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Hybrid membranes with Cu(II) loaded metal organic frameworks for enhanced desulfurization performance

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ABSTRACT

Tailoring the interface between the polymer matrix and filler to probe the structure-performance relationship is one of the critical research issues in hybrid membranes. In this study, metal organic framework (MOF) incorporated hybrid membranes are fabricated with polydimethylsiloxane (PDMS) as the matrix and Cu(II) loaded UiO-67-bpydc (bpydc refers to 2,2′-bipyridine-5,5′-dicarboxylic acid) as the filler, which are utilized for removing thiophene from model gasoline. The structure-performance relationship of the resultant membranes was investigated. The flux of the hybrid membrane shows a remarkable increase while avoiding obvious loss of selectivity. The loading of Cu(II) onto UiO-67-bpydc effectively tailors the interface between the polymer matrix and filler, which enhances the membrane separation performance. This study may offer a new example for designing MOF-based hybrid membranes towards efficient molecular separation.

1. Introduction

Metal organic framework (MOF) is a family of materials with diverse porosity, which have received intensive attention from worldwide researchers. The regular pores and channels, high surface area and functional groups endow MOFs with multiple functions and application fields. Particularly, MOFs have been widely applied in various separation processes, and a typical utility is the application as inorganic fillers in polymer-based hybrid membranes [1–4]. MOFs possess molecularly selective pores and intrinsic nano-scale transport pathways [5–7]. Besides, MOF particles can tune the membrane structure by disturbing the arrangement of polymer chains. Therefore, MOFs incorporated membranes can exhibit improved separation performance as well as physical and chemical properties [8,9]. Despite the advantages, challenges remain in preparing a uniformly dispersed MOF-based hybrid membrane. Fabricated through a physically blending method, hybrid membranes may suffer from particle aggregation and interfacial defects [10].

In order to optimize the properties of MOF-based hybrid membranes, the functionalization of MOFs is supposed to be one of the effective approaches [11,12]. First, the functionalization can improve the compatibility of MOFs towards polymer matrix, resulting in decreased interfacial defects. Wang et al. functionalized zeolitic imidazolate framework (ZIF) particles with ethanediamine [13] and dodecylamine [14]. The particles were modified hydrophilically and hydrophobically to show better compatibility towards different polymer matrices, leading to enhanced separation performance. Second, the functionalized MOFs may better interfere the arrangement of polymer chains and tune the interface between fillers and the polymer. Third, when it comes to the case of removing unsaturated molecules, grafting coordinative metal sites (known as facilitated transport carriers) on MOFs can promote the transport of such molecules through reversible π-complexation interaction [15].

As a subfamily, zirconium-based MOFs including UiO-66, 67 and 68 [16] have been investigated due to their extraordinary stability against heat (350 °C) and organic solvents over many other kinds of MOFs [17,18], which are promising for the separation or capture of organic mixture [19]. Up to now, UiO has been functionalized with various transition metal ions such as Fe, Mn, Co, Ni and Cu [20–22]. Among these elements, Cu(II) shows superior π-complexation capacity towards thiophene, which is suitable as UiO-functionalizing agent [23] for removing thiophene from model gasoline. In addition, if the 4,4′-biphenyl dicarboxylic acid ligands of UiO-67 are substituted with 2,2′-bipyridine-

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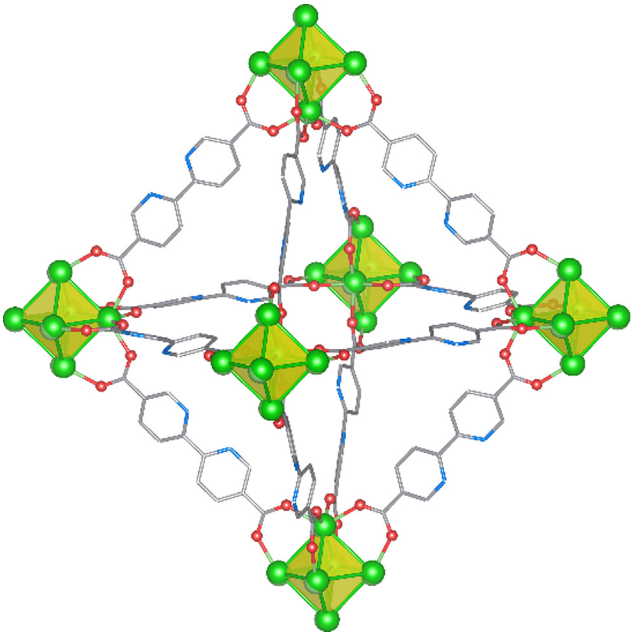

Fig. 1. Schematic representation of UiO-67-bpydc. For simplicity, the organic ligands are drawn as sticks while the grey sticks represent carbon atoms and blue sticks refer to nitrogen atoms. Hydrogen atoms are omitted. The $[Zr_6O_4(OH)_4]^{12+}$ clusters are represented as yellow octahedra with zirconium atoms (green spheres) at the vertices. Red spheres represent oxygen atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5,5′-dicarboxylic acid (H_2bpydc), a new kind of isostructural MOF denoted as UiO-67-bpydc will be generated [24] as illustrated in Fig. 1. The bipyridine groups can firmly coordinate with metal ions, which can avoid mutual deactivation of facilitated transport carriers that are too close to each other while allowing the exposure of metal sites towards unsaturated molecules [25,26]. Furthermore, the bipyridine groups show good affinity towards thiophene molecules through π–π stacking. By preparing Cu(II)-functionalized UiO-67-bpydc particles as well as corresponding hybrid membranes, the influence of functionalized MOFs towards the structure-performance relationship of hybrid membranes can be investigated in detail.

In this study, UiO-67-bpydc particles were loaded with Cu(II) through solvothermal method, subsequently incorporated in polydimethylsiloxane (PDMS) membranes, and then utilized in the desulfurization of model gasoline through pervaporation. The morphologies, chemical compositions, thermal stabilities, free volume properties, as well as mechanical, swelling and sorption properties of membranes were characterized via scanning electron microscope (SEM), positron annihilation lifetime spectroscope (PALS) and several other techniques. The effects of filler contents and Cu(II) loadings on the structure-performance relationship of hybrid membranes were investigated.

2. Experimental

2.1. Materials

Zirconium tetrachloride ($ZrCl_4$), 2,2′-bipyridine-5,5′-dicarboxylic acid (H_2bpydc), thiophene and 3-aminopropyl trimethoxysilane (APTMS) were purchased from Aladdin Industrial Corporation, Shanghai, China. *N*, *N*-dimethyl formamide (DMF), *n*-heptane, *n*-octane, and ethanol were offered by Guangfu Fine Chemical Research Institute, Tianjin, China. Copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) and acetonitrile (CH_3CN) were purchased from Jiangtian Chemical Technology Co., Ltd., Tianjin, China; hydroxyl-terminated polydimethylsiloxane (PDMS) oligomer with a viscosity of 5 Pa·s was acquired from Silicon Mountain Macromolecular Materials Co., Ltd., Shanghai, China. Dibutyltin dilaurate (a kind of organic tin catalyst) was purchased from Sihuan Antong Commercial and Trade Co., Ltd., Beijing, China; polyvinylidene fluoride (PVDF) ultrafiltration membrane sheets with a molecular weight cutoff (MWCO) of 30 kDa were acquired from Synder Membrane Technology Co., Ltd., Vacaville, USA. Octane was of chromatographical grade, while all other reagents were of analytical grade. Deionized water was used throughout this study. For convenience, the UiO-67-bpydc particle is denoted as "UiO-67b", and Cu(II) decorated UiO-67b particle is denoted as "Cu@UiO-67b" in this study.

2.2. Syntheses of UiO-67b and Cu@UiO-67b

2.2.1. Synthesis of UiO-67b

The solvothermal synthesis procedure of UiO-67b was directly from literature [24]. In a typical synthesis, $ZrCl_4$ and H_2bpydc powder were mixed in equal molar ratio and then put in a steel autoclave lined with polytetrafluoroethylene (PTFE). DMF was added to the autoclave as the solvent, and the molar ratio of DMF to Zr was 500:1. The autoclave was sealed and heated in a muffle furnace at a heating rate of less than 10 °C/min. The temperature of the muffle furnace was kept at 120 °C for 24 h. The product particles were separated by centrifugation, and then washed with ethanol for 4 times, each time for 6 h, in order to remove the residual H_2bpydc ligands. The final UiO-67b products were dried under vacuum at 40 °C for 24 h.

2.2.2. Synthesis of Cu@UiO-67b

The solvothermal method of loading Cu(II) to UiO-67b was derived from literature [26]. In a typical synthesis, UiO-67b particles, $Cu(NO_3)_2{\cdot}3H_2O$ and acetonitrile were added to a steel autoclave lined with PTFE. The molar ratio of $Cu(NO_3)_2{\cdot}3H_2O$ to H_2bpydc ligand in UiO-67b was 1:3, 2:3, 1:1, 2:1, 3:1. The molar ratio of acetonitrile to Zr was 300:1. The autoclave was put in a pre-heated oven under 65 °C for 24 h. The product particles were obtained by centrifugation, then washed with acetonitrile to remove the residual reactant, until the centrifugal supernatant became colorless. The final Cu@UiO-67b products were dried under vacuum at 80 °C for 12 h.

2.3. Fabrication of membranes

The fabrication method of PDMS pristine and hybrid membranes is identical with the method in our previous work [27,28]. In a typical fabrication, a certain portion of UiO-67b or Cu@UiO-67b particles was dispersed in heptane for 10 min under ultrasonication. Then, PDMS oligomer and APTMS were dissolved into heptane suspension under stirring to form the casting solution. Afterwards, the organic tin catalyst was added to the casting solution, and the solution was cast onto PVDF ultrafiltration membrane substrates. The mass ratio of heptane, PDMS oligomer, APTMS and organic tin catalyst was 1000:300:23:3. The product membranes were air-dried for 8 h at 30 °C, then put in a preheated oven for 4 h at 75 °C.

The mass ratio of UiO-67b to PDMS in PDMS-UiO-67b hybrid membranes are denoted as PDMS-UiO-67b (X), where X refers to 0%, 2%, 4%, 6% and 8%. The PDMS-Cu@UiO-67b hybrid membrane samples are denoted as PDMS-Cu@UiO-67b-1, PDMS-Cu@UiO-67b-2, PDMS-Cu@UiO-67b-3, PDMS-Cu@UiO-67b-4, and PDMS-Cu@UiO-67b-5, according to the increase of Cu(II) content in the hybrid membranes. Furthermore, the mass ratio of the "UiO-67b part" to PDMS for all the PDMS-Cu@UiO-67b hybrid membranes in this study is 4%. When investigating the effects of Cu(II) loadings on Cu@UiO-67b, denote "0" refers to UiO-67b particles without Cu(II) loadings.

2.4. Characterizations

The morphology of UiO-67b and Cu@UiO-67b was observed with