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Screening criteria and design principles for porous materials based mixed matrix pervaporation membranes

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ABSTRACT

Porous materials based mixed matrix pervaporation membranes have been paid much attention in recent years. Porous materials and polymers determine the pervaporation performance. In this short review, the screening criteria and design principles for porous materials and polymer for achieving anti-trade-off effects in solvent dehydration, organophilic pervaporation, and organic-organic mixtures separation are concluded and discussed respectively.

Keywords: Porous materials; Mixed matrix membranes; Pervaporation; Review; Screening criteria

1. Introduction

Pervaporation (PV), as a promising technology for liquid separation, possesses mild operating conditions, low energy consumption, environmental friendliness, and high separation efficiency [1]. PV has been widely employed for the removal of minor component from liquid mixture such as dehydration of organic solvents, removal of organics from aqueous solutions, and separation of organic-organic mixtures, demonstrating incomparable advantages especially in the separation of heat-sensitive, close-boiling, and azeotropic mixtures [2].

In PV, the feed liquid mixture contacts one side of a membrane, and vacuum or a sweep gas is applied at the permeate side of the membrane to generate a chemical potential difference [3]. Separation is achieved by the difference in sorption and diffusion of components in membranes [4]. Polymer membranes are usually employed in PV, whereas the swelling and plasticization of membranes often lead to the trade-off effects between separation factor and permeation fluxes, or deteriorated PV performance. Therefore, mixed matrix membranes (MMMs), composed of polymer and fillers (Fig. 1), emerged to enhance the permeation flux, selectivity and stability. The fillers include particles and porous materials. Particles are intrinsically impermeable and can alter the molecular packing of the polymer chains and thus affect the permeability and selectivity [5]. Porous materials, such as porous silica, zeolites, carbon molecular sieves (CMS), metal-organic frameworks (MOFs), polyhedral oligomeric silsesquioxane (POSS), covalent organic frameworks (COFs), carbon nanotubes (CNTs), etc., have gained more attention because the porous structure provide enormous and permanent channels for permeation through the membranes [6].

Apparently, the porous materials and polymers determine the PV performance of MMMs. In contrast to a trial-and-error approach, the rational screening and design of porous materials and polymers can avoid large amounts of tedious experiments and improve the pervaporation performance more effectively. Almost all of the properties of porous materials and polymers, including stability, hydrophobicity/hydrophilicity, pores size or free volume fraction, and functional groups, should be considered in the screening [2].

There is no doubt that the stability of porous materials and polymers in liquid should be firstly considered. For examples, triazole-, imine and hydrazone-based COFs are highly stable in water and most organic solvents, whereas the boron containing COFs are non-stable to polar media. Porous aromatic frameworks (PAFs), as a subclass of COFs, composed of tetrahedrally connected aromatic moieties, are prepared by irreversible cross-coupling reactions, and

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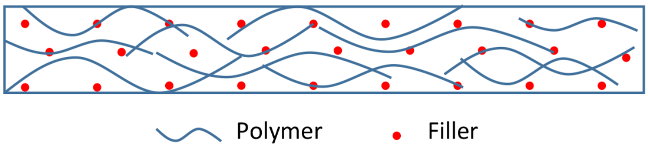

Fig. 1. Mixed matrix membranes.

display strong stability. Porous organic cages without imine linkages show high stability to water, or even to acids and bases [7].

Although there are several excellent reviews about MMMs [8,9], the criteria and principles of porous materials and polymers have not been addressed and concluded clearly. The synergy between sorption and diffusion should be considered for achieving anti-trade-off effects between separation factor and permeation fluxes. In this short review, the general screening criteria and design principles for porous materials and polymer in solvent dehydration, organophilic pervaporation, and organic-organic mixtures separation are concluded and discussed respectively for the first time.

2. MMMs for solvent dehydration

Solvent dehydration is important in the production of solvents, and we concluded three criteria for screening porous materials and polymers.

(1) Hydrophilic polymers or polymers with stiff structure. Hydrophilic polymers possesses high sorption centers (e.g. polar sites, charged sites) for water [10], and can interact with water by dipole-dipole, hydrogen bonding and/or ion-dipole interactions. Thus, hydrophilic polymers, such as cross linked poly (vinyl alcohol) (PVA), chitosan, polyacrylonitrile (PAN), poly electrolyte, etc., are usually used for dehydration to achieve sorption selectivity for water [11]. The polar groups in the membrane matrix act as the fixed carriers for mass transport in the membrane [1]. PVA membranes are the representative hydrophilic membranes especially for the industrial applications. The ideal structure for high fluxes appears to be one containing discrete domains of oppositely charged species with optimal size [12]. The PV performance is related to the cross linking degree and heat treatment of membranes, which affect the crystallinity and micro structure. Non-polar and low polar membranes (e.g. polystyrene and poly (vinyl chloride) often show relatively low separation factors and fluxes [11]. Recently, polymers with stiff and rigid chains have been paid attention to, and these polymers can improve the diffusivity selectivity of membranes in dehydration [3]. For examples, for the hydrophobicic perfluoropolymer, polybenzoxazole (PBO), polybenzoxazinone (PBOZ), and polybenzimidazole (PBI), polyimide (PI), etc., size exclusion is considered as the dominant separation mechanism in dehydration.

(2) Hydrophilic porous materials with small pores size. The hydrophobicity of porous materials can be predicted by hydrophobic constants [13], and determined by experimental and computational studies based on the heat of water adsorption or water uptake at low pressure [14]. As the dynamic diameter of water molecule (0.27 nm) is smaller than that of organic molecules (e.g. ethanol, 0.43 nm; n-butanol, 0.50 nm; benzene, 0.526 nm; cyclohexane, 0.606 nm), hydrophilic porous materials with pores size larger than water molecule while smaller than organic molecules are preferred to favor the sorption and diffusion selectivity towards water. It was reported that zeolite 4A and 13X enhanced both flux and selectivity of sodium carboxymethyl cellulose (NaCMC) and PVA in dehydration of ethanol [15]. Ag-exchanged NaY zeolite incorporated PVA/PAA cross linked membranes displayed improved PV performance due to the increased hydrophilicity of NaY zeolite after Ag-exchange [16]. The pores size of porous materials can tune by confining a third agent (e.g. ionic liquid) in the pores or employing mixed linkers [17]. It is worth noting that, the pores, especially the mesopores, may be blocked by the polymer chains during MMMs fabrication, leading to the probable decrease of membrane permeability and increase in selectivity.

(3) Strong porous materials/polymer interactions. Strong porous materials/polymer interactions can eliminate the inter facial defects and improve the structural rigidity of membranes, and thus enhance the diffusion selectivity for water. The incorporation of fillers can influence the aligned packing of polymer chains and then the free volume via the fillers' steric effect and inter facial interaction effects. The chemical structure of porous materials determines the interactions of porous materials with polymer and components. In comparison with inorganic fillers, MOFs and COFs display better compatibility with polymer matrix due to the presence of organic ligands or linkers. Using porous materials with chemical structure similar to polymer units or structure interacting strongly with polymer may eliminate interface defects and improve compatibility and selectivity. For instance, MOFs with amino and hydroxyl groups can form hydrogen bonds with many polymers such as PVA, PAN, and PI [18].

To introduce functional groups on porous materials, using of a functionalized ligand in synthesis, or post-synthetic modification can be adopted. For examples, MIL-53 (Al)-NH_2 nanocrystals were modified with heptanoic anhydride, valeric anhydride and formic acid (Fig. 2). With the decreased hydrophobic constants of the surface substitutes, the MOFs hydrophilicity and interactions with PVA matrix increased, and the water permeance and water/ethanol selectivity increased in

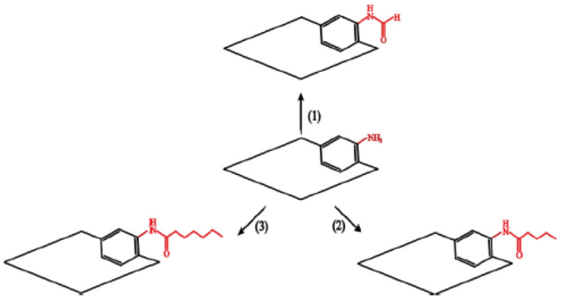

Fig. 2. Modification of MIL-53-NH$_2$ with formic acid (1), valeric anhydride (2) and heptanoic anhydride (3).

pervaporation of 92.5 wt% ethanol, and the PV performances were successfully tuned from trade-off to anti-trade-off effects between flux and separation factor [19]. By altering the organic linkers (1,4-benzenedicarboxylate acid, 2-hydroxyterephthalic acid, 2,5-dihydroxyterephthalic acid, and biphenyl-4,4-dicarboxylate), UiO-66, UiO-66-OH, UiO-66-(OH)$_2$ and UiO-67 were prepared, and anti-trade-off effects were demonstrated for UiO-66, UiO-66-OH and UiO-66-(OH)$_2$ PVA MMMs in PV of 90 wt% ethanol solution [20]. For zeolites, there are abundant hydroxyl groups on surface, and silylation reactions are usually employed for surface modification to enhance the zeolite/polymer interactions [21].

In a word, in solvent dehydration, water should be preferentially dissolved and transported in the hydrophilic MMMs, and the PV process is co-controlled by sorption and diffusion selectivity.

3. MMMs for organophilic pervaporation

Organophilic pervaporation is used for the removal of dilute organic compounds from aqueous streams, such as recovery of bio-alcohols from a fermentation broth, wastewater treatment, etc. Three criteria for screening porous materials and polymers should be followed for achieving anti-trade-off effects.

(1) Hydrophobic polymer. To enhance the sorption selectivity for organics, hydrophobic polymers, such as polydimethysiloxane (PDMS), poly(octylmethyl siloxane)(POMS), poly[1-(trimethylsilyl)-1-propyne](PTMSP), poly(vinyltriethoxysilane) (PVTES), polyether-block-amide (PEBA), polybenzimidazole (PBI), etc. are usually employed [22]. PDMS has been known as the most representative organophilic membrane materials with stable separation performance and cost-effective preparation. PTMSP, as a glassy polymer, is more permeable than PDMS, but PTMSP undergoes physical and/or chemical aging during the pervaporation process, leading to deteriorated separation performance [23]. It was reported that alkyl chains and CF$_3$ groups are alcohol-philic and water-repellency groups for pervaporation, and the interactions between these groups and alcohols weaken the coupling effect between alcohol and water molecules, and thus inhibit the diffusion of water along with alcohol [24,25]. To introduce the alkyl or CF$_3$ groups, Singh et al. introduced alkyl and perfluoroalkyl chains in PDMS membrane by utilizing n-octadecyltrichlorosilane and trichloro (1H,1H,2H,2H-perflourooctyl) silane as cross linkers [26]. Covalent grafting and co-polymerization are also utilized for improving the hydrophobicity of membranes [27].

(2) Hydrophobic porous materials with large pores size. Hydrophobic porous materials(e.g.silicalite-1, MOFs, COFs, PAFs, etc.) with pores size larger than water and organic molecules are preferred so that the porous materials favor the sorption of organics and simultaneously do not restrict the diffusion of organics. As an opposite example, in the separation of ethyl acetate from aqueous solutions, ZSM-5/PEBA displayed enhanced separation factor while declined fluxes [28] because of the small pore size of ZSM-5 (0.5 nm). It is worth emphasizing that the reversible gate-opening effects of MOFs should be addressed in considering the pores size. Some MOFs with small or comparable aperture size, such as ZIF-8, ZIF-71, ZIF-67 (aperture size of 0.43 nm), were used for organophilic pervaporation [29,30]. The high degree of flexibility of MOFs hinders the potential for shape-based molecular separation [31].

For instances, the butanol selectivity of PDMS membrane was increased over 2 times by the addition of silicalite-1 [32]. With the addition of 5 wt % CNTs, the flux of PEBA membrane was increased from 85 to 139 g m^{-2} h^{-1} with a constant separation factor of 18 [33]. In the PV of 4 wt% n-butanol solution, PAF-11/PDMS membranes (3 wt% loading, 28°C) displayed separation factor of 14.02 (increased 40.7 % in comparison with that of pristine PDMS) and flux of 2255 g m^{-2} h^{-1} (increased 10.8%) due to the hydrophobicity and large pores size (0.5–1.2 nm) of PAF-11 [34]. The permeation flux and separation factor of PAF-56/PDMS MMMs increased with the decreased PAF-56 particles size at the same loading. For MMMs with PAF-56 size of 0.83 μm and 2.5 wt% loading, the n-butanol permeance and selectivity were 156404 GPU and 23.2, increased by 203% and 238% respectively in comparison with that of pristine PDMS membranes. It was concluded that the hydrophobicity and larger pore size (1.2 nm) of PAF-56 favor the sorption and diffusion of alcohols [35]. In-situ prepared COF-LZU1 (pore size of 1.8 nm) in poly (ether-*block*-amide) membranes greatly improved the homogeneous dispersion of COFs, and the MMMs exhibited higher n-butanol/water sorption selectivity and pervaporation selectivity in comparison with that prepared by conventional blending methods [36].

(3) Relatively weak porous materials/polymer interactions. The relatively weak porous materials/polymer interactions favor the formation of loose micro structure of MMMs and then the diffusion of large organic molecules. However, too weak interactions may result in inter facial voids, agglomeration of fillers, and then large inter-filler channels and deteriorated selectivity [37]. Generally speaking, organophilic pervaporation should be a sorption selectivity dominated process.

4. MMMs for organic-organic mixtures separation

Organic-organic mixtures separation, e.g. benzene/cyclohexane, benzene/hexane, methyl *tert*-butyl ether (MTBE)/methanol, dimethyl carbonate (DMC)/methanol, ethylbenzene/xylene, etc., is crucial for chemical industries. Nevertheless, pervaporation saw least advance in the organic-organic separation over the past decades. Three criteria for screening porous materials and polymers are proposed as follows for breaking the trade-off effects.

(1) Polymer with special interactions with target compound. The special interactions can improve the sorption selectivity for the target compound. For the separation of aromatic and aliphatic compounds, the aromatics have delocalized π electrons and can be polarized under the induction of polar groups. Therefore, the membrane materials containing polar groups such as polyimide, display more preferential permeation for aromatics [38,39]. Blended membranes often show good balance between the permeation flux and separation factor. Glassy polymers can suppress the plasticization effects of the penetrants, and are generally more shape and size-selective [1].

(2) Porous materials with optimized pores size and special affinity to target compound. For small target molecule, the pores size of porous materials should be larger than the target molecule while smaller than the rejected one. For large target molecule, the pores size should be larger than the target and rejected molecules. For example, in the separation of toluene/n-heptane mixture (1:1), $Cu_3(BTC)_2$/PVA (BTC=benzene-1,3,5-tricarboxylate) membranes were fabricated on a ceramic tubular substrate. Compared with the pristine PVA membrane, the separation factor and permeate flux improved from 8.9 and 14 g m^{-2} h^{-1} to 17.9 and 133 g m^{-2} h^{-1} respectively due to the affinity of toluene to $Cu_3(BTC)_2$ as well as suitable pores size of $Cu_3(BTC)_2$ (0.56 nm) [40]. On the other hand, the affinity to target compound should be not be too strong. In the pervaporation of isooctane/toluene, the addition of graphene oxide (GO, 0.5 wt%) increased the affinity of membranes to aromatics and the selectivity increased to about four times while the permeation flux decreased because the GO/toluene interaction resulted in increased swelling [41].

(3) Optimized porous materials/polymer interactions. The proper porous materials/polymer interaction can be determined in term of the dynamic size of components. When the target molecule is small, the porous materials/polymer interactions should be strong so that the target molecules can permeate through while the others are rejected, favoring the diffusion selectivity. When the target molecule is large, the porous materials/polymer interactions should be relatively weak so that the target molecules can also permeate through the membranes, and the PV process is controlled by sorption-selectivity. The porous materials/polymer interactions can be characterized by molecular spectra (e.g. FTIR) and free-volume fraction [42]. Tuning the fractional free volume of membranes can effectively improve the diffusion selectivity.

Table 1
General screening criteria and design principles for porous materials and polymer

	Polymer	Porous materials	Porous materials/ polymer interactions	Process controlling factors
Solvent dehydration	Hydrophilic (e.g. PVA, PAN, PI, poly electrolyte, etc.) or polymers with stiff structure	Hydrophilic with small pores size (e.g. zeolite, UiO-66, UiO-66-OH, UiO-66-(OH)2, etc.)	Strong	Sorption and diffusion selectivity
Organophilic pervaporation	Hydrophobic (e.g. PDMS, POMS, PTMSP, etc.)	Hydrophobic with large pores size (e.g. silicalite-1, CNTs, COFs, PAFs, etc.)	Relatively weak	Sorption selectivity
Organic-organic separation	Special interactions with target compound	Optimized pores size and special affinity to target compound	Optimized interactions	Sorption and diffusion selectivity

Table 1 gives the summary of the general screening criteria and design principles for porous materials and polymer for achieving anti-trade-off effects between separation factor and permeation fluxes.

5. Conclusion and outlook

Porous materials based membranes exhibit great potential for achieving outstanding pervaporation performances due to the ease of design and modification of porous materials as well as the porous materials/polymer interactions. In the future research, the following issues may be paid more attention to: (1) Design and preparation of novel porous materials with high stability. (2) Aligning porous materials with 1D pores (such as 2D COFs, nanotubes) in polymers to improve the mass transfer. (3) Increasing the loading of porous materials to form more continuous diffusion channels. (4) Design and tuning porous materials/polymer interactions and micro-structure of membranes. (5) Exploring synergistic effects of porous materials and polymer. (6) Long-term running stability of MMMs, etc.

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