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Mixed matrix membranes with nano-sized functional UiO-66-type MOFs embedded in 6FDA-HAB/DABA polyimide for dehydration of C1-C3 alcohols via pervaporation

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ABSTRACT

This study demonstrated an effective method to enhance both the normalized flux and separation factor by molecularly designing mixed matrix membranes (MMMs) consisting of porous UiO-66-NH_2 nanoparticles and 6FDA-HAB/DABA polyimide. To investigate the effects of functional groups on UiO-66 particles on alcohol dehydration, MMMs containing (1) UiO-66-NH_2 nanoparticles with a particle size of 80–90 nm, (2) UiO-66 with a particle size of 90–110 nm and (3) UiO-66-F_4 with a particle size of 90–130 nm were fabricated and compared for alcohol dehydration. Three alcohol dehydration systems; namely, methanol/water, ethanol/water and isopropanol/water were studied. Results showed that UiO-66-NH_2 based MMMs have superior separation performance among these three MMMs because the hydrophilic amino-functional groups can facilitate water transport. Incorporation of UiO-66-NH_2 nanoparticles can greatly improve both the normalized flux and separation factor simultaneously if the particle loading is within the range of 0–20 wt%. Due to the good compatibility between UiO-66-NH_2 particles and the 6FDA-HAB/DABA polyimide resulting from the intermolecular bonding among the amine and imide groups, the UiO-66-NH_2 based MMMs exhibited stable isopropanol dehydration performance in uninterrupted 200-h tests. The excellent alcohol dehydration performance of UiO-66-NH_2 based MMMs opens up their potential for alcohol dehydration via pervaporation.

1. Introduction

The development of sustainable and renewable energy has received worldwide attention due to the highly fluctuated oil price and global warming. Bioalcohols are one of promising renewable and sustainable energy sources to substitute fossil fuels [1]. For bioalcohol dehydration, pervaporation is a promising technology due to its advantages of high energy efficiency, environmental benignity, mild operation conditions and small footprint [2–5]. More importantly, pervaporation is suitable for separation of azeotropic mixtures because it is not impeded by the vapor-liquid thermodynamic equilibrium [6].

In pervaporation, membrane is the most important part. Substantial works have focused on developing pervaporation membranes [7–10]. Polymeric membranes are widely used for pervaporation because they have reasonable separation performance. In addition, they can be fabricated easily and scaled up cost-effectively [6,11–13]. However, for polymeric membranes, there is a trade-off relationship between permeability and selectivity [14]. They are also vulnerable to the solvent-induced swelling issue that may deteriorate their separation performance. Inorganic membranes don't suffer from the swelling problem because of their superior thermal, mechanical and chemical stability [15]. Nonetheless, the fragility and high fabrication cost limit their wide applications. Mixed matrix membranes (MMMs) containing inorganic fillers and polymeric matrices were invented in 1988 by Kulprathipanja et al. to integrate the strengths of both polymeric and inorganic membranes [16]. The inorganic particles with an inherently high permeability and selectivity can help increase the separation performance, while the polymeric matrices can minimize the fragility issue and reduce the overall fabrication cost for MMMs [17–19].

Among numerous inorganic fillers, metal organic frameworks (MOFs) are regarded as a kind of promising materials due to their unique characteristics of ultrahigh porosities, tuneable chemical functionalities, controllable structures, good affinity with polymers and high adsorption capacity [20,21]. Among them, UiO-66-type MOFs have been extensively studied due to their noticeably high chemical, thermal and mechanical stability [22,23]. By altering ligands with various functional groups, one can easily manipulate the pore size and chemical characteristics of UiO-66-type MOFs [24,25]. UiO-66 functionalized with amine groups, UiO-66-NH_2 MOFs, have been widely applied in various applications [26–28]. For example, Anjum et al.

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reported that both selectivity and permeability were significantly improved by incorporating UiO-66-NH_2 into Matrimid because the amine groups inside MOF pores facilitated the CO_2 transport [26]. Nik et al. found that the existence of amine groups in UiO-66-NH_2 MOFs improved both the CO_2 permeability and selectivity in CO_2/CH_4 separation [27]. The study of Peterson et al. suggested that UiO-66-NH_2 MOFs could effectively remove nitrogen dioxide from air with the aid of amine groups [28]. In addition, UiO-66-NH_2 based membranes also show great potential for water treatment and dye removal [29,30].

Although UiO-66-NH_2 based membranes have a wide range of applications as aforementioned, there are limited studies for pervaporation [31,32]. However, none of them is related to alcohol dehydration. Therefore, the first objective of this work is to explore the feasibility of applying UiO-66-NH_2 based MMMs for alcohol dehydration. The proposed MMMs consist of 6FDA-HAB/DABA polyimide because it has a high separation factor [33]. The incorporation of UiO-66-NH_2 nanoparticles aims to improve the overall flux due to their high porosity and hydrophilic amino-functional groups. The other purposes of this work are to (1) explore the effect of functional groups of UiO-66-type MOF on alcohol dehydration and (2) investigate and compare their separation performances in three alcohol dehydration systems including isopropanol /water, ethanol/water and methanol /water as a function of MOF particle loading.

To meet the objectives, uniform UiO-66-NH_2 nanoparticles would be firstly synthesized for the fabrication of MMMs. To explain the effects of functional groups on dehydration performance, both UiO-66 and fluorine functionalized UiO-66 MOFs (referred to as UiO-66-F_4) nanoparticles would be synthesized and incorporated into MMMs for comparison. In addition, solvent uptake and positron annihilation lifetime spectroscopy (PALS) analyses would be carried out to reveal the fundamental science and mechanisms for the performance enhancement. 200-h stability tests would be carried out to study their long-term performance. This study suggests UiO-66-NH_2 based MMMs are very promising for dehydration of alcohols.

2. Experimental

2.1. Materials

For polyimide syntheses, all the information of the chemicals used has been described in detail in our previous study [33]. For MOF particle syntheses, zirconium (IV) chloride, 2-aminoterephthalic acid, tetrafluorobenzene-1,4-dicarboxylic acid, terephthalic acid and acetic acid (glacial) were acquired from Merck (Germany), Aldrich (Singapore), Matrix Scientific, Aldrich (Singapore) and Merck (Germany) respectively and used without further treatment. Dimethylformamide (DMF), methanol, ethanol, isopropanol (reagent grade or higher), from Fisher Scientific (UK), were also used as received.

2.2. Polyimide and MOF syntheses

The detailed synthesis procedures for 6FDA-HAB/DABA polyimide as well as their characterization methods can be found in our previous study [33]. Fig. 1(a) displays the chemical structure of the 6FDA-HAB/DABA polyimide where the diamine ratio of HAB to DABA was 9:1.

To synthesize UiO-66-NH_2, UiO-66 and UiO-66-F_4 nanoparticles, 0.080 g $ZrCl_4$, 0.062 g 2-aminoterephthalic acid (for UiO-66-NH_2) or 0.057 g terephthalic acid (for UiO-66) or 0.082 g tetrafluorobenzene-1,4-dicarboxylic acid (for UiO-66-F_4) and 0.6 mL acetic acid (glacial) were added into well-sealed blue cap bottles with 20 mL DMF, stirred at 100 °C (for UiO-66 and UiO-66-NH_2) or at room temperature (for UiO-66-F_4) for 24 h. After the reactions ended, the MOFs particles were separated by centrifugation and further purified by washing with fresh DMF for several times. After that, MOFs particles were immersed in fresh DMF until use. Fig. 1(b) illustrates the ligand structures of these UiO-66-type MOFs.

2.3. Preparation of MMMs

The dense flat-sheet MMMs in this study were made by the solution casting method. The 6FDA-HAB/DABA polyimide was firstly dissolved in DMF to form a 5 wt% solution, then filtered by a 5 μm PTFE syringe filter before mixing with the UiO-66-type MOF nanoparticles. The aforementioned MOF nanoparticles were sonicated in DMF for at least 1 h to avoid agglomeration and achieve a good dispersion. After that, the UiO-66-type MOFs in DMF were added into the polymer solutions and stirred for another 30 min. Subsequently, the polymer/MOF solutions were cast onto silicon wafers and dried in an oven at 80 °C to evaporate DMF slowly. The MMMs were formed and could be peeled off after a few days. Finally, the MMMs were dried in a vacuum oven at 200 °C for 12 h to eliminate the residual solvent. A Mitutoyo micrometer was used to test the thickness of the resultant MMMs.

2.4. Membrane characterizations

X-ray Diffraction (XRD) tests were conducted by an X-ray diffractometer (Bruker D8) with a radiation source of Cu K-α. The wavelength of the radiation source is 1.54 Å. A field emission scanning electron microscope (FESEM, JEOL, JSM-6700F) and an energy-dispersive X-ray spectroscopy (EDX) apparatus were applied to observe morphologies of MOFs particles and MMMs and do elemental mapping, respectively. All the FESEM samples for cross-section observations were prepared by cryogenically cracking in liquid nitrogen.

The thermal stability of MOFs particles was studied by thermogravimetric analyses (TGA) under air atmosphere using a Shimadzu Thermal Analyzer (DTG-60A/TA-60WS/FC-60A). The heating rate was 10 °C/min. The following equation was used to calculate the particle loading in MMMs:

$$Particle\ \ loading = \frac{Particle\ weight}{Particle\ \ weight + polymer\ \ weight} * 100\% \tag{1}$$

Positron annihilation lifetimes of the MMMs were measured using bulk PALS. ^{22}Na was the source of positrons and the counting rate of the system was around 165 counts s^{-1}. A description of experiment details and PALS system could be found elsewhere [4,34–40]. Three lifetime components (τ_1, τ_2 and τ_3) were obtained as raw data and the PATFIT program was used to analyze the data. The mean free-volume radius R (Å) was determined by the following equation [37–40]:

$$\tau_i^{-1} = 2\left[1 - \frac{R_i}{\Delta R} + \frac{1}{2\pi} sin\left(\frac{2\pi R_i}{\Delta R}\right)\right] \tag{2}$$

where $\tau_i = \tau_3$. It represents the o-Ps lifetime. ΔR refers to an empirical constant (1.66 Å). The fractional free volume (FFV) can be calculated by the following equation [39–41]:

$$FFV = \sum_i 0.0018 I_i \left(\frac{4}{3}\pi R_i^3\right) \tag{3}$$

where $I_i = I_3$. It represents the o-Ps intensity (%).

2.5. Solvent uptake tests

Before conducting the solvent uptake tests, the MMMs were placed in a vacuum oven overnight at 120 °C to remove the absorbed moisture. Subsequently, the pre-weighed dry membranes were weighted using a micro-balance. After that, the membranes were immersed in pure solvents including methanol, ethanol, isopropanol and water, separately. The swollen membranes were taken out from the solvents at different intervals and weighted again in a closed container after removing all solvents on the membrane surface by tissue papers. The sorption tests and measurements were continued until no prominent variations in their weights, which represented the achievement of sorption equilibrium. The following equation was used to determine the solvent uptake ratio: