Microporous and Mesoporous Materials 259 (2018) 255–263

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Direct synthesis of anion exchange polymer threaded in a metal-organic framework through *in situ* polymerization of an ionic liquid

Joseph Funso Olorunyomi [a], Kwong-Yu Chan [a, *], Liang Gao [a, b], Albert A. Voskanyan [a], Chi-Ying Vanessa Li [a, *]

[a] *Department of Chemistry, The University of Hong Kong, Pokfulam, Hong Kong*
[b] *School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong Province, China*

ARTICLE INFO

Article history:
Received 16 June 2017
Received in revised form
17 August 2017
Accepted 30 August 2017
Available online 8 September 2017

Keywords:
Metal-organic framework
Ionic liquid
UiO-66
Ion exchange
In situ polymerization

ABSTRACT

We report one step synthesis of anion exchange polymer threaded in a metal-organic framework (MOF) via *in situ* polymerization of an ionic liquid (IL) monomer. The ionic liquid 3-methyl-1-vinylimidazolium iodide (3MVIm-I) is water miscible and can be easily impregnated into hydrophilic UiO-66 before triggering in situ polymerization to produce the composite. This simple synthesis does not involve an amination step, which was previously required to incorporate anion-exchange function of a polymer threaded into ZIF-8. This method also avoids difficult impregnation of hydrophobic precursors into hydrophilic MOF for in situ ionic liquid formation and their removal. The synthesized P3MVim-I~UiO-66 composite is tested for anion exchange and cation rejection in aqueous solvent. P3MVim-I~UiO-66 demonstrates outstanding ion selectivity over pristine UiO-66 and commercial anion exchange resin (Amberlyst A26). Aside the high OH^- exchange capacity (6.05 meq g^{-1}), more than 95% of inorganic anions ($AuCl_4^-$) and 90% of anionic organic dye (Acid Blue 9) are exchanged by P3MVim-I~UiO-66 within 30 min. In addition, there is complete rejection of standalone cationic dye (Rhodamine B) by P3MVim-I~UiO-66 while the pristine UiO-66 exhibits no rejection. Crystallinity of the UiO-66 host is retained after impregnation and ion exchange.

1. Introduction

Though thousands of metal organic framework (MOF) structures are reported [1] and their applications explored in wide scope, only a few MOFs are intrinsically capable of ion-exchange [2–6]. Ionic functionality of the highly porous MOF is very attractive for applications related to the energy and environment. In particular, there is a strong interest for anion exchange materials [7–12] for lack of commercial materials meeting specific high performance requirements. Threading cavities of MOFs with ion-selective polymers via an *in situ* polymerization has been demonstrated previously [13,14]. While a one-step direct *in situ* polymerization of ionic monomer is reported for cation exchange polymer [14], an extra post-polymerization amination step is needed for producing anion exchange polyelectrolyte threaded in a zeolitic imidazolate framework (ZIF-8) [13]. ZIF-8 MOF is stable in alkaline, a multi-step anion polyelectrolyte incorporation is necessary since hydrophobic ZIF-8 prevents impregnation of an hydrophilic ionic monomer such as vinyl benzyl trimethyl ammonium chloride (VBTAC). Instead, a hydrophobic monomer, vinyl benzyl chloride (VBC) is impregnated, *in situ* polymerized, before providing anion exchange function with an amination reaction. Anion exchange PVBTAC~ZIF-8 showed better ion-exchange kinetics than the commercial macroporous anion-exchange resin Amberlyst A26 [13]. In addition to being a multi-step procedure, the amination step disfavours MOF hosts that cannot survive alkaline conditions. Therefore, it would be advantageous to impregnate MOFs with anion-exchange monomers and eliminate the concern of structural damage to the host during amination. Polymerizable ionic liquids (ILs) can be an alternative to amines for providing anion exchange function. Li et al. [15] employed the “ship-in-a-bottle” strategy for the preparation of MOF-polymer anion exchange composite, where precursors of an ionic liquid (IL) are forced into MIL-101(Cr) and form the ionic liquid benzyl-vinylimidazolium chloride in situ, which subsequently polymerized. There are, however, two inherent difficulties

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* Corresponding authors.
E-mail addresses: hrsccky@hku.hk (K.-Y. Chan), cyvli@hku.hk (C.-Y.V. Li).

https://doi.org/10.1016/j.micromeso.2017.08.054

of this approach. Hydrophobic IL precursors, vinyl benzyl chloride and vinylimidazole, cannot penetrate into the hydrophilic MIL-101(Cr) cavities. Separations of excess IL precursors and other impurities are needed after polymerization. On the other hand, H. Kitagawa et al. [16,17] reported a direct insertion of an IL but did not perform polymerization to synthesize a polyelectrolyte threaded MOF. It seems possible to extend H. Kitagawa's approach and perform *in situ* polymerization after direct insertion of the desired IL monomer which will have anion-exchange function. This approach avoids the difficulty of impregnation and needs of removing impurities and excess precursors required for in situ IL formation. Among the factors which determine the insertion of the IL guests into the pores of MOF are the molecular size of the IL, the size of the pore aperture for IL accessibility and similarities in hydrophilicity/hydrophobicity of the MOF to the IL [18,19]. We have chosen to impregnate a 'Universitetet i Oslo' MOF, UiO-66 (Zr), with 3-methyl-1-vinylimidazolium iodide because of the relatively smaller size and the hydrophilicity of the IL. UiO-66 is selected as the MOF host because of its chemical stability [20] which is crucial to ion-exchange study, and the structural stability of UiO-66 after the loss of some linkers leading to tunable porosity [21,22] and hydrophilicity of UiO-66 [23]. We present here the in-situ polymerization of the 3-methyl-1-vinylimidazolium iodide (3MVIm-I) to form a polyelectrolyte threaded in MOF. This strategy simplifies the steps of anion exchange composite preparation and avoids the amination step previously required to introduce anion-exchange polymer into MOF. Therefore, in-situ polymerization of cationic monomers can be achieved within MOFs thereby leading to the development of various MOF-polycation composites for anion exchange and related applications.

2. Experimental

2.1. Chemicals and reagents

N-vinyl imidazole (98%) was obtained from Tokyo Chemical Industry (TCI), Japan; Iodomethane (99%) was purchased from Honeywell Riedel-de-Haen. Zirconium (IV) chloride (99.5%), 1,4-benzenedicarboxylic acid (BDC; 98%) and Rhodamine B (HPLC grade; >95%) were purchased from Sigma Aldrich. Acid blue 9 (89%) was obtained from Warner Jenkinson Company. All chemicals were used without further purification and the reagents used are of ACS grade. The purity of the dyes was confirmed by strong absorbance at 553 nm (for Rhodamine-B) and 630 nm (for acid blue-9). 18.2 Ωcm deionized water dispensed from Milli-Q plus system was used for all preparations.

2.2. Synthesis of UiO-66

UiO-66 was synthesized based on a reported procedure [21]. Typically, 5.94 mmol of $ZrCl_4$ dissolved in a DMF-HCl mixture prepared by adding 11 ml of c.HCl to 55 ml of DMF in 250 ml beaker. BDC (8.25 mmol) was added to another 250 ml beaker containing 110 ml of DMF. The solutions in the two beakers were sonicated for 20 min until all chemicals were dissolved. Thereafter, the solutions were mixed together in a 500 ml capacity glass vessel and sealed. The vessel was heated at 80 °C for 15 h. The white solid product obtained was washed three times with DMF and separated by centrifugation at 7000 rpm. Thereafter, the as-synthesized UiO-66 was soaked in CH_3OH for 48 h to allow the exchange of entrapped DMF with CH_3OH. The product was dried in a vacuum oven at 100 °C overnight and used for further characterizations.

2.3. Ionic liquid (IL) preparation

N-vinyl imidazole was quaternized by iodomethane as documented in the literature [24]. To a 5 ml of ethylacetate contained in a 100 ml three-neck round-bottomed flask, 10 mmol of N-vinyl imidazole and 20 mmol of iodomethane were added. The flask was sealed and the reaction proceeded at 60 °C for 24 h under N_2 atmosphere. The product was washed in three batches of 10 ml ethylacetate and decanted to remove any unreacted substance. The solvent was removed under pressure in a rotary evaporator until a dark-yellow viscous liquid was obtained. The purified product is labelled 3MVim-I.

2.4. Bulk polymerization of 3MVim-I

In a three-neck round-bottomed flask of 100 ml, 0.318 ml of 3MVim-I was dissolved in water to make up 2 ml aqueous solution. The solution was purged in N_2 for 1 h. Then, 2 mol% of 2,2′-Azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044 radical initiator), was added, the reaction initiated at 50 °C and continuously stirred for 17 h under N_2 atmosphere. The obtained polymer was precipitated from acetone. It was re-dissolved in water to remove any unreacted substance and precipitated again using acetone. Finally, the product was dried under vacuum for 12 h at 40 °C. The polymer is alternatively referred to as a bulk P3MVim-I.

2.5. Confined polymerization of 3MVim-I in UiO-66

First, 1.2 ml of 3MVim-I was dissolved in water to make-up a 2 ml aqueous solution and then transferred to a 100 ml three-neck flask. 2 mol% of VA-044 was added and stirred continuously for 0.5 h under N_2 at room temperature. Meanwhile, UiO-66 had been degassed at 180 °C for 5 h. Then, 1 g of the evacuated UiO-66 powder was carefully added to the monomer solution until the powder was fully soaked and after that, sealed up for 24 h at 20 °C under N_2. Subsequently, the reaction was thermally initiated at 60 °C for another 24 h. The product obtained was washed in water thoroughly to remove any attached monomer and impurities. This was further soaked in acetone for 48 h to remove entrapped soluble species. The solid product was dried under vacuum at room temperature for characterizations. This product is hereafter referred to as P3MVim-I~UiO-66.

2.6. Materials characterization

The ^{1}H-NMR spectra were recorded by a Bruker 300 MHz spectrometer with D_2O as solvent. To obtain the spectrum of the confined polymer, the P3MVim-I~UiO-66 composite was digested with 4% HF acid in DMSO, the polymer was then precipitated from acetone. The obtained polymer was dissolved in water and precipitated again from acetone. The polymer was then dried under vacuum for 12 h at 40 °C after which dissolved in D_2O for ^{1}H-NMR experiment. The Fourier-transform infrared spectroscopy (FTIR) spectra of the ionic liquid, polymer and composite were measured with Shimadzu spectrometer in the range 4000–400 cm^{-1} at 16 cm^{-1} resolutions at room temperature. The X-ray diffraction patterns (XRD) were obtained from a Bruker Advance D8 diffractometer (CuKα). The simulated pattern obtained from the literature [25] was generated with the aid of Mercury 3.6 software from the Cambridge Crystallographic Data Centre (CCDC). Scanning electron microscope (SEM) and Energy-dispersive X-ray (EDX) characterizations were obtained from the Hitachi S-4800 microscope equipped with cold cathode field emission. The transmission electron microscope (TEM) images were acquired from the FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope.