacuum oven at $40^\circ C$ for 24 h.

2.2. Material characterization

CO_2 adsorption studies were performed on a BEL (Belsorpmax, BEL JAPAN INC) gas analyser. ZnO porous aggregates and the ZIF@ZnO hybrid structures were characterized by XRD for phase identification (PW1710 Philips, The Netherlands). Surface area and nitrogen adsorption–desorption measurements were performed using the previously described instrument (BEL) and surface area analyser (Micromeritics Gemini, USA). Thermo gravimetric analysis (TGA) was performed using a TGA apparatus (PerkinElmer STA1000 TGA) in the temperature range of 30 – $800^\circ C$ at a heating rate of $5^\circ C \text{ min}^{-1}$. TGA was also used to estimate the CO_2 adsorption capacity by the gravimetric method. Samples were first heated to $150^\circ C$ and CO_2 adsorption measurements were carried out after cooling to $50^\circ C$. A CO_2 gas flow of 30 mL/min was maintained throughout the adsorption duration. Morphological features of samples prepared were obtained by scanning electron microscopic imaging (SEM, Carl Zeiss, Germany). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM, Tecnai G2, FEI, The Netherlands, operated at 300 kV) images were also recorded for obtaining the finer details of the microstructures. The FTIR spectra were recorded on powders using Bruker αE FT-IR spectrometer.

3. Results and discussion

3.1. Phase analysis

The phase composition and crystallinity of “as prepared” ZnO aggregates, ZIF@ZnO65, ZIF@ZnO75 and ZIF@ZnO95 hybrid structures are provided in the XRD patterns presented in Fig. 1. The presence of (100), (002) and (101) peaks at 2 theta values between 30 and 40 confirmed the presence of hexagonal wurtzite phase in the ZnO aggregates (JCPDS 36–1451). The ZIF@ZnO hybrid structures provided peaks corresponding to (011), (002), (112), (022), (013), (222), (114), (233), (134) and (044) planes of ZIF-8 in addition to the peaks for ZnO. The XRD patterns of the samples obtained after solvothermal treatment of 65, 75 and $95^\circ C$ had one to one peak matching. The XRD patterns of samples obtained at different time intervals of solvothermal synthesis (at $65^\circ C$) are provided in Fig. S1.

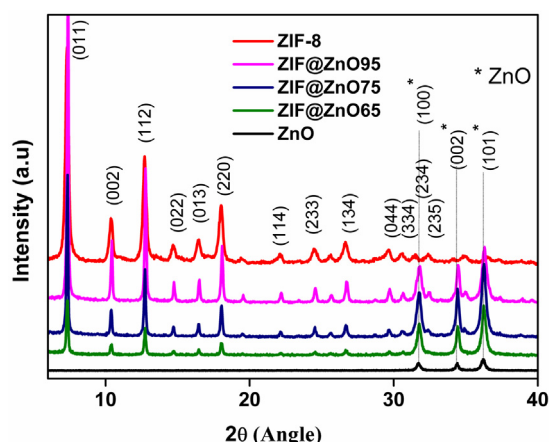


Fig. 1. XRD patterns of ZnO porous aggregates and ZIF@ZnO samples made at different reaction temperatures, in comparison with pure ZIF-8.

Download English Version:

<https://daneshyari.com/en/article/221627>

Download Persian Version:

<https://daneshyari.com/article/221627>

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