High-performance UiO-66/polyimide mixed matrix membranes for ethanol, isopropanol and n-butanol dehydration via pervaporation

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ABSTRACT

We have designed novel mixed matrix membranes (MMMs) consisting of UiO-66 nanoparticles and 6FDA-HAB/DABA polyimide for the dehydration of ethanol, isopropanol and n-butanol via pervaporation. The UiO-66 nanoparticles have a particle size of around 100 nm. They can be evenly dispersed in the 6FDA-HAB/DABA polyimide matrix without visible agglomeration even at the highest 30 wt% loading. The incorporation of UiO-66 into the 6FDA-HAB/DABA polyimide not only significantly enhances both free-volume radius and fractional free volume as confirmed by positron annihilation lifetime spectroscopy but also remarkably improves the normalized flux of MMMs for the dehydration of ethanol/water, isopropanol/water and n-butanol/water systems. The MMMs show excellent separation efficiency for the dehydration of isopropanol and n-butanol. At the highest UiO-66 loading of 30 wt%, the MMMs have the water permeability of 0.329 and 0.292 $mg\ m^{-1}\ h^{-1}\ kPa^{-1}$ and mole-based selectivity of 2209 and 14214 respectively for isopropanol/water and n-butanol/water systems, outperforming most literature data. These experimental results strongly suggest the newly developed UiO-66/polyimide MMMs have great potential for isopropanol and n-butanol dehydration via pervaporation.

1. Introduction

The global warming resulting from the heavy utilization of fossil fuels has raised the urgency to explore renewable and sustainable energy so that mankind can alleviate the reliance on fossil fuels. Biofuels, produced from biomass by biological processes, have been viewed as a promising candidate to substitute fossil fuels [1]. In the production of biofuels, the separation of biofuels from fermentation broth is the most expensive process, which can account for 60–80% of the total cost [1]. Therefore, the development of an economic and effective separation technology is essential to produce cost-effective biofuels. Pervaporation has been considered as a promising candidate to replace conventional separation technologies such as distillation and adsorption in chemical and energy industries as it has advantages of low energy consumption, environmental friendliness, small footprint and mild operation conditions [2–5]. What's more, pervaporation is powerful to separate azeotropic mixtures because it is not restricted by the vapour-liquid equilibrium [6].

Based on membrane materials, pervaporation membranes can be classified into inorganic membranes and polymeric membranes. Inorganic membranes have superior thermal, chemical and mechanical stabilities. They are not subjected to any solvent-induced swelling problem. Therefore, inorganic membranes have superior separation performance especially in harsh environments with strong solvents, low pH or high temperatures [7]. However, their fragility and high costs of fabrication limit their wide applications. Compared with inorganic membranes, polymeric membranes are more widely utilized for pervaporation due to the advantages such as ease of fabrication and scale-up, lower capital costs, better utilization of space and reasonable separation performance [6,8–10]. However, these membranes usually encounter the trade-off relationship between permeability and selectivity. They also suffer from the problem of long-term stability due to the solvent-induced swelling effect.

In order to combine the strengths of inorganic and polymeric membranes, mixed matrix membranes (MMMs) consisting of inorganic fillers dispersed in organic polymers were first developed by Kulprathipanja et al. in 1988 [11]. The incorporation of inherently high permeability and selectivity inorganic particles into polymeric matrices may result in MMMs that not only have better separation performance than the original polymeric membranes but also minimize the fragility issue in inorganic membranes [12,13]. Numerous inorganic fillers including zeolites, carbon molecular sieves, silica, metal oxides, carbon nanotubes, silicate, metal organic frameworks (MOFs), graphene oxide (GO), porous organic cages (POCs), covalent organic frameworks have

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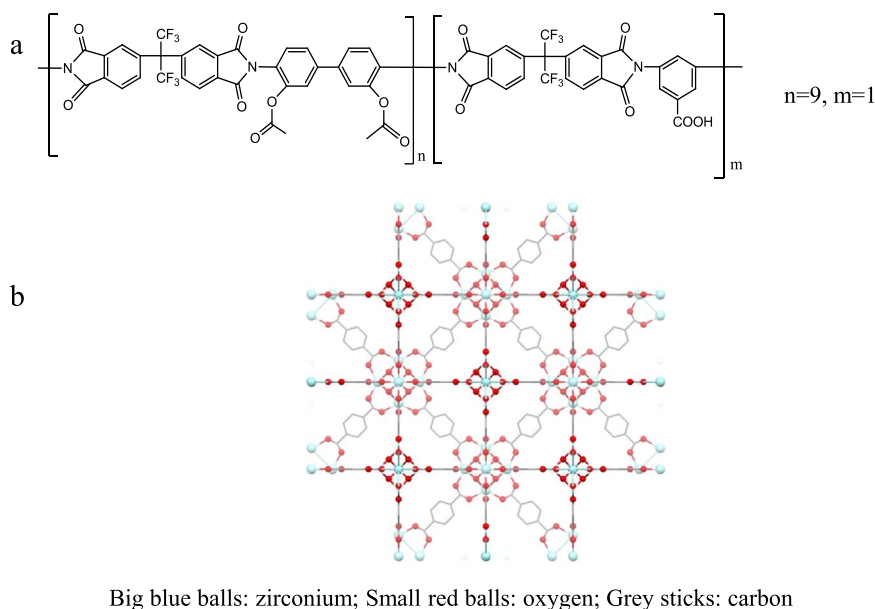Big blue balls: zirconium; Small red balls: oxygen; Grey sticks: carbon

Fig. 1. (a) Chemical structure of the 6FDA-HAB/DABA polyimide (b) Crystal structure of UiO-66. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

been investigated and employed in mixed matrix membranes [8,14–16]. Among them, metal organic frameworks (MOFs), have been demonstrated as promising materials for MMMs due to their unique characteristics such as large surface areas, controllable porosity, high adsorption capacity for certain gases and good affinity with polymer chains, as well as the tuneable chemical properties [14–16].

Among various MOFs, UiO-66, synthesized by $ZrCl_4$ and 1,4-benzene-dicarboxylate (BDC), possessing 12-coordinated zirconium-oxo clusters, has received significant attention since the pioneering work by Cavka et al. in 2008 [17]. UiO-66 based membranes have shown excellent gas separation performance especially in CO_2/CH_4 separation with high selectivity and good adsorption capacity [18–23]. Nik et al. reported CO_2 permeability of the UiO-66 based MMMs increased significantly compared to the neat polymer membrane without compromising the selectivity [18]. Besides, UiO-66 based membranes also show great potential in water reuse and desalination [24,25]. The pure-phase UiO-66 polycrystalline membranes fabricated on alumina hollow fibres exhibited excellent multivalent ion rejections with good permeability and outstanding water stability up to 170 h tests in a wide range of saline solutions [24,25]. The excellent chemical stability was attributed to the strong coordination covalent bonds between the hard-acid–hard-base interactions of the Zr atoms and carboxylate oxygens. Yin et al. combined amino-functionalized UiO-66 ($UiO-66-NH_2$) with ceramic membranes for adsorptive removal of Pb (II) from wastewater [25]. The resultant membrane was able to effectively remove most of Pb (II) (61.4%) and exhibited remarkably high adsorption capacity (1795.3 mg g^{-1}).

Although UiO-66 based MMMs have a wide range of applications as aforementioned, to our best knowledge, there is no study of UiO-66 based MMMs for pervaporation. Since UiO-66 possesses many important characteristics suitable for pervaporation such as high porosity, excellent chemical and thermal stability and tuneable chemical properties [26–29], this work aims to explore the feasibility of applying UiO-66 based MMMs for pervaporation and investigate the fundamental science behind the performance enhancement. To meet the objectives, uniform UiO-66 nanoparticles with a relatively small particle size would be firstly synthesized and subsequently employed to prepare UiO-66/6FDA-HAB/DABA polyimide MMMs with different particle

loadings for dehydration of ethanol, isopropanol and n-butanol via pervaporation. In addition, basic research on water and alcohol uptakes and free volume size would be characterized in order to reveal the actual mechanisms for the performance enhancement. This study may provide useful insights to develop high performance UiO-66 based MMMs for alcohol dehydration via pervaporation.

2. Experimental

2.1. Materials

For polyimide syntheses, 3,5-diaminobenzoicacid (DABA) and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) were purchased from Aldrich (Singapore) and Clariant (Germany) respectively and further purified by vacuum sublimation. 3,3′-dihydroxybenzidine diamine (HAB) was supplied by Tokyo Chemical Industry and used without further treatments. N-methyl-2-pyrrolidone (NMP, analytical grade) from Merck (Germany) was purified by vacuum distillation. Acetic anhydride, pyridine from Aldrich (Singapore) and methanol from Merck (Germany) of the reagent grade or higher, were used as received. For Uio-66 syntheses, zirconium (IV) chloride (≥98.0%), terephthalic acid (≥98%) and acetic acid (glacial) (≥99.8%) were obtained from Merck (Germany), Aldrich (Singapore) and Merck (Germany) respectively and used as received. Dimethylformamide (DMF), ethanol, isopropanol and n-butanol of the reagent grade or higher, from Fisher Scientific (UK), were also utilized as received.

2.2. Polyimide and UiO-66 syntheses

The 6FDA-HAB/DABA polyimide (PI) was synthesized by polycondensation of three monomers 6FDA, HAB and DABA in an anhydrous NMP solution under nitrogen environment. The two diamine ratio of HAB to DABA was 9:1. Firstly, the three monomers reacted to form a viscous poly(amic acid) solution. Then the poly(amic acid) was imidized to produce the 6FDA-HAB/DABA polyimide by a chemical imidization method where acetic anhydride and pyridine were added as the dehydration agent and catalyst, respectively. Fig. 1a illustrates its chemical structure with n and m equal to 9 and 1,