Enhanced ethanol recovery of PDMS mixed matrix membranes with hydrophobically modified ZIF-90

Sheng Xu[1], Hao Zhang[1], Fen Yu, Xiaoxu Zhao, Yan Wang*

Key Laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Wuhan 430074, China
Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT

In this study, dodecylamine-modified zeolitic imidazolate framework-90 (DLA-ZIF-90) particles with enhanced surface hydrophobicity are synthesized and incorporated into the polydimethylsiloxane (PDMS) matrix to fabricate novel PDMS/DLA-ZIF-90 mixed matrix membranes (MMMs) for ethanol recovery via pervaporation. The successful modification of ZIF-90 particles is investigated via various characterization techniques. The morphology and physicochemical properties of the PDMS/DLA-ZIF-90 MMMs are studied and characterized. Compared to the PDMS MMM with unmodified ZIF-90, PDMS/DLA-ZIF-90 MMM exhibits enhanced morphology homogeneity and separation performance, contributed by the flexible inner channels of ZIF-90-DLA particles with enhanced adsorption selectivity, as well as the improved affinity between ZIF-90-DLA particles and PDMS matrix. The MMM with 2.5 wt% DLA-ZIF-90 loading shows the best performance with the optimal flux of $99.5 \, \mathrm{g \, m^{-2} \, h^{-1}}$ and corresponding separation factor of 15.1 at 60 °C. The effect of operation temperature is also studied. The performance benchmarking shows that PDMS/DLA-ZIF-90 MMM exhibits superior pervaporation performance to most other PDMS-based membranes, and may therefore shed valuable insights to the development of high-performance ZIF-based MMMs for organic recovery.

1. Introduction

As one of the most valuable biofuel, ethanol is mainly generated from the biomass fermentation, which however faces two main bottleneck problems [1–3]. On one hand, the fermentation process may be terminated by the relatively high concentration of ethanol in the fermentation broth. On the other hand, the as-produced ethanol needs to be further purified from the fermentation broth to generate a high-quality ethanol product. Obviously, efficient separation processes for ethanol recovery is needed to address the above two issues. The conventional separation technologies, such as adsorption and distillation, usually need a high energy consumption and may lose the separation efficiency for liquid mixtures with close boiling points [4–6]. Alternatively, pervaporation, a promising membrane-based separation technology for ethanol recovery, exhibits its unique advantages of low operation cost, easy operation and high separation efficiency [7–10].

Based on the solution-diffusion mechanism, the heart of a pervaporation process is the suitable high-performance membrane, which is supposed to possess the superior permeability and selectivity, good mechanical stability and excellent durability [11]. For the organic recovery, hydrophobic polymers have long been established as the pervaporation membrane material because of their high chemical stability and desirable membrane-forming ability [7,9]. However, pristine hydrophobic polymeric membranes usually face low separation factors, and the "trade-off" phenomena between the flux and the separation factor [12]. Therefore, various modification routes have been developed to improve their physicochemical properties and separation performance, such as blending [13], crosslinking [14], and filler incorporation [15,16]. Among them, the incorporation of porous fillers into the polymer matrix could be an effective strategy to solve the above issues, for their rigid and porous structures [17–21].

Metal-organic frameworks (MOFs), as one class of porous fillers, possess tunable structures and favorable affinity with the polymer matrix as compared to most traditional inorganic particles [22–25]. They are therefore widely employed for the fabrication of mixed matrix membrane (MMM) by being incorporated into polymeric membrane, such as polydimethylsiloxane (PDMS) [26] polymethylphenylsioxane [27], and poly(ether block amide) [28]. However, the composite

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membranes fabricated by unmodified MOFs generally face severe particle aggregation and interface defects. To address this issue, one effective solution is to alter the particle addition route into the polymer matrix by the simultaneous spray self-assembly [29] or interfacial synthesis [30], to achieve the homogeneous membrane morphology and excellent pervaporation performance. Another strategy to enhance their affinity with the polymeric matrix could be physical or chemical modifications of MOF particles. Previous works showed that, zeolitic imidazolate framework (ZIF) particles physically pretreated with a hydrophilic sulfonated polyethersulfone primer [31] or polydopamine [32], could have the enhanced affinity with polyimide chains, contributing to the desirable performance of the MMM for pervaporation dehydration. In our recent work [33], by the chemical modification of ZIF-8 particles with ethanediamine, hydrogen bonding interactions between modified ZIF-8 and poly(vinyl alcohol) (PVA) chains could be formed, which therefore restricts the particle aggregation and improves the affinity of ZIF-8 particles with PVA chains, resulting in the enhanced membrane homogeneity and separation performance of the obtained MMM as compared to the MMM loaded with unmodified ZIF-8 particles.

It is clear that, all above modifications are on the hydrophilic enhancement of ZIF particles for the fabrication of pervaporation dehydration membranes. However, to the best of our knowledge, no study has been reported on the hydrophobic modification of ZIF particles to fabricated MMMs for pervaporation recovery of organic solvents.

In this study, the hydrophobic modification of ZIF-90 particles by dodecylamine (DLA) was performed to fabricate novel PDMS/DLA-ZIF-90 MMMs for ethanol recovery via pervaporation for the first time. ZIF-90 particles are selected for the following three factors. Firstly, ZIF-90 particles are porous and flexible, which can provide the promoted transport channels for both water and ethanol [34]. Secondly, ZIF-90 particles are relatively hydrophobic, which shows a certain adsorption selectivity towards ethanol [34]. Thirdly, ZIF-90 with aldehyde groups can be easily modified via the imine reaction; after the hydrophobic modification by DLA, ZIF-90 particles show a much higher adsorption selectivity towards ethanol and a better compatibility with PDMS chains, which may contribute to an improved separation factor of PDMS membrane. The morphology and physicochemical properties of DLA-ZIF-90 particles and resultant MMMs are studied by various characterizations. The properties and the separation performance of pristine PDMS membrane, PDMS/ZIF-90 and PDMS/DLA-ZIF-90 MMMs are investigated. The effects of DLA-ZIF-90 loading and operation temperature on the separation performance of PDMS/DLA-ZIF-90 are also carried out.

2. Experimental

2.1. Materials

Poly (vinylidene fluoride) (PVDF) was obtained from Alfa Aesar. PDMS (Sylgard® 184 Silicone Elastomer) and the corresponding curing agent were purchased from Dow Corning. Sylgard® 184 Silicone Elastomer consists of the vinyl-terminated oligomeric dimehtylsiloxanes and platinum-based catalyst, while the curing agent is the crosslinker with functional -SiH groups. The PDMS networks of Sylgard® 184 is formed by a hydrosilylation reaction between the vinyl-terminated oligomeric dimehtylsiloxanes and the crosslinker. Imidazole-2-carboxaldehyde (ICA), zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O) and DLA were all purchased from Aladdin. N,N-dimethylformamide (DMF), N-methyl pyrrolidone (NMP), methanol (MeOH), ethanol (EtOH) and n-hexane of analytical purity and hydrochloric acid of 36.0–38.0 wt% were provided by Sinophatm Chemical Reagent Co., Ltd. The deionized water was generated in lab by Wuhan PinGuan Ultrapure LAB system with a resistivity of 18.25 MΩ cm. All reagents were used as received unless otherwise stated.
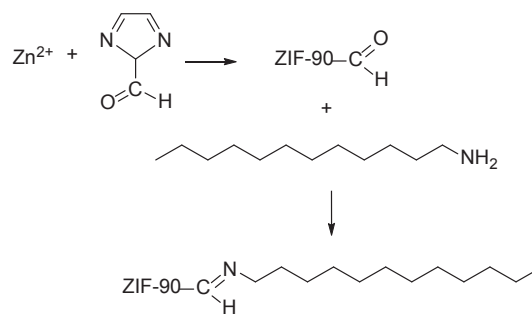
Scheme 1. Schematic diagram of synthesis and DLA modification of ZIF-90 particles.

2.2. Synthesis and modification of ZIF-90 particles

ZIF-90 crystals were synthesized according to a previous work [31]. Firstly, ICA/DMF and Zn(CH$_3$COO)$_2$/DMF solutions were prepared separately, by dissolving ICA (0.845 g) or Zn(CH$_3$COO)$_2$·2H$_2$O (0.964 g) in the solvent DMF (50 mL) at 65 °C for 1 h, followed by the filtration with 1.0 μm PTFE syringe membrane filter. Subsequently, Zn (CH$_3$COO)$_2$/DMF solution was rapidly added into the ICA/DMF solution and stirred at ambient temperature for 4 h to form a stable particle suspension. The product was collected by centrifugation (10000 rpm, 15 min) and further washed with fresh DMF and MeOH for three times to remove the unreacted components. The as-synthesized ZIF-90 particles were finally dried at 80 °C under vacuum for 24 h.

For DLA modification, the as-prepared ZIF-90 particles (DLA-ZIF-90) were added in 10 wt% DLA/MeOH solution, and refluxed at 60 °C for 30 min. After that, DLA-ZIF-90 particles were recovered by centrifugation (10000 rpm, 10 min), washed with MeOH for three times, and dried completely in the vacuum oven at 80 °C for 24 h. The reaction mechanism was shown in Scheme 1, where DLA was grafted to the ZIF-90 via imine condensation. The mass loading of DLA in DLA-ZIF-90 is about 4 wt%, estimated by the residue weight of zinc oxide from the combustion of ZIF-90 and DLA-ZIF-90 particles under air atmosphere [31].

2.3. Membrane preparation

The PVDF membrane was fabricated by the non-solvent induced phase inversion process. The 15 wt% casting solution was prepared by dissolving PVDF in NMP under magnetic stirring at 50 °C for 72 h. After degassed in vacuum oven at room temperature overnight, the solution was cast onto a clean glass plate using a casting knife with the thickness of 150 μm at room temperature. The as-cast solution layer was then quickly placed into a water coagulation bath to induce the phase-inversion separation. Subsequently, the as-fabricated membrane was immersed in the deionized water for 24 h and then dried under vacuum at 60 °C overnight. The PVDF membrane was used as the support for the preparation of PDMS MMMs.

For the fabrication of PDMS MMMs, a certain amount of ZIF-90 or DLA-ZIF-90 particles (0–5 wt% of PDMS mass weight) were added into the 60 wt% PDMS/hexane solution, stirred for 12 h vigorously and sonicated for 2 h to minimize particle aggregation. Subsequently, the curing agent (10 wt% of PDMS) was added in the above solution under magnetic stirring at 60 °C for another 2 h to form a viscous solution. After degassed overnight, the mixed solution was cast onto the PVDF substrate with a casting knife at a thickness of 150 μm, and dried at 60 °C overnight under vacuum. The as-fabricated MMMs were annealed at 100 °C for another 6 h to remove the retained solvent completely. The pristine PDMS membrane is denoted as PDMS. And PDMS MMMs with ZIF-90 or DLA-ZIF-90 were denoted as PDMS/ZIF-90-m or PDMS/DLA-ZIF-90-m, where m (wt%) is the weight percentage of ZIF-90 or DLA-ZIF-90 to PDMS.