Inorganic Chemistry Communications 46 (2014) 9–12

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Carbon dioxide selective adsorption within a highly stable mixed-ligand Zeolitic Imidazolate Framework

Lin Huang, Ming Xue *, Qingshan Song, Siru Chen, Ying Pan, Shilun Qiu *

State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University, Changchun 130012, China

ARTICLE INFO

Article history:
Received 14 March 2014
Accepted 25 April 2014
Available online 6 May 2014

Keywords:
Zeolitic Imidazolate Frameworks
Mixed ligand
Stability
Selective adsorption
Carbon dioxide

ABSTRACT

A new mixed-ligand Zeolitic Imidazolate Framework $Zn_4(2\text{-mbIm})_3(\text{bIm})_5\cdot4H_2O$ (named JUC-160, 2-mbIm = 2-methylbenzimidazole, bIm = benzimidazole and JUC = Jilin University China) was synthesized with a solvothermal reaction of $Zn(NO_3)_2\cdot6H_2O$, bIm and 2-mbIm in DMF solution at 180 °C. Topological analysis indicated that JUC-160 has a zeolite GIS (gismondine) topology. Study of the gas adsorption and thermal and chemical stability of JUC-160 demonstrated its selective adsorption property for carbon dioxide, high thermal stability, and remarkable chemical resistance to boiling alkaline water and organic solvent for up to one week.

Zeolitic Imidazolate Frameworks (ZIFs) are porous crystalline materials with tetrahedral networks that resemble those of zeolites; transition metals such as zinc and cobalt replace the sites of tetrahedrally coordinated silicon atoms, and Im (imidazolate) links replace oxygen bridges [1–4]. The exceptional thermal and chemical stabilities of many ZIFs have made them suitable for many applications, such as gas separation [5–9], sensors [10], catalysts [11] and other potential applications [12,13]. To date, over 100 ZIF structures with several interesting zeolitic topologies (e.g. GIS, LTA, ANA, GME, SOD, RHO, DFT, MER, POZ, MOZ etc.) have been reported [14,15]. Among these, only 16 form single-phase materials that are synthesized from mixed linkers. The mixed-ligand ZIFs provide a greater level of complexity in their pore composition and structure, and this affects the selectivity and multifunctionality of the pores.

Overwhelming scientific evidence shows that CO_2 emissions from fossil fuels have caused climate change, and a dramatic selective removal of CO_2 from gaseous mixtures is of paramount importance for the purification of the atmosphere [16,17]. Effective systems for CO_2 removal must combine high selectivity and capacity with minimal energetic input to liberate the captured CO_2. Amine solutions, zeolites, porous carbon and MOFs are used to capture CO_2, but all fall short in one or more of these categories [18–22]. ZIF materials have been widely studied for their potential use as adsorbents for carbon dioxide capture and separation [23,24]. Strategies that have been developed for designing high-efficiency CO_2-selective ZIFs include using mixed ligands and tailoring suibable pore sizes. For instance, Yaghi et al. reported a series mixed-ligand ZIFs with GME (gmelinite) topology [25]. In this series of ZIFs, every tetrahedral Zn atom was connected to two nIm (2-nitroimidazole) ligands and two other substituted Im ligands. By incrementally varying the bulk of the substituted Im ligand, the pore aperture of these ZIFs was varied degressively from 13.1 Å (ZIF-70) to 3.8 Å (ZIF-78), and showed that ZIF-78 had the best CO_2 sorption selectivity for air or methane.

Inspired by that result, we examined a new mixed-ligand ZIF with GIS topology, $Zn_4(2\text{-mbIm})_3(\text{bIm})_5\cdot4H_2O$ (JUC-160). This is the first time that the big bulky 2-mbIm ligand has been observed to construct the ZIF structure. Pure JUC-160 was synthesized from a solvothermal reaction of $Zn(NO_3)_2\cdot6H_2O$, bIm and 2-mbIm in DMF (N,N-dimethylformamide) at 180 °C. It is worth noting that JUC-160 showed high thermal and chemical stability and CO_2-selective capture properties.

Single-crystal X-ray diffraction analysis revealed that JUC-160 crystallizes in an orthorhombic space group *Pnma* (no. 62) [26–28]. There were two kinds of coordination environments of the zinc atoms in JUC-160 (Fig. 1). Zn1 coordinates to two N atoms (N1A, N5) from 2-mbIm ligands and two other N atoms (N2A, N7A) from bIm ligands. Zn2 coordinates to one N atom (N4) from the 2-mbIm ligand and three other N atoms from bIm ligands. The Zn–N distances and the N–Zn–N angles ranged from 1.966(10)–2.004(9) Å and 102.1(4)–119.0(4) Å (Table S2).

The topological analysis indicated that JUC-160 has a uninodal network, in which two crystallographically unique zinc atoms, Zn1 and Zn2, are in the same short Schläfli symbol of $[4^6\cdot8^4]$. The framework can also be described as 4- and 8-ring SBUs (Fig. S1). The Second Building Units (SUBs) parallel to the (100) plane were linked with each other

---

* Corresponding authors. Tel./fax: +86 431 85168589.
E-mail addresses: xueming@jlu.edu.cn (M. Xue), sqiu@jlu.edu.cn (S. Qiu).

http://dx.doi.org/10.1016/j.inoche.2014.04.026
1387-7003/

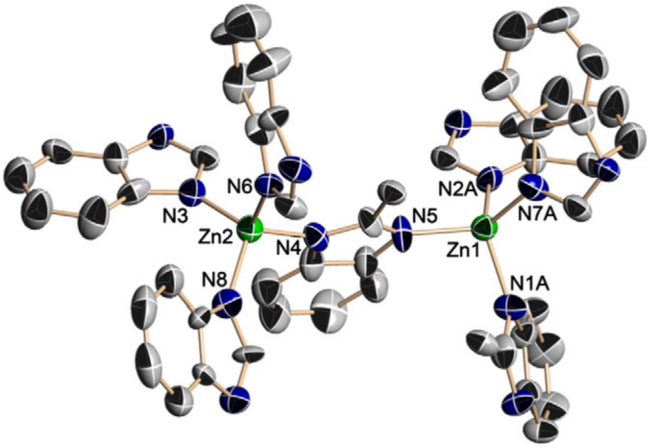

Fig. 1. Coordination environment of Zn^{2+} ions in JUC-160. (Hydrogen atoms have been omitted for clarity.)

up and down in the [100] direction, giving rise to a three-dimensional network by completing the four-way connection of the nodes (Fig. 2a). This is exactly the network related to zeolite GIS topology (Fig. 2b) [29–31]. With the topology of natural zeolite GIS, JUC-160 consisted of identical cages (5.8 Å) of 8-ring openings in the structure. These cages intersected each other to form a one-dimensional channel (1.8 Å × 4.2 Å) in the [100] direction. The water guest molecule could be detected with a single crystal X-ray determination in the cage and established by thermogravimetric analysis (TGA) [32]. The effective free volume of JUC-160 was calculated by PLATON analysis as being 18.9% [33].

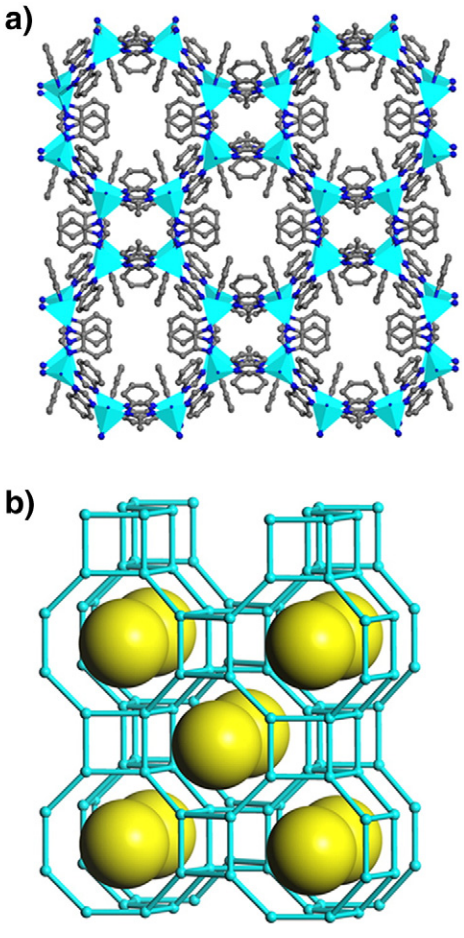

Fig. 2. (a) View of the 3D framework of JUC-160 with ZnN_4 tetrahedra along the [100] direction; (b) the GIS topology and the cage (yellow ball) of JUC-160. Color code: Zn, cyan; N, blue; C, gray. (Hydrogen atoms and guest molecules have been omitted for clarity.)

It is worth noting that pure JUC-160 has to be synthesized at 180 °C solvothermally (Scheme S1). When the reaction was performed at 100 °C and 140 °C, pure ZIF-7 or a mixture of JUC-160 and ZIF-7 phases was obtained, respectively (Fig. S3). More interestingly, ZIF-7 crystals could be turned into JUC-160 crystals in the equimolar 2-mbIm DMF solution at 180 °C, exhibiting the crystal-to-crystal transformation phenomenon (Fig. S4).

To verify the thermal stability of JUC-160, an in situ Powder X-Ray Diffraction (PXRD) experiment was performed. As shown in Fig. S5, the positions and intensities of the diffraction peaks only changed slightly and the structure was retained up to 500 °C, which is more stable than many other mixed-ligand ZIFs, such as ZIF-68 (390 °C) or ZIF-69 (400 °C) [23,25]. Furthermore, the chemical stability of JUC-160 was analyzed by suspending the powder sample for 7 days in benzene, water and even 8 M (mol L^{-1}) aqueous NaOH at 100 °C conditions that reflect the extreme operational parameters of typical industrial chemical processes. After such extensive treatments, JUC-160 maintained its fully crystalline integrity as confirmed by the sharp, unshifted diffraction lines in PXRD patterns (Fig. 3), demonstrating that JUC-160 has exceptional chemical stability.

Encouraged by the stability of JUC-160, nitrogen, oxygen, methane and carbon dioxide adsorption properties were investigated. The activated JUC-160 was heated to 200 °C under a vacuum for 24 h. It was found to be essentially non-porous to nitrogen at 77 K, and thus CO_2 was used to determine the BET surface area. As shown in Fig. 4, a significant increase was observed in the amount of CO_2 gas adsorbed by JUC-160, which is a typical Type-I sorption behavior. The BET surface area was calculated to be 210.6 $m^2\ g^{-1}$ according to the data at 195 K (Fig. S8). CO_2 uptake in ZIF materials is of great interest given the need for effective CO_2 capture and separation over gas mixtures. Hence, the CO_2, CH_4, O_2, and N_2 adsorption properties of JUC-160 were measured up to 1 bar at 273 K to examine the selective CO_2 adsorption. As shown in Fig. 5a, it is clear that JUC-160 has a higher capacity for CO_2 than for other gases. The CO_2 uptake is 24.51 $cm^3\ g^{-1}$ (1.09 $mmol \cdot g^{-1}$) at 273 K, which is comparable to other ZIF materials, such as ZIF-95 (0.9 $mmol \cdot g^{-1}$) and ZIF-8 (1.2 $mmol \cdot g^{-1}$). From the ratio of the initial slope, the separation ratios of CO_2/CH_4, CO_2/O_2 and CO_2/N_2, were calculated to be 5.6:1, 28:1 and 65:1 [25]. To the best of our knowledge, ZIF materials with such high CO_2 selectivity over gas mixtures have rarely

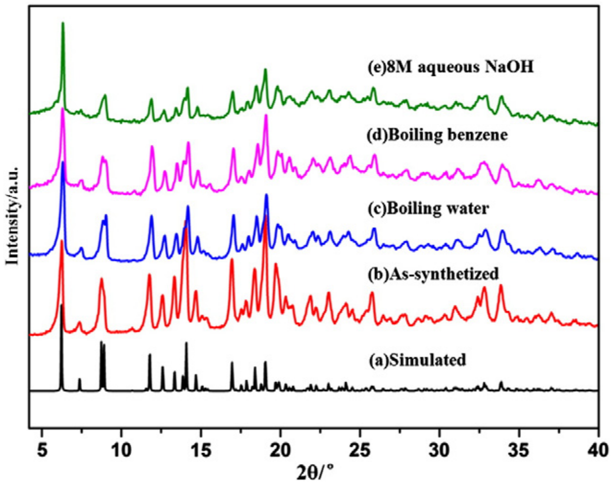

Fig. 3. The PXRD patterns for JUC-160 (a) simulated; (b) as-synthetized; (c) in water at 100 °C for up to 7 days; (d) in benzene at 100 °C for up to 7 days; and (e) in 8 M aqueous NaOH at 100 °C for up to 7 days.