Microporous and Mesoporous Materials 219 (2016) 190–198

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Dual-ligand zeolitic imidazolate framework crystals and oriented films derived from metastable mono-ligand ZIF-108

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ARTICLE INFO

Article history:
Received 14 June 2015
Received in revised form
31 July 2015
Accepted 10 August 2015
Available online 17 August 2015

Keywords:
Metal-organic frameworks
Zeolitic imidazolate frameworks
ZIF-108
Ligand exchange
ZIF-78 film

ABSTRACT

Post-synthetic ligand exchange of metal-organic frameworks (MOFs) is a feasible target-oriented method of preparing dual-ligand MOF crystals with fine-tuneable compositions and functions. Herein, a series of dual-ligand zeolitic imidazolate framework (ZIF) crystals with SOD, GME and GIS topologies were constructed by ligand exchange of the mono-ligand parent materials ZIF-108, Zn(2-nitroimidazolate)$_2$. In-depth investigations on the formation processes of the daughter ZIFs indicated that ligand exchange is a heterogeneous nucleation process using ZIF-108 as seeds. The metastability of ZIF-108 makes the ligand substitution of ZIF-108 require lower activation energy than homogeneous nucleation. This ligand exchange process paves the way for facile synthesis of dual-ligand and dual-metal-dual-ligand ZIF crystals with diverse porous networks. Based on these results, *c*-out-of-plane oriented dual-ligand ZIF-78 films were synthesized through the evolutionary selection in a van der Drift's type growth originated from randomly oriented ZIF-108 seed layer.

1. Introduction

Metal-organic frameworks (MOFs), a subset of crystalline porous materials, are coordination polymers established from metal ions or clusters bridged by organic ligands. These porous solids have aroused tremendous interest due to their capacity for gas adsorption and capture [1–3], membrane separation [4–16], catalysis [17], sensing [18] and drug delivery [19–21]. Substantial attention has been paid to target-oriented design and synthesis of functional MOF materials. Post-synthetic modification (PSM) methods are particularly attractive due to their diversity and ease of manipulation [22,23]. Aiming at “metal nodes and ligands” in MOFs [24–27] or “metal-organic polyhedra” (MOP) [28], post-synthetic metal substitution and ligand exchange is confirmed to be a feasible modification method with the purpose of fine-tuning of compositions and functions.

During the past few years, ligand exchange of MOFs has been extensively studied. A representative example, reported by Choe and co-workers, was stepwise ligand exchange in pillared paddle-wheel MOFs [29]. An intriguing 2D to 3D structural transformation was observed upon insertion of excess pillaring ligands. Similarly, pillared 3D MOF crystals with partial or complete substitution of the ligands in the alternating layers, reported by Lah et al., could be harvested by controlling the concentrations of pillaring ligands in the ligand exchange step [30]. Cohen et al. stated that the ligand exchange approach was even suitable for relatively robust and inert MOFs [31,32].

Zeolitic imidazolate frameworks (ZIFs), a sub-family of metal-organic frameworks, consist of transition metal ions and imidazolate ligands, forming 3D tetrahedral frameworks frequently with zeolite topologies [33,34]. Dual-ligand ZIF crystals commonly have different topologies, porosities and chemical properties with mono-ligand ones. Nair and co-workers demonstrate a direct synthetic strategy for dual-ligand ZIF materials, achieving tuneable pore size distribution and gas adsorption properties [35,36]. Ligand exchange is an attractive way to synthesize dual-ligand functional ZIF crystals that cannot be easily synthesized via conventional direct routes. Recently, Hupp and co-workers synthesized ZIF-8 derivatives with partial ligands exchanged by imidazole, and the crystals displayed a more open structure and remarkable catalytic

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http://dx.doi.org/10.1016/j.micromeso.2015.08.013
1387-1811/

properties [37]. Dual-ligand ZIF materials with excellent hydrothermal stability were also prepared using shell-ligand-exchange-reaction (SLER), as demonstrated in our previous work [38].

In the present study, ZIF-108 crystals consisting of Zn^{2+} ions and 2-nitroimidazolate (nim^-) in 1:2 stoichiometry and featuring SOD topology were employed as parent materials to synthesize dual-ligand ZIF materials with diverse porous networks by ligand exchange with imidazole (im), 5-nitrobenzimidazole (nbim), 5,6-dimethylbenzimidazole (dmbim), 2-ethylimidazole (eim) and 2-methylimidazole (mim) (Scheme 1). ZIF-108 was appropriate parent materials for ligand exchange owing to its metastability (Zn—N bond length of 2.007 Å for ZIF-108, compared to 1.987 Å for ZIF-8 and 1.984 Å for ZIF-7) resulting from the electron-withdrawing effect of the nitro-group [39]. An in-depth investigation was performed to explore the derivations of dual-ligand and dual-metal-dual-ligand ZIF crystals as well as oriented dual-ligand ZIF-78 films.

2. Experimental section

2.1. Materials

All chemicals and solvents were purchased from commercial suppliers and used without further purification, including $Zn(OAc)_2\cdot 2H_2O$ (99%, Sigma—Aldrich), $Zn(NO_3)_2\cdot 6H_2O$ (99%, Sigma—Aldrich), 2-nitroimidazole (nim, 98%, Tongchuang pharma Co., Ltd), 5-nitrobenzimidazole (nbim, 98%, Alfa-Aesar), imidazole (im, 99%, Sigma—Aldrich), 5,6-dimethylbenzimidazole (dmbim, 99%, Aldrich), 2-ethylimidazole (eim, 98%, Aldrich), 2-methylimidazole (mim, 99%, Aldrich), N, N-dimethylformamide (DMF, 99.5%, Bodi) and triethylamine (TEA, 99.0%, Tianjing Bodi chemical holding Co., Ltd).

A hierarchically ordered stainless-steel-mesh (HOSSM) was employed as the film support. The HOSSM support consists of top, intermediate and bottom layers with an average pore size of 6.5 μm, 2.0 μm and 6.5 μm, respectively.

2.2. Synthesis of the parent material ZIF-108

ZIF-108 nanocrystals were synthesized as reported previously [40]. Approximate 0.636 g of $Zn(OAc)_2\cdot 2H_2O$ and 0.656 g of nim were dissolved separately in 56 ml of DMF with the assistance of an ultrasonic bath. These two solutions were mixed together and stirred for 2.5 h at room temperature. The precipitate was recovered using centrifugation and washed repeatedly with DMF. The yield of ZIF-108 based Zn is 85%.

2.3. Synthesis of dual-ligand ZIFs from ZIF-108

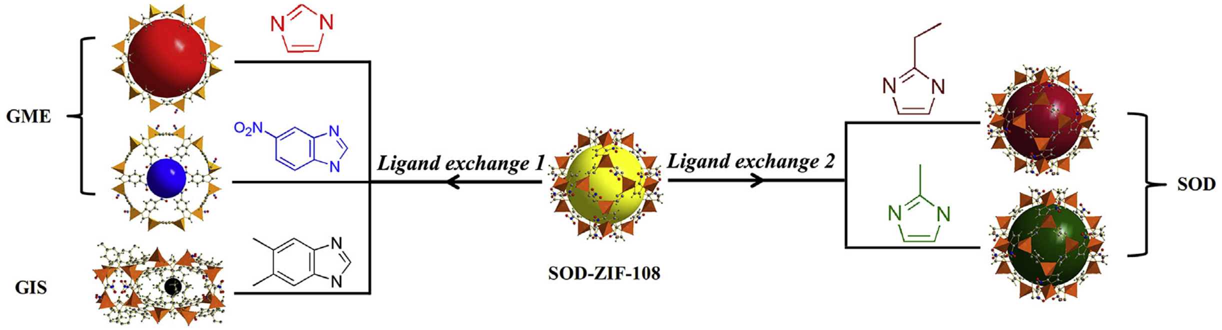
Dual-ligand ZIFs were synthesized by ligand exchange under mild conditions. A typical synthesis procedure for ZIF-78 was as follows: nbim (0.0958 g, 0.587 mmol) was dissolved in DMF (16 ml). ZIF-108 powder (0.1097 g, 0.291 mmol equiv. of Zn of ZIF-108) was then added and stirred for 10 min. The mixture was heated at 60 °C to promote the ligand exchange process. After 52 h, the product was separated using centrifugation and washed with fresh DMF (3 × 20 ml) to remove residual reactants in the ZIF pores. The product was finally dried at 60 °C overnight. Similarly, im, dmbim, eim and mim ligands were employed to synthesize dual-ligand ZIF crystals with a molar ratio of ligands: ZIF-108: DMF = 2.0: 1: 716. The overall yield of ligand exchange reaction was the product of the yields of the two-step reaction (from Zn^{2+} to ZIF-108 then to dual-ligand ZIF products). Dual-metal-dual-ligand ZIF crystals were synthesized by using metal-substituted ZIF-108 as the parent material.

2.4. Synthesis of oriented ZIF-78 films

ZIF-78 films were synthesized via secondary growth with ZIF-108 as seeds. ZIF-108 was plugged into a HOSSM support by hand scrubbing to form a thick seed bed. Two drops of PEI/DMF solution (2.56 wt.%) was coated onto the surface of the seed bed to prevent it from peeling off. After drying thoroughly at 50 °C, the seeding support was immersed vertically into the clear mother solution with the assistance of a PTFE holder. The reaction mixture was heated at 120 °C for 60 h. After cooling naturally to room temperature, the support was carefully removed from the PTFE holder, briefly washed with fresh DMF and dried in a beaker covered with filter paper. Significantly, the mother solution was prepared as follows: 0.432 g of $Zn(NO_3)_2\cdot 6H_2O$ was dissolved into 16 ml of DMF (solution A) and then 0.206 g of nim, 0.296 g of nbim and 0.728 g of TEA were dissolved in 40 ml of DMF (solution B). Solution A was poured into solution B to give a reaction mixture ratio of Zn^{2+}/nim/nbim/DMF/TEA = 1:1.25:1.25:500:5.0. After stirring for 0.5 h, the reaction mixture was transferred into a DURAN® laboratory bottle and heated at 393 K for 30 min. Gel-like seeds were removed by centrifugation, and the clear mother solution was eventually used for the film synthesis.

2.5. Characterizations

PXRD patterns were recorded on a Rigaku D/MAX 2500/PC instrument using Cu Kα radiation ($\lambda = 0.154$ nm at 40 kV and 200 mA), with a scan speed of 5°/min and a 2θ range of 2–40°. The morphology of products was observed using SEM (Quanta 200 FEG,



Scheme 1. Illustration of ligand exchange processes using ZIF-108 as parent materials.