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ZIF-90/P84 mixed matrix membranes for pervaporation dehydration of isopropanol

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ABSTRACT

By modifying the synthesis route, we have synthesized ZIF-90 nanoparticles with an average particle size of 55 nm and embedded them into P84 polymeric membranes with excellent dispersion for the dehydration of isopropanol (IPA)/water mixture via pervaporation. The effects of ZIF-90 loading as well as feed temperature on pervaporation performance of the mixed matrix membranes (MMMs) were systematically investigated. The flux of MMMs increases with increasing ZIF-90 loading due to the enhanced fractional free volume, while the separation factor of water/IPA can be maintained at 5432 when the ZIF-90 loading is less than 20 wt%, but reduced to 385 when the ZIF-90 loading is 30 wt%. Interestingly, the application of sulfonated polyethersulfone (SPES) as a primer to ZIF-90 nanoparticles before fabricating MMMs consisting of 30 wt% ZIF-90 recovers the separation factor without sacrificing the flux. The best MMM showed the separation performance with a flux of 109 g m^{-2} h^{-1} and a separation factor of 5668 at 60 °C. This encouraging performance suggests a promising future of ZIF-90/P84 composite membranes for the dehydration of IPA via pervaporation process.

1. Introduction

Driven by concerns on energy security and global warming, there is an urgent need to explore and develop both energy-saving and environmentally benign processes for chemical industries. Previous studies indicate that separation alone currently accounts for 60 to 80% of the process cost in most mature chemical processes [1]. Distillation, gas stripping and molecular sieve adsorption are the conventional unit operations applied to separate and purify alcohols from alcohol/water mixtures. However, these processes often require large footprints and intensive energy [2]. Moreover, it is costly to achieve a complete dewatering of alcohol via single-step ordinary distillation process due to the formation of azeotropic mixtures between alcohols and water. In contrast, the pervaporation process (a combination of permeation and evaporation processes) is an economic and eco-friendly separation process. It has been considered as one of potential candidates to outperform the conventional separation processes in dehydration of alcohols as it has the flexibility in process design and integration, lower energy consumptions coupled with simplicity in the process control [3,4]. For instance, the energy demand for purification of isopropanol (IPA) from aqueous solutions may be lowered by 87% when comparing pervaporation vs. azeotropic distillation [5]. In addition, the risk of cross-contamination using the entrainers in azeotropic distillation can be eliminated by using the pervaporation process [6,7]. Hence, pervaporation is a promising technology for the dehydration of alcohols from alcohol/water mixtures [2–5,8].

In the past decades, substantial works have been devoted to explore high performance pervaporation membranes for alcohol separation. An ideal pervaporation membrane should have superior permeability and selectivity, excellent durability, high mechanical stability, and economic viability. Generally, inorganic membranes offer good mechanical stability and high performance, but their wide applications are often limited by their expensive costs and fragility. On the other hand, polymeric membranes that are relatively inexpensive and easy to fabricate usually encounter the trade-off between permeability and selectivity. Therefore, heterogeneous mixed matrix membranes (MMMs) consisting of nanometric inorganic fillers embedded in a polymeric matrix may provide synergistic characteristics of both organic and inorganic membranes in energy and environment related separations [9,10]. Since the compatibility between the inorganic and organic phases as well as the elimination of interface defects are among the essential aspects in the development of MMMs for pervaporation processes, significant researches have been focused on elucidating these issues [4,10,11].

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Zeolitic imidazolate frameworks (ZIFs) are a subfamily of metal-organic frameworks (MOFs), which have been demonstrated as promising membrane materials due to their extremely large surface areas as well as superior hydrothermal and chemical stabilities [12–14]. In general, ZIFs are regarded to possess flexible structures that have a better affinity with polymer chains, as compared with traditional inorganic particles (e.g. zeolites, silica, carbon nanotubes, etc.) with "rigid" frameworks [8,13,15]. Therefore, MMMs with the incorporation of ZIFs as additives (fillers) are expected to exhibit enhanced flux and possibly selectivity when compared to the pristine polymeric membrane. A variety of MMMs consisting of ZIF materials have recently been studied in order to explore their prospects for gas separation [15–25]. However, only limited studies are for pervaporation.

Shi et al. prepared ZIF-8/PBI mixed matrix membranes for pervaporation dehydration of C_2–C_4 alcohols and studied their fundamental properties of sorption and permeability [26,27]. Liu et al. fabricated an organophilic ZIF-8/polymethyl-phenylsiloxane membrane to recover bioalcohols by taking the advantage of ultrahigh adsorption selectivity of ZIF-8 nanoparticles [8]. Recently, their group employed a novel "plugging–filling" method to fabricate ZIF-8-silicone rubber nanocomposite membranes with interesting performance [28]. Kang et al. also designed ZIF-7/chitosan MMMs by incorporating microporous ZIF-7 particles into chitosan membranes [29]. They found that ZIF-7 particles have a strong affinity with the chitosan due to the nature of organic linkers within ZIF-7. Jin et al. immobilized the organophilic ZIF-71 particles into polyether-block-amide (PEBA) membranes for the recovery of biobutanol via pervaporation [30]. Since ZIF-71 particles with an appropriate loading of ≤ 20 wt% exhibited excellent compatibility with the polymer matrix, the resultant separation performance was significantly improved.

Among various ZIFs, zinc(2-carboxyaldehyde imidazolate)$_2$ (ZIF-90) has gained particular attention since the pioneering work by Yaghi et al. in 2008 [31]. The imidazole linker of ZIF-90 contains a carbonyl group, which has a favorable noncovalent interaction with the polymer matrix. Therefore, ZIF-90 based MMMs may have the advantage to suppress the delamination between the filler and polymer phases. In addition to better affinity with the polymer phase, ZIF-90 possesses the free aldehyde groups in the framework which can be covalently functionalized with amine groups through the imine condensation reaction. Huang et al. employed 3-aminopropyltriethoxysilane (APTES) as a covalent linker between the ZIF-90 layer and Al_2O_3 support via imine condensation and the resultant ZIF-90 membranes exhibited excellent separation of H_2 from CO_2, N_2, CH_4, and C_2H_4 [32]. All these salient features facilitate their promising applications in the field of membrane separation.

To our best knowledge, there are limited reports regarding the fabrication of ZIF-90 based MMMs for gas-separation [17,33] but no study of ZIF-90 MMMs for pervaporation. Moreover, the particle sizes of ZIF-90 reported in literatures are relatively big (>100 nm), which are unfavorable in the fabrication of MMMs [11]. Therefore, this study aims to synthesize ZIF-90 nanoparticles with a relatively small particle size and a narrow particle size distribution via a modified room-temperature synthesis method. The ZIF-90 nanoparticles were subsequently applied to fabricate high performance ZIF-90/P84 MMMs for dehydration of IPA/water mixtures via pervaporation. Moreover, the sulfonated polyethersulfone (SPES) primer method was adopted during the membrane fabrication process to further enhance the separation performance of the MMMs. The newly developed ZIF-90/P84 MMMs show great potentials for pervaporation applications.

2. Experimental

2.1. Materials

Chemicals were used as received: zinc acetate dihydrate (reagent grade, Sigma-Aldrich), imidazolate-2-carboxyaldehyde (ICA, reagent grade, Alfa Aesar), methanol (reagent grade, Merck), N,N-dimethylformamide (DMF, HPLC grade, Fisher), and isopropanol (IPA, reagent grade, Fisher). P84 powders were purchased from HP Polymer GmbH, Austria. Its structure of the repeating unit is shown in Fig. 1a. Sulfonated polyethersulfone (SPES) granules

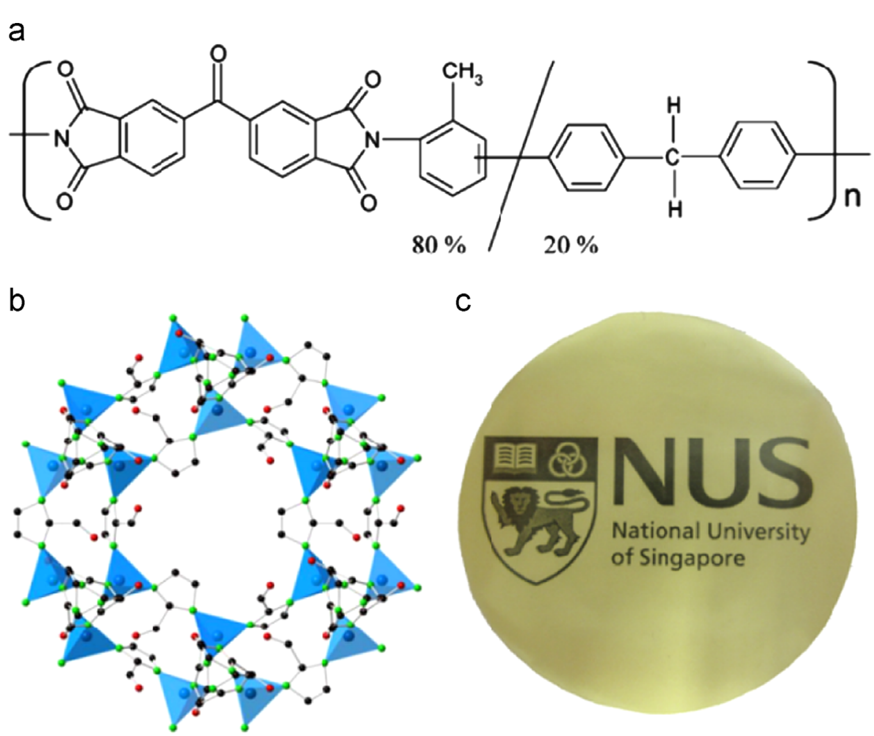

Fig. 1. Chemical structures of (a) P84 and (b) ZIF-90, and (c) a photo of a 30/70 (w/w) ZIF-90/P84 membrane (15.2 cm^2) on top of the NUS logo.