



Gas sorption and transition-metal cation separation with a thienothiophene based zirconium metal–organic framework



Mostakim SK^a, Maciej Grzywa^b, Dirk Volkmer^b, Shyam Biswas^{a,*}

^a Department of Chemistry, Indian Institute of Technology Guwahati, 781039 Assam, India

^b Institute of Physics, Chair of Solid State Science, Augsburg University, Universitätsstrasse 1, D-86135 Augsburg, Germany

ARTICLE INFO

Article history:

Received 21 May 2015

Received in revised form

14 September 2015

Accepted 29 September 2015

Available online 8 October 2015

Keywords:

Zirconium-based metal–organic framework

Thienothiophene ligand

Modulated synthesis

Gas adsorption

Transition-metal cation separation

ABSTRACT

The modulated synthesis of the thienothiophene based zirconium metal–organic framework (MOF) material having formula $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{DMTDC})_6] \cdot 4.8\text{DMF} \cdot 10\text{H}_2\text{O}$ (**1**) (H_2DMTDC = 3,4-dimethylthieno [2,3-*b*]thiophene-2,5-dicarboxylic acid; DMF = *N,N'*-dimethylformamide) was carried out by heating a mixture of ZrCl_4 , H_2DMTDC linker and benzoic acid (used as a modulator) with a molar ratio of 1:1:30 in DMF at 150 °C for 24 h. Systematic investigations have been performed in order to realize the effect of ZrCl_4 /benzoic acid molar ratio on the crystallinity of the material. The activation (i.e., the removal of the guest solvent molecules from the pores) of as-synthesized compound was achieved by stirring it with methanol and subsequently heating under vacuum. A combination of X-ray diffraction (XRD), Fourier transform infrared (FT-IR), thermogravimetric (TG) and elemental analysis was used to examine the phase purity of the as-synthesized and thermally activated **1**. The material displays high thermal stability up to 310 °C in an air atmosphere. As revealed from the XRD measurements, the compound retains its crystallinity when treated with water, acetic acid and 1 M HCl solutions. The N_2 and CO_2 sorption analyses suggest that the material possesses remarkably high microporosity ($S_{\text{BET}} = 1236 \text{ m}^2 \text{ g}^{-1}$; CO_2 uptake = 3.5 mmol g^{-1} at 1 bar and 0 °C). The compound also shows selective adsorption behavior for Cu^{2+} over Co^{2+} and Ni^{2+} ions.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Research activity on metal–organic frameworks (MOFs) [1–5] has aroused great attention in recent years. MOFs are a comparatively new type of highly crystalline and nanoporous materials. They have shown potential applications in a large variety of areas such as gas storage [6–8], chemical separation [9], catalysis [10,11] and chemical sensing [12]. They are composed of inorganic building units that are cross-linked by polytopic organic linkers. A wide variety of porous MOF structures possessing different types of pore systems (channels, cages, etc.) have been reported till date owing to the availability of a huge combination of metal ions and organic linker molecules. In sharp contrast to conventional porous adsorbents such as zeolites, mesoporous silicas, carbon nanotubes and activated carbons, the pore surface characteristics of MOFs can be changed in a systematic way by grafting various functional groups (with different sizes, polarities, acidities, hydrophilicities, etc.) to the organic linker [13–16]. The attachment of functional groups to the organic moiety can be attained by (i) using pre-

functionalized [13–18] organic linkers during synthesis or (ii) employing post-synthetic modification strategy [19]. The introduction of functional groups into the MOF structures has been demonstrated to influence their sorption/separation [20,21] behavior as well as thermal and chemical stability [22,23]. Moreover, the MOFs functionalized with desired functional groups can be applied for a target application.

Sulfur (in the form of $-\text{SO}_3\text{H}$, $-\text{SO}_2-$, $-\text{SH}$ or thiophene) containing MOFs show distinct advantages which is dependent on the nature of functional group. For example, MOFs bearing sulfonic acid groups have shown potential for proton conduction [24–28], Brønsted acid catalysis [29–31] and CO_2/CH_4 separation [15]. Sulfone-functionalized MOFs have been demonstrated to accomplish not only CO_2/CH_4 separation [32–34] but also shape-selective adsorption [35] of linear and branched alkanes. MOFs containing thiol groups have exhibited prospective for effective mercury sorption [36] and grafting of Pd(II) ions [37] for Suzuki–Miyaura coupling reactions. The potential of thienothiophene based MOFs for mercury vapor sorption [38] as well as separation [39] of transition-metal ions has been documented. However, the number of reports describing the utilities of sulfur-tagged (especially thienothiophene based) MOFs is still relatively less. It should be noted that selective transition-metal cation sorption behavior has

* Corresponding author. Fax: +91 3612582349.

E-mail address: sbiswas@iitg.ernet.in (S. Biswas).

previously been observed in a zinc MOF containing uncoordinated carboxyl groups [40], in addition to a thienothiophene-based [39] zinc MOF.

The development of MOF compounds bearing high physicochemical stability (air, water, thermal, acid–base, etc.) is a challenging goal for their applications in industry. The low physicochemical stabilities of several well-known MOF materials [41–45] have made them unsuitable for industrial applications, instead of their potential performances [8,46–50] for adsorption and separation. One strategy to synthesize MOF compounds with relatively higher physicochemical stabilities is to use transition-metal ions possessing higher oxidation states (e.g. Ti(IV) [51], Zr(IV) [52], etc.). The MOF material UiO-66 (UiO=University of Oslo) [52], which incorporates Zr(IV) ions and 1,4-benzenedicarboxylate linkers, has recently fascinated researchers with its high thermal and chemical stability as well as potential capabilities for CO₂/CH₄ gas separation [53,54]. The three-dimensional cubic framework of this compound is composed of a centric octahedral cage, which is linked with eight corner tetrahedral cages via trigonal windows. The presented thienothiophene based Zr(IV) MOF material (compound **1**) bears the same framework topology as the UiO-66 compound.

Modulators or additives have been employed for tuning the size and morphology of MOF crystals [55]. They have been used during the solvothermal synthesis of many Zr(IV) based MOF materials having UiO-66 structural topology in order to enhance their crystallinity [15,16,23,33,38,56–80]. Typically, modulators include monocarboxylic acids (e.g. benzoic acid, formic acid, acetic acid, trifluoroacetic acid, etc.), whereas additives involve water or hydrochloric acid. In this work, the thienothiophene based Zr(IV) MOF (compound **1**) has been successfully prepared in *N,N*-dimethylformamide (DMF) by using ZrCl₄ as the Zr(IV) source and benzoic acid as the modulator. The influence of ZrCl₄/benzoic acid molar ratio on the crystallinity of compound **1** has been investigated in a systematic fashion. Herein, we wish to report on the modulated synthesis, thorough characterization, thermal and chemical stability as well as gas sorption and transition-metal cation separation properties of compound **1**. During the preparation of the manuscript, the stability and mercury vapor sorption behavior of this MOF have been reported [38]. However, the synthesis and activation routes of our compound are different. Moreover, we have studied transition-metal cation separation properties of this material.

2. Experimental

2.1. Materials and general methods

The H₂DMTDC ligand was synthesized as described previously [81]. All other starting materials were of reagent grade and used as received from the commercial suppliers. Fourier transform infrared (FT-IR) spectra were recorded in the region of 4000–440 cm⁻¹ with a Perkin Elmer Spectrum Two FT-IR spectrometer. The following indications are used to characterize absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh) and broad (br). Elemental analyses (C, H, N) were carried out on a Thermo Scientific Flash 2000 CHNS-O analyzer equipped with a TCD detector. Thermogravimetric analyses (TGA) were performed with a Netzsch STA-409CD thermal analyzer in a temperature range of 25–600 °C under air atmosphere at a heating rate of 4 °C min⁻¹. Ambient temperature X-Ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser X-ray diffractometer (30 kV, 10 mA) or a Seifert XRD 3003 TT diffractometer (40 kV, 40 mA) equipped with a Meteor 1D detector and fixed divergence slits (0.5 mm), using Cu-Kα (λ = 1.5406 Å) radiation. Energy dispersive

X-ray (EDX) analyses were carried out with Hitachi S3400N and Zeiss Supra 55VP SEM-EDX (SEM = scanning electron microscope) instrument. Inductively coupled plasma-optical emission spectrometry (ICP-OES) experiments were performed with a Perkin Elmer Optima 5300 DV instrument. Le Bail fit of the XRD pattern of activated **1** was performed by using the Jana2006 program [82]. The nitrogen sorption isotherms were recorded using a Quantachrome Autosorb iQ-MP gas sorption analyzer at –196 °C. The carbon dioxide adsorption measurements were performed using a Belsorp Max instrument combined with a BELCryo system. Prior to the sorption experiments, the compound was degassed at 100 °C under vacuum for 24 h. It was degassed at 100 °C under vacuum for 2 h between the CO₂ sorption measurements.

The modeling of the crystal structure of compound **1** was carried out by utilizing the Materials Studio V7.0 (Accelrys Software, Inc., San Diego, CA, USA) software package. The constructed model with an artificially symmetrized version of the organic linker was refined using universal force field (UFF) molecular mechanics geometry optimization (Forcite module in Materials Studio). The constructed structure of the H₂DMTDC linker (*cf.* Fig. 2) was approximately a symmetrical overlay (without the two carboxylate groups) of the two positions of the actual linker.

2.2. Synthesis

Synthesis of [Zr₆O₄(OH)₄(C₁₀H₆O₄S₂)₆]·4.8DMF·10H₂O (as-synthesized **1**): a mixture of ZrCl₄ (100 mg, 0.43 mmol), H₂DMTDC (110 mg, 0.43 mmol) and benzoic acid (1.57 g, 12.87 mmol) in 3 mL of DMF was heated in a sealed glass tube at 150 °C for 24 h using a block heater. After spontaneous cooling to room temperature, the white precipitate was collected by filtration, washed with acetone and dried in air. The yield was 117 mg (0.04 mmol, 60%) based on the Zr salt. Anal. calcd for C_{74.4}H_{93.6}N_{4.8}O_{46.8}S₁₂Zr₆: C, 32.66 H, 3.45 N, 2.46. Found: C, 32.32 H, 3.28 N, 2.37%. FT-IR (KBr, cm⁻¹): 3427 (br), 2959 (w), 2930 (w), 1661 (m), 1577 (m), 1499 (s), 1387 (vs), 1161 (m), 1119 (w), 1027 (m), 781 (m), 724 (m), 661 (s), 618 (m), and 492 (m).

2.3. Activation of the as-synthesized compound

The as-synthesized **1** was activated in two steps. In the first step, the as-synthesized compound (0.2 g) was stirred in methanol (30 mL) at room temperature for 24 h. In the second step, the white compound was collected by filtration and heated at 100 °C under dynamic vacuum for 24 h.

3. Results and discussion

3.1. Synthesis and activation

The optimized synthesis conditions for compound **1** were determined by performing solvothermal reactions of the H₂DMTDC linker with different Zr(IV) salts (ZrCl₄, ZrO(NO₃)₂·xH₂O or ZrOCl₂·8H₂O) in polar amide solvents like DMF, *N,N*-diethylformamide (DEF) and *N,N*-dimethylacetamide (DMA) in presence of various modulators or additives (H₂O, conc. HCl, benzoic acid, formic acid or acetic acid). As described in the Supporting information, solvothermal reactions were carried out in all possible combinations of the Zr(IV) salts, modulators/additives and amide solvents. When ZrCl₄ was used as the metal source and benzoic acid as the modulator in DMF, compound **1** was obtained with very high crystallinity. The ZrCl₄/H₂DMTDC/benzoic acid molar ratio used for achieving the optimum crystallinity was 1:1:30. The reactions in all other combinations of reactants did not yield any crystalline compound. The influence of ZrCl₄/benzoic acid molar

Download English Version:

<https://daneshyari.com/en/article/1329459>

Download Persian Version:

<https://daneshyari.com/article/1329459>

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