Pervaporation membrane materials: Recent trends and perspectives

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A R T I C L E   I N F O

Keywords:
Pervaporation
Polymeric membrane
Inorganic membrane
Mixed-matrix membrane
Two-dimensional-material membrane

A B S T R A C T

Pervaporation is a molecular separation membrane technology for selective permeation of water or organic compounds from organic-water mixtures or organic-organic mixtures. The pervaporation process is controlled by thermodynamic partitioning and kinetic mobility of molecules in the membrane. The chemical property and morphology of membrane materials can be engineered to tailor the complementary sorption and diffusion coefficients and selectivity, and thus the permeability (or flux) and selectivity (or separation factor). In this review, we highlight the latest progresses of pervaporation membrane materials, including pure polymeric membranes and inorganic membranes, as well as mixed-matrix membranes and emerging two-dimensional-material membranes. Challenges and future opportunities in materials design, fabrication and structure-performance relationship are identified to develop next-generation pervaporation membranes with enhanced separation efficiency.

1. Overview of pervaporation membranes

The energy required for separation process is about half of the total energy consumption in chemical industry [1]. It is increasingly important to develop energy efficient separation processes including membrane technology [2–4]. Pervaporation is a separation process in which liquid contacts the feed side of a semi-permeable membrane, and vapor emerges from the permeate side of the membrane by using either vacuum or a sweep gas to generate a chemical potential difference as the driving force [5]. The separation property of pervaporation process relies on the preferential sorption and diffusion of the components in the membrane. Therefore, the pervaporation process can overcome the limitation of thermodynamic vapor-liquid equilibrium (VLE) and consume less energy as only the latent heat of evaporation is required compared with conventional distillation technology [6]. A third component that is added as an entrainer to alter the VLE behavior in distillation can be also eliminated in pervaporation process to prevent contamination of the final products. In addition, pervaporation technology is favorable for purification of thermally sensitive organics such as aromatic substances in food industry [7].

The origins of pervaporation can be traced to the 1910s when Kober proposed the term of “pervaporation” from “permeation” and “evaporation” of selective transport of water through collodion or parchment [8]. Binning and coworkers at American Oil conducted initial systematic investigations on pervaporation process for the separation of organic mixtures in the 1960s [9]. Other lab-scale pervaporation experiments were also carried out by academic researchers such as Aptel and Néel at University of Toulouse [10]. Until the 1980s, with the advance of membrane material and module, the commercialization of pervaporation process was realized by Gesellschaft für Trenntechnik (GFT) company (now owned by Sulzer Chemtech). The pervaporation membrane prepared by casting a crosslinked polyvinyl alcohol (PVA) layer on a porous poly (acrylonitrile) (PAN) support was applied for dehydration of ethanol [11]. By the 2010s Sulzer installed over 200 small pervaporation plants and most of them were used to dehydrate solvents such as ethanol and isopropanol produced in pharmaceutical and fine chemicals industries [3].

Pervaporation is suitable for separation of liquid mixtures containing small molecules such as water and organic solvent. Until now, solvent dehydration is still the majority of both academic and industrial research on pervaporation process, which can break the azeotropes (e.g., alcohol/water) based on water affinity and size discrimination effect of a hydrophilic membrane rather than addition of entrainer. In recent two decades, pervaporation has been widely studied for separation of small amounts of volatile organic compounds (VOCs) from water [12]. Main focus of this aspect is recovery of bio-alcohol (e.g., ethanol, butanol) from aqueous solution using hydrophobic pervaporation membranes. It can not only enrich alcohol product, but also reduce the inhibition effect.

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https://doi.org/10.1016/j.memsci.2021.119557
Received 30 April 2021; Received in revised form 22 June 2021; Accepted 24 June 2021
Available online 26 June 2021
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of alcohol on microbial growth to enhance alcohol productivity when applied in a fermentation process. Despite of great challenge in membrane selectivity and stability, separation of organic/organic mixtures with close physicochemical properties (aromatic/aliphatic) that is a key and energy intensive process in chemical industry, has also been explored by pervaporation process [13].

Mass transport through pervaporation membrane generally follows solution-diffusion model that is also widely applied for reverse osmosis and gas separation membranes [14]. Specifically, components are adsorbed from the feed liquid into the membrane and then diffuse through the membrane as vapor phase in the permeate side. Different from membrane filtration processes primarily based on hydrodynamic sieving effect, pervaporation process involving molecular separation is controlled by thermodynamic partitioning (sorption coefficients) and kinetic mobility (diffusion coefficients) [15]. The permeability \( P_i \) is the product of the sorption coefficient \( S_i \) and diffusion \( D_i \) in the membrane:

\[
P_i = S_i \times D_i
\]

The sorption coefficient \( S_i \) can be obtained by the sorption measurement of membrane materials under the identical conditions of pervaporation process. The diffusion coefficient \( D_i \) can be calculated by \( P_i/S_i \) or measured by inverse gas chromatography technique or time-lag method involving a mass spectrometer to analyze the vapor permeating through the membrane. The selectivity \( \alpha \) is the ratio of the permeability \( P \) or permeance \( P/l \) of components \( i \) and \( j \):

\[
\alpha = P_i/P_j = (P_i/l)/(P_j/l)
\]

Like gas separation membrane, the permeability and selectivity reflect the intrinsic transport property of pervaporation membrane materials [16]. In experimental, the productivity of pervaporation membrane is evaluated by measuring the weight of permeate \( W \) within a given period \( t \) and membrane area \( A \) to obtain the total flux \( J \):

\[
J = W/(A \times t)
\]

The permeation flux of a component \( J_i \) through pervaporation membrane is direct proportion to the permeability \( P_i \) and driving force (gradient of partial vapor pressure across the membrane, \( \Delta p_i \)) whereas is inversely proportional to the membrane thickness \( l \):

\[
J_i = P_i \times \Delta p_i/l
\]

The separation efficiency of pervaporation membrane is characterized by separation factor \( \beta \):

\[
\beta = (y_j/y_i)/(x_j/x_i)
\]

or enrichment factor \( E \):

\[
E = y_i/x_i
\]

in some cases, where \( x \) and \( y \) are weight percent of components \( i \) and \( j \) in the feed and permeate, respectively.

According to the solution-diffusion model, both the chemical property (e.g., affinity of functional groups) and morphology (e.g., cavity size, membrane thickness) of pervaporation membrane can be engineered to tailor the complementary sorption and diffusion coefficient and selectivity, and thus the permeability (or permeation flux) and selectivity (or separation factor). Apparently, both the intrinsic property and fabrication approach of membrane materials play critical roles in determining the separation performance of pervaporation membrane. Affinity and size sieving property are two main criteria to identify suitable membrane materials for pervaporation separation of given mixtures. Generally, hydrophilic pervaporation membranes are used for solvent dehydration, namely selective permeation of water from solvent-water mixtures; hydrophobic pervaporation membranes, which are usually organophilic, are used for solvent recovery, namely selective permeation of solvent from solvent-water mixtures. The size sieving effect of pervaporation membranes could promote the diffusion selectivity of components with smaller molecular size (e.g., water) over

Fig. 1. Pervaporation process and transport channels created by various membrane materials.
larger molecular size (e.g., solvent), which is the case of solvent dehydration.

In recent decade, there are several comprehensive reviews related to pervaporation separation, with emphasis on one or a few specific kinds of membrane materials [17–21] or specific applications [6,22,23]. It is necessary to provide an overview of the state-of-the-art membrane materials for pervaporation. To serve this purpose, this Review Article focuses on membrane materials recently developed for pervaporation separation technology (Fig. 1). They include pure polymeric membranes and inorganic membranes, as well as mixed-matrix membranes and emerging two-dimensional-material membranes. Continuing progresses are highlighted and future opportunities are identified in developing next-generation pervaporation membranes with enhanced separation efficiency.

In Section 2, polymers, the largest family of membrane materials for pervaporation, are discussed in terms of the relationship between materials affinity and separation system: hydrophilic polymers for solvent dehydration, hydrophobic polymers for organic recovery and polymers for organic-organic separation. The next section reviewed inorganic membranes that show higher pervaporation performance than polymeric membranes owing to the highly connected and relatively rigid transport channels. With the development of microporous crystalline materials, inorganic pervaporation membranes have been sequentially synthesized by zeolite, silica, metal-organic framework (MOF) or covalent-organic framework (COF). In addition to the conventional polymeric and inorganic membranes, Section 4 introduced a new family of membrane materials for pervaporation: two-dimensional (2D)-material membranes possessing interlayer channels (e.g., graphene oxide) or in-plane pores (e.g., COF nanosheet) for molecular transport. The atomic thickness of 2D material offers great opportunities to fabricate ultra-thin membrane layer and precisely tune the channel size. In comparison to the above pervaporation membranes made by a single type of material, Section 5 discusses the hybrid mixed-matrix membrane (MMM) combining inorganic materials or 2D materials as fillers in a polymer matrix. The filler endows the membrane with high performance and the matrix offers good membrane processability. Based on the recent progresses, the last section gives conclusions and perspectives in pervaporation membrane materials from the aspect of design, fabrication and application.

2. Polymeric membranes

Polymeric membranes for pervaporation separation are mainly based on the preferential absorption of polymers towards the components and the diffusion through the free volumes of the polymers. Generally, affinity is the first criterion to screen polymers for pervaporation membrane. Size discrimination effect of the free volume cavities provides additional contribution to the permeation of small-sized molecule (e.g., water) over large-sized one (e.g., organics). According to the affinity, hydrophilic polymers and hydrophobic polymers are used to develop membranes for selective permeation of water over organics and organics over water, respectively. There is a large number of hydrophilic polymers for pervaporation membranes, such as poly (vinyl alcohol) (PVA), polyelectrolyte complex (PEC), polyamide (PA) and polyimide (PI). By contrast, the number of hydrophobic membranes identified for pervaporation is much less than hydrophilic pervaporation membranes, because limited hydrophobic materials are available and only a few of them, mainly including polydimethylsiloxane (PDMS) and poly (ether-block-amide) (PEBA), can be formed into suitable pore structures for molecular separation. For pervaporation separation of organic-organic mixtures, hydrophilic PI and hydrophobic PEBA are both studied. The affinity of polymers towards one organic over the other is still the dominant factor for the separation, and the membrane stability in the organic mixtures is another key point.

2.1. Hydrophilic polymers

Hydrophilic polymeric membranes are suitable for selective removal of water from organic solvent (i.e., pervaporation dehydration of solvent). The hydrophilicity favors preferential sorption towards water over organic solvent and the diffusivity of water is faster than organic solvent with larger molecular size. One of the first commercialized pervaporation membrane materials is PVA, which remains the benchmark polymer of hydrophilic membranes for solvent dehydration [24]. The hydrophilicity of PVA comes from the pendant hydroxyl groups while semicrystalline structure is resulted from the two carbon atoms in the backbone of PVA. Therefore, despite of excellent perm-selectivity towards water, PVA membrane exhibits relatively low permeation flux (usually less than 300 g/m²h). On the other hand, PVA is water soluble, causing the membrane swelling in aqueous solution, which can be suppressed by various crosslinking approaches but with a loss of permeation flux [6]. Blending PVA with other hydrophilic polymers with less compact structure (e.g., chitosan, CS [25]; sodium alginate, SA [26]) was demonstrated to reduce the crystallinity of PVA and thus improve the permeation flux of PVA membrane. Early studies mainly focused on blending [25] and crosslinking [27] approaches to modify the molecular structure of PVA membrane. While the modified membranes generally suffered the trade-off between permeability (or flux) and selectivity (or separation factor) for polymeric membranes. To overcome this trade-off, incorporating high-performing fillers into PVA matrix to fabricate mixed-matrix membranes is received increasing attention in recent two decades, which will be discussed in Section 5.

In addition to the main application for solvent dehydration, hydrophilic pervaporation membrane can be coupled with reaction involving water as byproduct (e.g., esterification) where the in-situ removal of water could enhance the conversion rate [28]. Recently, catalyst was introduced into the PVA casting solution to prepare a catalytic membrane to further promote the reaction efficiency (Fig. 2) [29]. The reaction occurs with the aid of catalyst embedded in the membrane and meanwhile the byproduct water was removed by the PVA-based membrane via pervaporation process. The potential in catalytic membrane would extend the application spectrum of PVA membranes from separation process into process intensification. More attention should be paid to the effect of introduced catalyst on the structure and transport property of PVA membrane in the following study. To further enhance mass transfer rate, the current design of catalytic/separation bi-layer might be modified as asymmetric single-layer where the catalyst can be combined into the porous structure.

Polyelectrolyte is a large family of hydrophilic polymers for fabricating pervaporation dehydration membranes (Fig. 3a). PEC is formed as oppositely charged polyelectrolyte chains contacting with each other at interface or in solution (Fig. 3b–c). Accordingly, two main types of PEC membranes were consecutively developed: multilayered membranes fabricated by layer-by-layer (LBL) assembly of polyelectrolyte solution, and homogenous membranes made by solution processable PEC [21]. The LBL approach can precisely control the membrane thickness at molecular scale with deposition of very dilute polyelectrolyte solution for each cycle [30]. Ultra-thin membrane layer can be produced to obtain high permeation flux. On the other hand, the complexation structure is loose and defect-free deposition of PEC layer on porous substrate is challenging, resulting in relatively low selectivity of multilayered PEC membranes for solvent dehydration (e.g., water/ethanol) separation factor is basically less than 10000) and stability issue.

 Compared with time-consuming LBL approach, solution casting is more favorable towards scalable fabrication of PEC membranes. However, direct mixing oppositely charged polyelectrolytes would easily form PEC aggregate particles that are insoluble in solution. To resolve the processability problem of PECs, acid was added as mixing the polyelectrolytes to depress the ionic complexation and inhibit the precipitation of PECs to produce a homogeneous casting solution. An “protection de-protection” method was further developed to realize
synthesis of processable PEC bulk solids, in which the ionization degree of polyelectrolyte was controlled by acid and the as-prepared PEC solids can be re-dispersed in alkali solution (Fig. 3d) [31]. As a result, homogeneous PEC membranes with larger thickness while denser complexation structure exhibited balanced permeation flux and selectivity during pervaporation dehydration of solvent (e.g., total flux of 2100 g/m²h and separation factor of 2134 in dehydration of 90 wt% ethanol/water mixture at 70 °C) [32]. In future study, the multilayered and homogeneous PEC membranes can be investigated with correlation to each other to further understand their differences in structures and performance. Moreover, prior to practical application, the long-term stability of PEC membranes should be systematically evaluated.

Several polymeric membrane materials widely used for nanofiltration (NF), reverse osmosis (RO) and gas separation, have also been explored for pervaporation separation with the idea of sharing similar hydrophilicity and/or morphology. In terms of the molecular size of separation components and size discrimination as dominant effect of separation, pervaporation membranes require moderate cavity size that is smaller than that of NF or RO membranes while larger than that of gas separation membranes. Therefore, although using the similar fabrication techniques such as interfacial polymerization and dry-wet spinning, the casting or dope solution may need to be re-formulated to form favorable structures for selective permeation of water over organic solvent. Another different aspect compared with water filtration and gas separation membranes is the operating conditions. With liquid in feed and vapor in permeate, pervaporation membranes are no need to be fed with high pressure while are often operated at elevated temperature to enhance the productivity. Thus, the thermal stability and solvent resistance are of particular importance for the pervaporation membranes made by the materials originally used for water filtration or gas separation membranes.

PA membranes, typically prepared by interfacial polymerization between acyl chloride in organic phase and amine in aqueous phase at surface of porous substrate, are the dominant commercial product for NF and RO. The formed thin-film composite (TFC) structure and the intrinsic hydrophilicity of PA motivated the exploration the application...
of PA TFC membranes in pervaporation dehydration of solvent \[33,34\]. Compared with NF or RO membranes, pervaporation membranes require smaller cavity size to discriminate water from organic solvent (e.g., ethanol) that is smaller than most solute (e.g., salts). Thus, the conditions of interfacial polymerization including monomer structure, temperature and annealing process need to be redesigned to fabricate PA TFC membranes that are capable for solvent dehydration. Interfacial polymerized PA TFC membrane by using triethylenetetramine and trimesoyl chloride exhibited total flux of 115 g/m²h and separation factor of 1491 for dehydration of 90 wt% ethanol/water mixture at 25 °C \[35\]. With the well-established interfacial polymerization technique for fabricating NF or RO membranes, TFC membranes based on PA materials may have wider applications in pervaporation. Again, the thermal, chemical and mechanical stability of PA TFC membranes during long-term operation of solvent dehydration process should be further evaluated.

Towards dehydration of aggressive solvents at elevated temperature, chemically and thermally stable polymeric membranes are necessary to be developed. To address this challenge, aromatic PIs with rigid chains such as polybenzoxazole (PBO) \[36\] and polybenzimidazole (PBI) \[37\] were employed to fabricate membranes for solvent dehydration. These polymers feature thermally rearranged (TR) property that is useful to tune the molecular structure and thus the membrane permeation property in terms of diffusivity. As thermally treating at ~450 °C under vacuum, the ortho-functional PI will be occurred a condensation reaction to form TR polymer, which has shown excellent membrane performance for H₂ and CO₂ separation \[38\]. However, due to the essentially tight free volumes and insufficient hydrophilicity, such TR polymeric membranes exhibited relatively low flux during solvent dehydration \[36\]. Nevertheless, TR polymers with heterocyclic and aromatic structure are thermally stable and resistant to swelling, which is in favor of application in solvent dehydration operated under harsh conditions. Hollow fiber spinning approach to form asymmetric membrane with a thin, dense skin layer and porous substrate layer is industrially preferred to improve the flux of TR polymeric membranes.

### 2.2. Hydrophobic polymers

Hydrophobic polymeric membranes possessing preferential sorption of organic compounds over water are used for selective removal of organic compounds from aqueous solution via pervaporation process. Different from the membrane for solvent dehydration, the hydrophobic (sometimes also called organophilic) membrane can only rely on its sorption selectivity but not diffusion selectivity to realize the selective permeation of organics over water, because the diffusivity of organics is lower than water in terms of molecular size. Thus, thermodynamic sorption of components in the membrane is critical for identifying and designing hydrophobic membrane materials, which can be indicated by the solubility parameters. Generally, the closer solubility parameter of a component to that of membrane material, the stronger affinity of the membrane towards the component. The solubility parameters of small molecules can be calculated by considering hydrogen bonding, polar

![Fig. 4. Molecular structure of PDMS precursor and crosslinked network based on (a) condensation reaction; (b) hydrosilylation reaction \[40\].](image-url)
and dispersive force contributions according to theory of Hansen solubility parameters. Likewise, a group contribution method was proposed to estimate the solubility parameter of membrane materials [39].

PDMS, an important kind of silicon rubber, is the most widely studied and benchmark hydrophobic material for pervaporation [17]. PDMS membranes exhibit excellent separation performance for recovery of organics from aqueous solution, as well as additional advantages in hydrophobicity, processability and stability. PDMS needs to be crosslinked to fabricate dense and robust membrane. According to the terminal groups, two types of commercial PDMS precursors are most frequently used for developing pervaporation membranes. One is hydroxyl-terminated PDMS that is often crosslinked by tetraethoxysilane (TEOS) via condensation reaction to form a three-dimensional network structure (Fig. 4a). The other is vinyl-terminated PDMS reacting with hydrosilyl-containing crosslinker via addition reaction to form a linear architecture (Fig. 4b).

It was demonstrated that the four-armed quaternary-siloxy groups can create additional free volumes and hydrogen bonding to enhance the sorption and diffusion of phenol molecules in the crosslinked hydroxyl-PDMS membrane [40]. Besides of the molecular structure, the precursor’s molecular weight and crosslinker amounts were found to be crucial to optimize the transport and mechanical properties of PDMS membrane [41]. Recently, an UV-induced crosslinking was developed based on a methacrylate-functionalized PDMS precursor, realizing an ultra-fast and continuous fabrication of PDMS membrane [42]. Other PDMS derivatives such as polyoctylmethylsiloxane (POMS) [43] and polymethylphenylsiloxane (PMPS) [44] were also studied for hydrophobic pervaporation membranes. The introduced long alkyl or aromatic groups are expected to enhance the membrane affinity towards C₈+ hydrocarbons, and affect the packing of polymer chains as well. Alternative approach to introduce side groups into the crosslinked PDMS network is using crosslinker attached with the side groups. For instance, fluoroalkyl groups were enriched on the surface of PDMS membrane by using fluoroalkylsilane (FAS) to crosslink hydroxyl terminated PDMS [45]. Compared with conventional TEOS crosslinker, the FAS crosslinked PDMS membrane with stronger water repellency showed much higher butanol/water separation factor (52 vs 32) without sacrificing the butanol flux.

To obtain sufficient flux and mechanical strength, a thin PDMS layer was usually coated on porous substrate to develop composite membranes. Ideally, PDMS layer determines the separation performance and porous substrate only provides mechanical support. However, more and more studies demonstrated that substrate layer plays non-negligible role in the formation of separation layer and transport properties of the composite membrane. The surface functionality of substrate would affect the wetting of coating solution and the surface nanostructures of the substrate including roughness and pore size have significant influence on controlling the membrane integrity and the thickness of membrane layer and interface [46,47]. Accordingly, the surface properties of substrate should be carefully designed for matching with the properties of coating solution (e.g., viscosity) to form a defect-free PDMS layer as thin as possible [48]. An intermediate layer with ultra-low transport resistance could be designed to tune the surface morphology and chemistry of a highly porous substrate to reduce the thickness of defect-free membrane layer. Recently, a 200 nm-thin defect-free PDMS membrane was realized by alternately spin-coating PDMS and crosslinker on substrate decorated with a layer of copper hydroxide nanofibers (Fig. 5) [49]. The ultra-thin PDMS membrane exhibited outstanding permeation flux of 6.18 kg/m²h with separation factor of 31 for 1 wt% n-butanol/water at 60 °C.

The infiltration of PDMS solution into the pores of substrate forms separation layer-substrate layer interface of the composite membrane [50]. Excessive infiltration should be avoided to ensure the integrity of the separation layer or maintain low transport resistance, while suitable infiltration was found to be favorable for enhancing the structural stability of PDMS composite membrane [51]. At the interface, different from organic substrate, rigid inorganic substrate can inhibit the excessive swelling of PDMS membrane layer in the feed of organic-water solution during pervaporation process [41]. As a result, the perm-selectivity and structural stability of such inorganic substrate-supported PDMS composite membrane can be well maintained even under harsh conditions (e.g., elevated temperature) [52]. Nano-indentation/scratch test was proven as a powerful technique to measure the mechanical properties (e.g., hardness, elastic modulus) of the thin separation layer and its interfacial adhesive force onto the porous substrate layer [50,51]. Towards biofuels recovery from fermentation process, hydrophobic PDMS membrane face the challenge of biofouling. It was demonstrated that surface chemistry of PDMS membranes not only determined the preferential adsorption of permeant molecules, but also affected the attachment of bio-fouling in real separation system [53]. A new kind of anti-biofouling PDMS membrane was fabricated by a facile crosslinking reaction between fluorosilane and PDMS. By keeping the excellent hydrophobicity, the introduced fluoroalkyl groups endowed the PDMS membrane with an ultra-low surface energy, thereby alleviating microbial adhesion onto the membrane surface [54].

PEBA is another large family of polymers for hydrophobic pervaporation membranes and gas separation membranes. It is a block copolymer consisting of polyamide (PA) and polyether (PE). The rigid PA part provides mechanical strength while the PE part provides affinity towards organic compounds and polar gases. Different types of PEBA products (called Pebax) are available with variable PE/PA molar ratios. Pebax 1657 with a moderate PE/PA weight ratio of 60/40 to balance the affinity and size discrimination ability of the membrane is mostly used
for CO₂ separation [55]. Pebax 2533 with the highest PE content of 80 wt% to maximize the organophilicity exhibits the optimal membrane performance for recovery of organics among the PEBA materials [56]. With the intrinsically hydrophilic PA segments, the hydrophobicity of PEBA is insufficient. Compared with PDMS membrane, the water contact angle of PEBA membrane is much lower (60°–70° vs 110°–120°) [57], which can account for the lower alcohol/water separation factor (3–4 vs 7–8 for ethanol/water; ~20 vs ~40 for butanol/water) [56,58,59]. However, PEBA membrane exhibited much higher phenol/water separation factor than PDMS membrane (30 vs 6), suggesting an excellent organophilicity that enables PEBA membranes to be favorable for selective permeation of organics with large molecular size (e.g., phenol) [60].

Other hydrophobic polymers with high free volume fractions were explored as highly permeable membrane materials for pervaporation recovery of organics from aqueous solution. Previous studies focused on poly (1-trimethylsilyl-1-propyne) (PTMSP), in which the bulky trimethylsilyl side groups create a large number of free volumes for selective permeation of molecules [61,62]. Recently, polymers of intrinsic microporosity (PIMs), whose special ladder-like structure with contorted sites can prevent polymer chains from close packing and rotating, were demonstrated to be an emerging membrane material for alcohol recovery from water [63]. The main challenge for using these high-free volume polymers is the significant decline of permeability (or flux) during operating time, because the accessible free volumes were reduced by the chain relaxation. For instance, after aging over one year, PIM-1 membrane exhibited a 9-fold decline in butanol permeability and 30% decline in water permeability [64]. Moreover, the physical aging rate was found to be closely related to the membrane thickness, which would be faster in thinner film. Recent studies demonstrated that incorporation of nanofillers acting as physical barriers into the polymer can slow down the aging process that will be discussed in the following section [65].

2.3. Polymeric membranes for organic/organic separation

Separation of organic/organic mixtures is of great importance in chemical industry and an energy-intensive process [22]. Polymeric pervaporation membranes have been studied for separating three main kinds of organic mixtures: i) aromatic/aliphatic such as benzene/cyclohexane and toluene/n-heptane; ii) polar/non-polar such as methanol/methyl tert-butyl ether (MTBE); iii) gasoline desulfurization (e.g., model mixtures: thiophene/n-heptane). Compared with organic/water mixtures, organic/organic mixtures are more challenging separation task for polymeric membranes, because much larger swelling of polymers in pure organic solution would reduce the size discrimination ability and stability of the membrane. Besides, organics in some mixtures (e.g., aromatic/aliphatic) exhibit quite similar physicochemical properties, resulting in insufficient difference in solubility and diffusivity of the membrane.

Pls are a kind of common glassy polymers for gas separation and nanofiltration, which are synthesized by carboxylic acid anhydrides and primary diamines [66]. The rigid and stiff chains enabled Pls as chemically and thermally robust membrane materials for organic/organic separations. Generally, Pl shows stronger affinity towards aromatic over aliphatic owing to the favorable interactions between the polar imide and/or benzene groups with π electrons of aromatic rings. Thus, Pl membranes can selectively separate aromatics from its mixtures with aliphatic. For instance, the solubility parameter (δ) of toluene (18.2 MPa⁴/³) is closer to that of aromatic Pls (Matrimid: 22.1 MPa⁴/³; PBI: 23.4 MPa⁴/³) and compared with iso-octane (14.1 MPa⁴/³), where δ is Hansen solubility parameter, δ = δp + δd + δh, where δp is dispersive force contribution, δd is polar contribution and δh is hydrogen bonding contribution [66]. Meanwhile, the molecule of toluene is smaller than that of iso-octane (Lennard-Jones molecular size: 0.593 nm vs 0.762 nm). As a result, Matrimid/PBI blending PI hollow fiber membrane exhibited separation factor of 200 and flux of 1.35 kg/m²h for pervaporation separation of 50 wt% toluene/iso-octane at 60 °C [67]. In contrast, for separation of toluene/n-heptane, or benzene/cyclohexane with much closer physicochemical properties, PI membranes exhibited much lower separation factor (mostly less than 10) [22]. Like the achievements in gas separation membranes, introducing bulky fluorine groups such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dihydride (6FDA) into PI structures can increase the free volumes of PI membranes and crosslinking is often employed to enhance the swelling resistance of PI membranes [68]. In addition to the remarkable developments in highly permeable and robust asymmetric hollow fiber for gas separation, PI-based membranes would play an increasingly important role in pervaporation separation of organic/organic mixtures.

Block copolymers with soft-hard segment such as PEBA [69] and polyurethane (PU) [70] are another important capable membrane material for separation of organic/organic mixtures, in which the hard segments can suppress the excessive swelling and the soft segments provide affinity towards organics. The size and chemistry of the soft/hard segments can be tuned to achieve comparable separation performance in terms of permeation flux, separation factor and structural stability in organic/organic mixtures. Among them, PEBA was attracted more attention owing to its available commercial products with variable soft (PE)-hard (PA) ratios and good processability in fabricating composite membranes (Fig. 6). Because of the favorable interactions between PE segments and aromatics, PEBA had a higher affinity to aromatics (e.g., benzene, toluene) than aliphatic (e.g., n-heptane, cyclohexane). The results of liquid sorption measurement and inverse gas chromatography (IGC) technique indicated that Pebax 2533 exhibited higher solubility and diffusivity towards toluene over n-heptane. The thermally crosslinked PEBA composite membrane showed a good and stable performance for 50 wt% toluene/n-heptane mixtures at 80 °C (separation factor: 4.0 and flux: 280 g/m²h) [69]. Apparently, PEBA TFC membranes that have been intensively studied for CO₂ capture can be adopted for organic/organic separation. Besides of the stability of PEBA layer, more attention should be paid to enhance the stability of the substrate and interface that may not be a primary issue for this membrane applied in CO₂ separation with low feed pressure.

3. Inorganic membranes

Inorganic pervaporation membranes are generally made by crystalline microporous materials such as zeolite, MOF and COF. On the one hand, with well-defined and rigid pore structures, inorganic membranes exhibited higher separation performance and stability compared with polymeric membranes. On the other hand, the fabrication of defect-free inorganic membranes mainly based on hydrothermal synthesis faces more challenges than easily processable polymeric membranes. Zeolite is the first and still the largest family of inorganic materials for pervaporation. The zeolitic pores with tunable hydrophilicity and subnanometer size offer strong preferential adsorption, fast and selective diffusion to the intergrown crystalline membrane to realize efficient molecular separations. Like polymers, many types of hydrophilic zeolites (e.g., NaA, CHA, T-type), and only a few hydrophobic zeolites (e.g., MFI), can be used to fabricate pervaporation membranes for organic dehydrogenation and organic recovery (separation), respectively. As another kind of intensively studied hydrophilic membrane, amorphous silica membranes are promising for high-temperature organic dehydrogenation once addressing the primary issue of hydrothermal stability. Crystalline membranes derived from organic framework materials with versatile pore structures and functionality are ideally suitable for pervaporation separations with the prerequisites of solving the water stability issue of MOFs and reducing the intrinsically large pore size of COFs.
Zeolites, an important kind of microporous aluminosilicate crystals, are the major building blocks of inorganic membranes for pervaporation separation [71]. The pore size of zeolite is controlled by the TO₄ tetrahedral unit (T = Si, Al or P) framework. Zeolites with 8- (e.g., LTA, CHA, DDR type), 10- (e.g., MFI, FAU type) and 12- (e.g., MOR type) members framework ring have pore sizes varying from 0.38 to 0.74 nm. The hydrophilicity of zeolite is dependent on the Si/Al ratio (1~∞). Zeolite with low Si/Al ratio exhibits high hydrophilicity but low acid stability [72]. The uniform and well-defined pore with sub-nanometer size, tunable hydrophilicity and high thermal stability of zeolites endow the pervaporation membranes outstanding separation performance for water/organic or organic-organic mixtures at elevated temperature. To utilize the intrinsic pores for selective and fast molecular transport, zeolite crystals are intergrown on a porous substrate without intercrystalline defects to form an integrated crystalline membrane layer with minimal thickness [73]. Generally, zeolite membranes are prepared by hydrothermal synthesis via in-situ growth or secondary growth method (Fig. 7) [74]. Initial works mainly used in-situ growth method to fabricate zeolite membranes, in which surface of the substrate can be functionalized to
NaA (LTA-type) membranes, the first commercialized zeolite membranes by Mitsui Engineering and Shipbuilding Co., Japan in 1999, have been widely studied for pervaporation dehydration of alcohols or solvents [74]. A general formula of NaA is \([\text{Na}_8(\text{Al}_2\text{Si}_12\text{O}_{40})\cdot 27\text{H}_2\text{O}]\), in which the cation is \(\text{Na}^+\) and Si/Al ratio is 1. The pore for molecular transport of NaA zeolite is defined by the 8-membered oxygen ring with diameter of 0.41 nm \(\times\) 0.41 nm. This molecular sieving pore allows highly selective diffusion of water with molecular size of 0.29 nm over other organics with molecular size larger than 0.41 nm (e.g., ethanol: 0.43 nm; butanol: 0.51 nm). Meanwhile, the low Si/Al ratio of NaA zeolite results in a hydrophilic pore structure that favors preferential sorption of water. Therefore, NaA membranes are ideally suitable for selective removal of water from its organic mixtures. Many studies have focused on optimizing the seeding layer to fabricate thin and defect-free NaA membranes. A dip-coating/wiping approach [77] was proposed to deposit a uniform layer of zeolite seeds with highly reduced amount on the substrate, producing a NaA zeolite membrane with separation factor of 10,000 and flux of 9.0 kg/m²h for pervaporation dehydration of 90 wt% ethanol/water mixtures at 75 °C. Such high flux is also attributed to the usage of ceramic hollow fiber substrate with low transport resistance. It was demonstrated that four-channel ceramic hollow fiber substrate [78] endowed NaA membrane with water flux up to 12.8 kg/m²h and the same separation factor under the above separation conditions. Like polymeric composite membranes, macroporous substrates are desirable due to the low cost and transport resistance, which however bring more challenges for fabricating a thin and defect-free membrane layer because zeolite crystals are easily penetrated into substrate pores to form defects or increase transport resistance. Continuous efforts have been made to achieve reproducible fabrication of high-quality NaA membranes on cost-effective substrates with sufficient mechanical strength and packing density that are preferred in industrial applications.

One challenge of NaA membrane is inhibition of inter-crystalline defects during membrane fabrication and separation process. The inter-crystalline defects can be shrunk or enlarged due to the adsorption amount of water inside the NaA zeolite framework with certain crystal flexibility [79]. This explained a common observation that highly selective NaA membranes showed sharp decrease of selectivity as feed water concentration below 5 wt%. Besides of optimizing the synthesis conditions, post-treatment methods such as surface coating and molecular deposition were developed to repair the defects of zeolite membranes. These methods improved the membrane selectivity while often declined the flux due to the blocking of zeolite pores or adding additional transport resistance. A recent study [80] demonstrated that deposition of a loose layer of highly flexible and hydrophilic WS₂ nanosheets on NaA membrane can inhibit the inter-crystalline defects (Fig. 8), increasing the separation factor from 60 to 10000; meanwhile well maintain the original flux with a slight loss of 18.6% during dehydration of 90 wt% isopropanol/water at 100 °C.

The high aluminum content in zeolite framework (Si/Al \(\approx\) 1) causes poor stability of NaA membrane in acid solution due to the dealumination [81]. Zeolites such as FAU, MFI and MOR with higher Si/Al ratio exhibit higher acid stability than NaA (Fig. 9) [82]. However, their pores (0.56 or 0.74 nm) are too large to exclude organics from water molecules, and the lowered hydrophilicity reduces the preferential adsorption towards water, thereby sacrificing the selective water permeation. Alternatively, CHA zeolite is a promising candidate to balance the trade-off between acid stability and dehydration performance. Its 8-membered ring generates pore diameter of 0.38 nm \(\times\) 0.38 nm showing even higher molecular sieving ability than NaA zeolite with pore diameter of 0.41 nm \(\times\) 0.41 nm. Meanwhile, the Si/Al ratio of CHA zeolite can be tuned from 2 to \(\infty\) to achieve

![Fig. 9. Attributes of various zeolite frameworks with pore size, hydrophilicity, and acid stability trend [82].](image)
both high acid stability and hydrophilicity. To fabricate high-quality CHA zeolite membranes, it was demonstrated that introducing seed crystals can increase the nucleation sites and inhibit the generation of other types of zeolite (e.g., MER), obtaining a pure phase CHA zeolite membrane [83]. Moreover, transparent suspension (so-called clear solution) of precursor was in favor of growing a thinner CHA membrane compared with precursor in a milk-like gel form. The reported water flux of CHA membranes was up to 13.3 kg/m²h, with separation factor of 6000 for dehydration of 90 wt% ethanol/water mixture at 75 °C [84]. Importantly, the CHA membrane showed excellent acid stability when dealing with solution with pH ~3 for 550 h.

Other zeolites with good acid resistance include T-type and DD3R. T-type zeolite (OFF-ERI intergrowth) with pore size of 0.36 nm × 0.51 nm and Si/Al ratio of 3–4 also exhibited good acid stability (pH ~3–4) while lower flux due to the smaller pore size compared with CHA [85,86]. To pursue even higher acid stability, all-silica Decadodecasil 3R (DD3R) zeolite membrane, despite its hydrophobic character, can be used for removing water from organic solvents based on the molecular sieving effect of the zeolitic pore with 0.36 nm × 0.44 nm [87]. DD3R zeolite membrane can dehydrate 90 wt% acetic acid/water mixtures (with intermittently adding 0.1 M HCl or 0.05 M H₂SO₄) at 75 °C with total flux of 0.185 g/m²h and separation factor of ~250 during 120 h continuous operation [88].

Apparent the dehydration performance was compromised by the strong hydrophobicity of all-silica DD3R framework with smallest pores among the zeolites for solvent dehydration. Detailed progress in zeolite membranes for dehydration of acetic acid can be found in a recent review paper [82].

As discussed above, zeolite membranes are mostly studied for solvent dehydration by utilizing both the hydrophilicity and size sieving effect of the zeolite framework. As another aspect of pervaporation application, recovering organics from water requires a hydrophobic zeolite with suitable pore size for selective permeation of organic molecules over water. Up to date, only a few zeolites fit such purpose. MFI type zeolite, possessing desirable hydrophobicity and pore size of 0.55 nm, is the most promising zeolite for hydrophobic pervaporation membranes [89,90]. Over the past two decades, several attempts have been made to improve the quality and pervaporation performance of MFI membranes by enhancing the hydrophobicity, eliminating non-selective defects or reducing membrane thickness. The hydrophobicity of zeolite is increased by the Si/Al ratio and pure-silica MFI (also called silicalite-1) shows the highest hydrophobicity. An important direction to fabricate sufficient hydrophobicity of MFI membrane is trying to avoid alumina contamination from commonly-used ceramic substrate during secondary growth or solid-state diffusion of calcination. Properly designed seeding layer (e.g., seed size/shape/density, deposition approach) is crucial to obtain a defect-free and ultra-thin MFI zeolite layer. Recently, a dual-seed-layer and varying temperature secondary growth method was proposed to improve the quality of MFI membranes with high Si/Al ratio of 187 and minimum defect, achieving ethanol/water separation factor of 160 and total flux of 2.9 kg/m²h for 5 wt% ethanol/water at 25 °C (Fig. 10) [91]. As the flux of zeolite membrane layer is sufficiently

![Fig. 10. Dual-seed-layer and varying temperature secondary growth method to fabricate MFI hollow fiber membranes: (a) schematic, (b) morphology and (c) ethanol/water separation performance [91].]
high, the transport resistance of the substrate layer should not be ignored. In this regard, highly porous hollow fiber substrate with low transport resistance is often adopted to achieve high-flux MFI membranes [91–93] (e.g., 9.8 kg/m²h with ethanol/water separation factor of 58 for 5 wt% ethanol/water at 60 °C [93]).

Until now, the total flux and separation factor of reported silicalite-1 membranes did not exceed 10 kg/m²h and 100, respectively, for ethanol/water mixtures, a typical system for evaluating hydrophobic pervaporation membranes. Compared with hydrophilic zeolite membranes for solvent dehydration, hydrophobic zeolite membranes generally showed lower flux and much lower separation factor towards organic recovery from aqueous solution. The reason is similar to abovementioned polymeric pervaporation membranes: organic compound with larger molecular size transports slower than water, and pore size sieving effect is against preferential molecular diffusion of large-sized organic over small-sized water. Moreover, the rigid zeolite pore (0.55 nm) limits the size of organics that are able to permeate through MFI membranes. This cut-off effect accounts for the few reports on MFI membranes for selective permeation of C8 hydrocarbons from water.

Another issue related to the application of MFI membranes in aqueous solution is the long-term stability at elevated temperature. It was found that both flux and ethanol/water separation factor of MFI membrane declined during 177 h pervaporation process at 100 °C. This instability was attributed to the loss of Si atoms of the zeolite framework and formation of Si-OH in aqueous solution [94]. Despite of great challenge [95], the stability issue of MFI membranes has to be overcome prior to practical application in recovery of organics from aqueous solution.

Another widely studied application of MFI membranes is separation of xylene isomers via vapor permeation [96–98] or pervaporation [99] process by utilizing the molecular sieving property of zeolitic pore. It is of great importance in the petrochemical industry to separate p-xylene (molecular size ~0.58 nm) from its buklier m-xylene and o-xylene isomers (~0.68 nm). Besides of optimizing the synthesis conditions to inhibit inter-crystalline defects, particular efforts have been devoted to fabricating MFI membranes with reduced transport resistance to enhance xylene flux. Two approaches are mostly followed: b-channel-oriented membrane and thin nanosheet membrane. MFI zeolite possesses 0.55 nm × 0.51 nm sized channels along the a axis in a sinusoidal manner, and 0.56 nm × 0.53 nm sized channels running straight along the b axis. Thus, separation performance of MFI membrane can be highly enhanced as the b channels are uniformly oriented normal to the substrate. Typically, b-oriented MFI membranes were obtained by growth of an oriented seed layer with the aid of structure-directing agent, which can offer p-xylene permeance of ~2 × 10⁻⁷ mol/m²-s-Pa with p-xylene/o-xylene separation factor up to ~500 [100]. The key challenge of achieving highly oriented MFI membrane lies in how to control the orientation of zeolite seed layer and the subsequent secondary growth [101]. The progresses in preparation, mechanism and applications of oriented MFI zeolite membranes were reviewed recently [102].

The crystal dimension of MFI zeolite is longer along the c axis and smaller along the b axis. It means that formation of plate-like MFI with the thin crystal dimension along the b axis, ultimately MFI nanosheet, is favorable for membrane separation. The straight zeolitic pores along this direction (b-oriented) and the possibility of fabricating much thinner selective layer (~100 nm) could highly improve the separation efficiency. Top-down [103] and bottom-up [104] methods were successively invented to fabricate MFI nanosheets during the last decade. Top-down method involves exfoliation of layered MFI and subsequent removal of non-exfoliated particles, which is time-consuming, low-yield, and produces limited lateral dimensions (in submicron scale). Bottom-up synthesis of MFI nanosheets can overcome these disadvantages, while faces the challenge of orthogonal intergrowths (MFI twins).

Until recently, nanocrystal-seeded growth method triggered by a single rotational intergrowth in the presence of bis-1,5 (tripropyl ammonium) pentamethylene diiodide (dC5, an optimal structure-directing agent [105]) was developed to synthesize MFI nanosheets with a thickness of 5 nm (2.5 unit cells) (Fig. 11) [104]. The MFI membranes with thickness of 250 nm to 1 μm were prepared by coating the nanosheets on a porous substrate via vacuum filtration, followed by gel-free secondary growth [106] to form an inter-grown zeolite layer. The membrane exhibited outstanding molecular sieving performance for xylene isomers with p-xylene permeance of 5.6 × 10⁻⁷ mol/m²-s-Pa and p-/o-xylene separation factor of ~2000 at 150 °C. Further attempt will be needed to remove the seed crystals in the MFI nanosheets by chemical or mechanical methods and control the influence of the resulting tens of nanometer holes on the separation performance.

Compared with polymeric membranes, zeolite pervaporation membranes have shown much higher permeance and selectivity, owing to the regular, rigid zeolitic pores with tunable molecular sieving property and hydrophilicity. Under the condition of defect-free intergrown membrane layer, zeolite membranes are pursued for higher flux by reducing the membrane thickness and substrate transport resistance. Acid stability is a key test for zeolite membranes applied in pervaporation dehydration that often involves low pH. The oriented growth and nanosheet seeding are two directions to improve the separation productivity of MFI membranes dealing with permeation of large molecules (i.e., xylene).

3.2. Silica membranes

Microporous silica membranes have been studied for pervaporation separation three decades ago [107]. Due to the hydrophilic nature of silica and the sub-nanosized pores, silica membranes were mostly used for organic dehydration. The preparation of silica membranes is based on sol-gel method that is commonly used for fabricating ceramic nanofiltration membranes with pore size down to a few nanometers. Like most inorganic membranes, silica membrane is prepared on top of a porous substrate to provide sufficiently high flux and mechanical strength. In a typical sol-gel process, a silica sol was synthesized via hydrolysis with a condensation of alkoxysilane precursors, and then coated on the surface of a porous substrate to form a thin silica gel layer that was subsequently calcined at 200–600 °C to form the silica membrane layer. Two kinds of pores are considered in silica membrane: sub-nanosized pores of three-dimensional silica networks and nano-sized pores of interparticle pores and/or grain boundaries [108]. Apparently, the sub-nanosized pores (controlling the selectivity) and nano-sized pores (providing sufficient permeance) should be interconnected to endow silica membrane with selective and efficient permeation of components during pervaporation process. The pore structures can be varied by the synthetic conditions, such as the type and concentration of precursors and catalyst, the solvent and the precursor/water ratio.

The first generation of silica membranes is derived from acid-catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS). The resulting amorphous silica membranes consisting of randomly connected SiO₄ tetrahedra showed high separation performance for pervaporation dehydration of alcohols or organic acids. ECN (Energy Research Centre of the Netherlands) reported silica membranes [109] (up to 1 m length tube) with thickness of 150–200 nm and pore size of ~0.4 nm, exhibiting water flux of 4.5 kg/m²h and separation factor of 600 for dehydration of 95 wt% n-butanol/water mixtures at 75 °C. Although the acid stability is much higher than NaA zeolite membranes [82], the pure silica membranes were found to be unstable under hydrothermal conditions. Typically, the flux of silica membrane was declined within a few days (feed: 95 wt% butanol/water mixtures at 80 °C) (Fig. 12) [110]. A possible reason was that water or alcohol would react with the hydroxyl groups on silica, decreasing the hydrophilicity of silica. This reaction may also reduce the surface energy associated with the surface area of the pores, generating dense silica particles with formation of large non-selective pores. Another explanation [111] was considering pore blocking by water molecules bound to the internal pore surface through interactions that are stronger than
those of physisorption, e.g. hydrogen bonding or chemisorption.

To enhance the hydrothermal stability of pure silica membranes, one strategy is incorporating metal such as zirconia and titania into the silica networks to develop silica composite membranes. By controlling the pore size less than 1 nm, silica-zirconia composite membranes \[112\] exhibited permeation flux of 9.0 kg/m\(^2\)/h with separation factor of 1500 in the boiling feed of 90 wt\% isopropanol/water, and were stable as increasing the water concentration to 30.7 wt\%. The enhancement of hydrothermal stability in the silica-metal composite membranes is attributed to the more stable M\(\ldots\)O (M: metal) bonds than Si\(\ldots\)O bonds.

Another strategy is incorporation of hydrolytically stable groups with hydrophobic character to protect the siloxane bonds by shielding them from water. Typically, alkoxyisilane precursors with non-reactive side groups (e.g., \(-\text{CH}_3\)) was co-condensed with the conventional TEOS precursor, forming an inorganic network consisting of hydrolytically stable Si\(\ldots\)C links. It was demonstrated that introducing methyl into the silica network enabled silica membrane dehydrating 95 wt\% \(n\)-butanol/water mixtures at 95 °C with water flux of \(~4\) kg/m\(^2\)/h and separation factor of 500–2000 for more than 18 months \[111\]. However, the two strategies based on incorporation was limited to a low doping content (e.g., C/O molar ratio of 0.5), and moderate improvement of durability was achieved.

Fig. 11. Nanosheet MFI membrane: morphology of nanosheet and membrane, and p-o-xylene separation performance \[104\].

Fig. 12. Pure and hybrid silica membranes: precursor and network structure \[108\], morphology and long-term butanol dehydration performance \[113\].
In the recent decade, organic-inorganic hybrid silica membranes are considered as a new generation of silica membranes showing both high separation performance and stability. Rather than incorporation, TEOS was replaced with bis-silyl-type precursor such as 1,2-bis(triethoxysilyl)ethane (BTESE) or bis(triethoxysilyl)methane (BTESM) to generate Si-O-Si hybrid networks with higher bonding energy than pure Si–O–Si networks. Outstanding pervaporation dehydration performance and superior hydrothermal stability were simultaneously achieved in BTESE hybrid membrane [113]. The water flux was only changed by almost 2% per month with initial water flow of 10 kg/m²h, and the water concentration in the permeate was maintained at ~98 wt% during almost 2 years towards dehydration of 95 wt% n-butanol/water mixtures at 150 °C (Fig. 12). By contrast, conventional silica membranes and methylated silica membranes failed within days at 95 and 115 °C, respectively. The BTESE hybrid membranes also showed excellent stability in the dehydration of acetic acid solutions with water flux of 2–4 kg/m²h and separation factor of 200–500 for 90 wt% acetic acid/water mixtures at 75 °C, and the performance was stable after 70 days exposure at the same feed condition [114]. It was also demonstrated that the methylene groups inserted between Si atoms could enlarge the pore size of pure silica networks formed by TEOS [115]. Thus, the network pore size of hybrid silica membranes can be tuned by the number of methylene groups and the precursor/water ratio during sol-gel preparation process.

Overall, the pervaporation performance of silica membranes is basically between that of polymeric membranes and zeolite membranes [116]. This is determined by the intrinsic pore structures of silica membranes derived from sol-gel process: more rigid and highly porous compared with polymers, but without uniform and highly interconnected as zeolite. The organic-inorganic hybrid silica membranes, with excellent high acid and hydrothermal stability, could be competitive candidates compared with the counterparts in application of organic dehydration under harsh conditions (high water content, temperature and/or low pH) [82]. Different from zeolite membranes with easily tuned pore size and hydrophilicity based on various zeolithic frameworks, silica membranes face much more challenges in precisely controlling the pore size. In this regard, more attention could be paid to the molecular design of the silica sol, and the sintering conditions of the silica gel layer.

3.3. MOF membranes

Metal-organic framework (MOF) is a new type of microporous materials, attracting substantial attention for membrane separation in the last decade. Although of hybrid structure constructed by coordinating metal cluster with organic ligands, MOF are often categorized as inorganic membrane materials because its crystalline structure with well-defined pores and membrane fabrication generally follows the methods for zeolite membranes (e.g., hydrothermal synthesis). Two prerequisites should be met when applying pure MOF membranes for pervaporation separation: suitable pore size matching the permeant size and sufficient liquid stability. Like most pervaporation membranes, the primary criterion of determining the separating systems for MOF membranes is the hydrophilicity of MOFs. Currently, most MOFs are hydrophobic and suitable for organic dehydration, while few of them are hydrophobic that can be used for organic recovery from aqueous solution (Table 1) [117]. The separation of organic-organic mixtures can be based on affinity and/or size sieving effect of MOFs.

Compared with gas separation, much less kinds of MOF membranes were studied for pervaporation, including MIL-53 [118], ZIF-71 [119, 120], ZIF-8 [121], MOF-5 [122] and UiO-66 [123]. An early work [118] reported MIL-53 membranes prepared by reactive seeding method demonstrated more than 200 h stable performance for dehydration of 93 wt% ethyl acetate/water mixtures at 60 °C with total flux of 454 g/m²h and separation factor of 1300. The window size of MIL-53 is 0.73 nm × 0.77 nm, which can accommodate both water (0.29 nm) and ethyl acetate (0.52 nm) molecules. The selective permeation of water was not only attributed to the molecular sieving effect, but also to the hydrophilic framework of MIL-53 form hydrogen bonds with water. This also explained the observation that no separation performance of this membrane for dehydration of ethanol (0.43 nm) or butanol (0.5 nm) that with smaller molecular size and more hydroxyl groups. ZIF-71 is an RHO-type zeolitic imidazolate framework with window size of 0.48 nm, exhibiting high hydrophobicity and organophilicity [124]. This motivated the development of ZIF-71 membranes for organic recovery from aqueous solution. Based on the preferential affinity towards ethanol over water, initial attempt [119] demonstrated potential ethanol/water separation performance of ZIF-71 membrane with separation factor of ~6. Later on, an improved ZIF-71 membrane was synthesized via counter-diffusion method on a ceramic hollow fiber substrate [120], showing one order of magnitude higher permeation flux (2600 g/m²h) with equivalent separation factor for 5 wt% ethanol/water mixtures at 25 °C. It can be noticed that the above MOF membranes, either for organic dehydration or organic separation, showed moderate separation performance as polymeric membranes while much lower than zeolite membranes. The reasons could be the poor size discrimination property or insufficient hydrophobicity of these MOFs compared with zeolites.

The discovery of UiO-66 shed light on the water-stable MOFs for pervaporation separation. With the strong coordination bonds between the hard-acid-hard-base interactions of the Zr(IV) atoms and carboxylate oxygens, this Zr-MOF family exhibits exceptional chemical and thermal stability. Moreover, the triangular window size of 0.6 nm and high hydrophilicity enables UiO-66 a promising membrane material for organic dehydration. A well-intergrown UiO-66 membrane was achieved by controlling the in-situ solvothermal synthesis conditions such as composition of mother solution, duration of synthesis and substrates. Selective transport of water molecules from salt solution (desalination) was reported for the first UiO-66 crystalline membrane [125]. The aperture of UiO-66 highly rejected multivalent ions with hydrated diameters of 0.66–0.95 nm on the basis of size exclusion with moderate water permeance of 0.14 L m⁻² h⁻¹ bar⁻¹. Importantly, excellent stability of the UiO-66 membrane was demonstrated by continuous saline filtration of 170 h under 10 bar. By further optimizing the synthesis conditions and microstructures of ceramic hollow fiber substrate, UiO-66 membranes exhibited high flux of up to ~6.0 kg/m²h and excellent separation factor of more than 45000 for dehydration of several solvents including i-butanol and furfural with 5 wt% water concentration at 70 °C (Fig. 13) [123]. The permeance for each permeant follows the order of its kinetic diameter, suggesting that the molecular sieving of UiO-66 aperture dominated the separation performance. Additionally, the UiO-66 membrane remained robust during ~300 h pervaporation test involving exposure to boiling benzene, boiling water and sulfuric acid. Another work [126] using micro-patterned substrate with larger surface area achieved one-fold higher apparent water permeation flux over UiO-66 membrane using

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<th>Table 1 Summary of MOFs with water/hydrothermal-stable ability for pervaporation [117].</th>
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<td>MIL-53 (Al)</td>
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The intrinsic pores of MOFs are suitable for dehydration of organic compounds but cannot be used for separation of water from water-glycerol mixtures without pre-treatment (e.g., the Pd-based catalyst in Ni-promoted water-glycerol mixtures [127]). Additionally, the performance of these MOFs is highly dependent on the synthesis condition such as the synthesis time, temperature and etc. Therefore, there is a need for more investigations and improvements to make these MOFs more applicable for practical applications.
The UiO-66-NH$_2$ membrane demonstrated promising desulfurization performance with permeation flux of $\sim$2.0 kg/m$^2$h and enrichment factor of 16.0 for $\sim$1300 ppm thiophene/n-octane mixtures at 40 °C during 70 h continuous pervaporation test. The thiophene/n-octane selectivity is higher than polymeric membranes, which was due to the enhanced preferential thiophene sorption in amine functionalized UiO-66.

Overall, the lack of water stability for most MOFs hampers their crystalline membranes for pervaporation separation of organic-water mixtures [131]. According to the hard/soft acid-base principle, high-valence metal ions with high charge density could form a stronger coordination bond towards the ligands. Moreover, high-valence metal units with higher coordination number normally result in a rigid structure, making the metal sites less susceptible to water molecules. Considering the sub-nanosized window size and presumed solvent stability, MOFs could be promising membrane materials for separation of organic-organic mixtures. However, this potential was far more demonstrated yet. Possible challenges include enhancing size sieving property of flexible MOF window, preferential adsorption for specific permeant that can be easily desorbed as well, membrane structural stability against the swelling of solvent at high temperature.

3.4. COF membranes

Covalent organic framework (COF), a new class of porous crystalline polymers, are promising membrane materials owing to their well-defined and highly ordered pore channels [132]. The covalent bonds render COFs with higher stability in liquids than MOFs with coordination bonds. Although a polymer in nature, COF is considered as a kind of materials for fabricating inorganic membranes in terms of its well-defined crystalline pores. Three methods have been well developed to fabricate crystalline COF membranes: in-situ growth, interfacial polymerization and LBL assembly. The last method stacks COF nanosheets into laminar membrane structure that is often regarded as two-dimensional-material membranes and will be discussed in the next section. The in-situ growth of COF membranes basically follows the COF synthesis method. Besides of growing in an autoclave [133], the polymer nature of COF enables its precursor with desirable viscosity that can be casted on a porous substrate to form a continuous COF membrane [134]. If two linkers of COF can be respectively dissolved in organic solvent and water, like PA membranes, interfacial polymerization is able to fabricate the COF membrane at the solvent/water interface [135,136]. Mediator is often added into the membrane formation to promote the formation of crystalline structure instead of amorphous polymer.

The pore structures of COFs are derived from the geometry and connectivity of the linkers, whose sizes range from 0.5 nm to 4.7 nm. Most reported COFs for membrane separation are hydrophilic because of the chemical structures of organic linkers. Up to date, COF membranes were mostly studied for nanofiltration owing to the appropriate pore size and high chemical resistance. The intrinsic crystalline pore sizes of COFs are not suitable for separation of small molecules involved in pervaporation separation, which need to be further reduced to sub-nanometer to realize the sieving of small molecules. It was demonstrated that the aperture size of TpPa COF (Tp: 2,4,6-triformylphloroglucinol, Pa: p-phenylenediamine) membranes can be shrunk from 0.8-1.3 nm to 0.49-0.51 nm by the offset-eclipsed stacking or unoriented assembly of COF nanosheets. Bronsted acid was introduced to mediate the TpPa COF transformation from amorphous to crystalline structure, thereby confining the TpPa COF membrane growth at the interface during interfacial polymerization synthesis [137]. The TpPa COF membrane mediated by n-octanoic acid displayed total flux of 10.57 kg/m$^2$h and separation factor of 5534 for pervaporation dehydration of 90 wt% n-butanol/water mixtures at 80 °C. In another study, a post-synthetic linker exchange method [138], using a short linker hydrazine hydrate (H$_2$) to partially replace the long linker Pa of the synthesized TpPa COF membrane, was proposed to reduce the average

![Fig. 13. UiO-66 crystalline membrane: morphology (inset: framework window aperture) and solvent dehydration performance [123].](image-url)
pore size from ~1.2 nm to ~0.5 nm (Fig. 14). With the improved molecular sieving property, the separation factor of the COF membrane for butanol dehydration was highly enhanced. The TpPa@Hz membrane with thickness of ~80–90 nm exhibited total flux up to ~12 kg/m²h and separation factor of ~3500 for pervaporation dehydration of 90 wt % n-butanol/water mixtures at 80 °C during 15 days long-term operation.

Despite of many COF structures available, only a few of them have been translated into separation membranes. More facile synthesis approaches should be developed to fabricate thin and robust COF membranes. To further realize an efficient pervaporation process, the pore size of COFs is still needed to be reduced by using the established or new strategies. Industrially preferred membrane configuration (e.g., tubular) and fabrication method (e.g., casting) have been realized for COF nanofiltration membranes, providing insights for the long-term development of COF pervaporation membranes.

4. Two-dimensional-material membranes

Since the discovery of graphene, two-dimensional (2D) materials are received increasing attention in membrane separation, and regarded as a new family of membrane materials [139]. Due to the atomic thickness of 2D materials, significant reduction in membrane thickness and ultra-fast transport behavior through the in-plane pores or interlayer channels are expected in the membranes, thereby achieving both high permeance and selectivity for molecular separations. Considering the affinity and size sieving effect, currently 2D-material pervaporation membranes are mostly used for organic dehydration. Among them, laminar graphene oxide (GO) membranes with hydrophilic nature and molecular sieving interlayer channels are the most widely studied and have shown excellent organic dehydration performance as high as that achieved in inorganic membranes. Another kind of promising 2D-material membrane is assembled by COF nanosheets, in which both in-plane regular pores and interlayer channels can be utilized for molecular transport. In addition, other 2D materials such as MXene and layered double hydroxide (LDH) are also explored to develop pervaporation membranes for organic dehydration showing moderate separation performance.

4.1. Graphene oxide membranes

Graphene-based membrane is the first and mostly studied 2D-material membranes since the 2010s [140,141]. Compared with other 2D materials for membrane separation, graphene-based materials own the advantages in single-carbon-atom thin and large lateral size up to hundreds of micrometers. Monolayer or a few-layered graphene membranes are generally fabricated by chemical vapor deposition with/without subsequent perforation process. The complex fabrication with very small area and low pore density limits this kind of graphene membranes to theoretical study [142,143]. Alternatively, as an important derivate of graphene, GO can be readily synthesized and assembled into large-area laminar membranes by utilizing the functionality of oxygen-containing groups (e.g., –OH, –COOH) on graphene nanosheet. As a result, GO membranes are the majority of graphene-based membranes or even 2D-material membranes, which have shown great potential in various membrane processes including ultrafiltration, nanofiltration, reverse osmosis, forward osmosis, pervaporation and gas separation [139].

Filtration, driven either by downstream vacuum [144] or upstream pressurization [145], is the most popular method to assemble GO nanosheets into laminar membranes (Fig. 15). Other approaches have been also developed to fabricate GO membranes, including spinning coating [146], spray coating [147], dip-coating [148], solution casting [149] and LBL assembly [150]. Ordered stacking of GO nanosheets with controlled interlayer channel size and thinner GO membrane layer without non-selective defects are always pursued by using these assemble methods. Owing to the hydrophilic nature of GO nanosheets and the molecular sieving property of interlayer channels, GO membranes are ideal for selective transport of water molecules from molecules with larger size, corresponding to the process of organics dehydration. Solution-diffusion model can be applied to describe the GO membranes for pervaporation separation process [151]. Compared with conventional pervaporation membrane materials discussed above, GO membranes exhibit similar surface sorption behavior whereas different diffusion pathways due to the unique laminar structure. Due to the non-porous structure of GO nanosheet, interlayer channels are considered the main diffusion route for molecular diffusion, and the slit-like pores and in-plane holes provide additional or shortcut pathways.
through the GO laminar membranes. An initial attempt [144] on GO membranes for pervaporation is realized by vacuum-filtrating GO nanosheets onto a porous ceramic hollow fiber substrate to form a laminar GO membrane layer with \( \sim 1 \mu m \) thickness. The GO membrane could dehydrate 2.6 wt% DMC/water mixtures at room temperature, with permeation flux of 1.7 kg/m\(^2\)h and separation factor of 740. Another work used pressurized filtration to prepare GO laminar membrane as thin as 231 nm, showing high flux of 4.14 kg/m\(^2\)h and separation factor of 1164 for dehydration of 70 wt% isopropanol/water at 70 °C [145]. It was demonstrated that the amphiphilic GO provided water transport channels where water molecules were preferentially adsorbed at the hydrophilic edge of GO and then diffused through the hydrophobic core of GO (Fig. 15). The initial studies suggested two approaches to enhance the organic dehydration performance of GO membranes: improving the membrane hydrophilicity and tuning the size of interlayer channels.

Surface modification is a straightforward method to improve the hydrophilicity of GO membranes and enhance the pervaporation dehydration performance. It was considered that the ultra-fast water transport property of interlayer channels would be compromised if there are no sufficient water molecules adsorbed on the surface of GO membrane. With this in mind, a highly hydrophilic polymeric coating was introduced onto the surface of GO laminates to form a water-capturing layer (Fig. 16a) [152]. To minimize the transport resistance, a dilute CS solution was used to ensure a loose (rather than dense) and ultrathin \(<10 \) nm polymeric coating. The surface hydrophilization afforded the GO membrane excellent dehydration performance: water flux of \( \sim 10 \) kg/m\(^2\)h and separation factor of 1523 for 90 wt% n-butanol/water mixtures at 70 °C, which is competitive even compared with inorganic membranes. A synergistic effect of highly enhanced water sorption from the polymeric layer and intrinsic interlayer channels from the GO laminates was proposed to explain the fast and selective water transport through the CS@GO membrane.

The preferential water sorption property of GO membranes is not only dependent on the surface hydrophilicity, but also related to the water affinity of interlayer channels. Intuitively, introducing functional groups onto the GO nanosheets or intercalating molecules that have strong affinity towards water into GO interlayer could be an efficient approach to enhance the water sorption within the laminate. Unfortunately, the assembly behavior of GO nanosheets and the interlayer structure of GO laminates would be deteriorated if the functionality approach is not properly designed. Recently, sodium 1,4-phenylenedi-amine-2-sulfonate (PDASA (Na\(^+\))) was rationally introduced into GO interlayer channels, whose amine groups could form covalent bonding with oxygen groups of GO, leading to a highly ordered laminate even as thin as 30 nm (Fig. 16b) [153]. More importantly, the PDASA (Na\(^+\)) acts as water transport promoter by taking advantage of strong water affinity and facilitated transport property of the ionized sulfonate groups, as revealed by both experimental results and theoretical simulation. The introduction of PDASA (Na\(^+\)) generated 38.5% higher permeation flux and 11-fold higher water/n-butanol separation factor compared with pure GO membranes. It was noticed that GO membranes perform excellent dehydration performance towards organic compounds (e.g., DMC, butanol) with weak molecular interaction and large molecular size difference with water molecules. However, precise separation of molecules with a strong coupling effect and small size discrepancy (e.g., water/ethanol), remains a challenge for GO membranes. A recent study addressed this challenge by LBL assembling GO laminate with zwitterion-functionalized GO nanosheets and hydrophilic, positively-charged polyelectrolytes [154]. The carefully introduced high-density ionic hydrophilic groups decoupled the strong water-ethanol interactions by adsorbing water molecules through hydrogen bonding or ionic solvation and meanwhile repelling ethanol molecules due to surrounding hydration layer. With the exclusive and fast water channels, water/ethanol separation factor of 2248 with flux of 3.23 kg/m\(^2\)h were unprecedentedly achieved in the GO membranes as

![Fig. 15. GO laminar membrane: filtration fabrication and transport of water and alcohol [145].](image1)

![Fig. 16. Tuning the water affinity of GO membranes: (a) surface [152], (b) interlayer channels [153].](image2)
dehydration of GO nanosheets, including boronic acid [160], 1,3,5-benzenetricarbonyl trichloride (TMC) [161] and thiourea [162] have been successively developed to fabricate GO laminar membranes with enhanced separation performance and structural stability.

Intercalation is another useful approach to control the stacking behavior of GO laminates and tune the interlayer distance. Positively charged polyelectrolytes can form electrostatic attractions with negatively charged GO nanosheets, and thus can be easily intercalated between GO nanosheets via LBL assembly. It was demonstrated that the electrostatic attraction between CS and GO can drive the assembly of GO nanosheets into ordered interlayer channels [150]. The interlayer height (interlayer spacing subtracts graphene thickness) of GO membrane was reduced (from 0.53 to 0.43 nm) and stabilized in 90 wt% ethanol/water mixtures (from 0.65 to 0.43 nm) with the intercalation of CS. The constant interlayer height of 0.43 nm is highly desirable for dehydration of C2–C4 alcohols because it is much larger than the kinetic diameter of water (0.29 nm) but is not larger than the alcohols (ethanol: 0.43 nm, isopropanol: 0.47 nm, and n-butanol: 0.51 nm). In dehydration of 90 wt% alcohol/water mixtures at 70 °C, the CS/GO membrane exhibited total flux of 2.35, 2.98, and 4.69 kg/m²h and separation factor of 3390, 5790, and 4680 for ethanol/water, isopropanol/water, and n-butanol/water, respectively. It suggested that the CS intercalation enhanced the water discrimination property of the GO laminate without losing the fast diffusion of water.

In principle, nanoparticles can be intercalated into GO laminates to enlarge the interlayer distance and reduce the transport resistance. Sufficiently small particle size and molecular interactions with GO nanosheets are often required to fabricate nanoparticles intercalated GO membranes for pervaporation separation. Otherwise, the ordering of GO stacking might be damaged to generate non-selective defects or the interlayer distance was excessively enlarged to sacrifice the size discrimination property. Nanoporous and hydrophilic UiO-66-(COOH)₂ MOF with particle size of 20–30 nm was intercalated into GO laminar membranes, leading to higher hydrophilicity and more water transport channels [163]. The MOF intercalated GO membrane showed total flux of 2.4 kg/m²h and separation factor of 9751 for pervaporation dehydration of 98 wt% ethyl acetate/water mixtures at 30 °C, which were 159% and 244% higher than those of pristine GO membrane, respectively. Another work [164] introduced calcium lignosulfonate to functionalize GO nanosheets to obtain an ordered interlayer channels with interaction sites for subsequent intercalation. As a result, positively charged polyelectrolyte PEI and TiO₂ with particle size of 2–4 nm can be uniformly introduced into the GO interlayer to form the integrated membrane structure. The permeation flux was up to 6.25 kg/m²h with separation factor of 891 when applying the PEI/TiO₂ intercalated GO membrane for dehydration of 90 wt% n-butanol/water at 70 °C. It was demonstrated that both the interlayer distance and slit-like pores could be precisely controlled by the formed favorable molecular interactions (cation-π, π-π, hydrogen bonding, electrostatic attraction) and spacing effect of the additives.

With the diverse requirements in sub-nanosized channels, affinity and liquid stability, GO membranes for pervaporation have not been studied as much as that for water purification and gas separation. Excellent alcohol dehydration performance was achieved in GO membranes with carefully controlled surface and/or interlayer properties. Further efforts on these GO membranes could be exploring scalable fabrication approaches and evaluating the stability in practical pervaporation process. Additionally, the complex molecular transport pathways and separation mechanism for GO pervaporation membranes deserve more fundamental studies.

4.2. 2D COF membranes

Most COFs have 2D lamellar structures resulting from the planar organic linkers. 2D COFs with uniform in-plane pores (i.e., ordered one-dimensional nanochannels) enable ultrathin membranes with fast and selective transport channels [132]. Similar to fabrication of GO laminar
membranes, COF nanosheets are firstly synthesized via top-down method (e.g., exfoliation of COF) and then stacked into laminar membranes via filtration or LBL assembly on a porous substrate. As discussed in Section 3.4, intrinsic pores of reported COFs, with size of 0.5–4.7 nm, are too large for pervaporation separation of organics and water with molecular kinetic diameters less than 0.5 nm. Recent studies on 2D COF membranes towards pervaporation are mainly focused on developing ultra-thin membranes with sub-nanopores. Another challenge is the weak interlamellar π–π interactions between stacked COF nanosheets resulting in poor mechanical strength of the 2D COF membranes.

A new kind of 2D COF membranes were fabricated via a so-called mixed-dimensional assembly of 2D COF nanosheets and 1D nanofibers [165]. The nanofibers with highly anisotropic shape were covered on the surface of COF nanosheets to decrease the size of COF pore entrance using the sheltering effect of 1D nanofibers. It was found that the pores of TpTG\(_2\) COF membrane (TG\(_2\): triminoguanidinium chloride) was reduced from 1.3 nm to 0.45 nm by mixing assembly with cellulose nanofibers. The highly shrunk membrane pores are favorable for strictly sieving water (0.29 nm) molecules from its mixtures with butanol (0.5 nm). Meanwhile, only a minor decline in permeance of the COF membrane is expected due to the ultra-low transport resistance of 1D nanofiber porous network. In addition, the pristine 2D COF membrane based on weak interlamellar π–π interactions can be reinforced by the introduced multiple interactions with cellulose nanofibers, as well as the robust nanofiber network. The resulting 2D COF membrane exhibited total flux of 8.53 kg/m\(^2\)h with separation factor of 3876 for pervaporation dehydration of 90 wt% n-butanol/water mixtures at 80 °C.

Besides of the physical sheltering effect, the pores of 2D COF membranes can be narrowed by chemical bonding. Recently, a vapor-liquid interfacial synthesis approach was proposed to in situ generate a TPz COF layer onto a pre-assembled TPzHBD COF (DHBD: dihydroxybenzidine) layer to form a heterostructured 2D COF membrane (Fig. 19) [166]. By anchoring TP amine monomers of TPzH (pore size: 0.8 nm) onto the carboxyl groups of TPzHBD (pore size: 1.2 nm) via covalent bonding, narrowly distributed interfacial pores with averaged size of ~0.39 nm were formed in the membrane. The resulting membrane with a thickness of 28 nm exhibits superior permeation flux of 14.35 kg/m\(^2\)h with separation factor of 4464 for dehydration of 90 wt% n-butanol/water mixtures at 80 °C. Moreover, the vapor-liquid interfacial synthesized ultrathin 2D COF membrane can be stably run by pervaporation process up to 30 days. Such excellent stability was not achieved in the simply filtration stacked 2D COF membranes due to the loose structures and weak interfacial interactions.

The reported high-quality 2D COF membranes exhibited outstanding pervaporation dehydration performance, which was even higher than GO membranes, highlighting the advantages of well-defined in-plane pores for fast molecular transport. However, very limited 2D COF membranes have been successfully fabricated, due to the challenges in synthesis of defect-free and large lateral size COF nanosheets, and their highly ordered stacking. Furthermore, the structure-performance relationship in 2D COF pervaporation membranes with in-plane pores and interlayer channels was not clear so far.

### 4.3. Other kinds of 2D-material membranes

MXene, a new family of 2D transition metal carbides and carbonitrides, has been explored as building blocks of molecular separation membranes for water purification [167], desalination [168], pervaporation [169–171] and gas separation [172,173]. Compared with graphene-family materials, MXene with large variety of transition metals offer diverse structures (>30 synthesized compositions reported to date) and higher mechanical stability. Similar to GO, a perfect MXene nanosheet is nonporous, possessing negative charge and hydrophilic characteristic due to the –F, –OH, and/or –O groups on the surface. Thus, MXene nanosheets were assembled into laminar membranes that are capable for pervaporation dehydration of organics.

Vacuum filtration is also the most frequently used approach to fabricate laminar MXene membranes. Initial works on MXene membranes realized high separation performance for water purification [167]. However, the channel sizes of these MXene membranes (~1 nm) are too large for pervaporation separation. The first pervaporation study on MXene membrane was related to desalination by using the nano-channels and hydrophilicity of Ti\(_3\)C\(_2\)T\(_x\) laminate. The MXene membrane was as thin as 60 nm, showing water flux up to 85.4 L/m\(^2\)-h and salt rejection of 99.5% for pervaporation desalination of 3.5 wt% NaCl solution at 65 °C. Molecular sieving property of the MXene nanochannels was not confirmed in this study since the separation of water over salt is essentially based on the evaporation difference. Another study [171] fabricated a 2 μm-thick Ti\(_3\)C\(_2\)T\(_x\) laminate membrane for pervaporation dehydration of 95 wt% ethanol/water mixtures. Moderate performance was obtained with permeation flux of 0.26 kg/m\(^2\)-h and separation factor of 135, which was evaluated at room temperature and decreased at elevated temperature. The reason could be the thick membrane layer and non-selective defects or inappropriate channel size of the MXene membrane.

To pursue integrated and ordered nanochannels, positively charged PEI was electrostatically intercalated with negatively charged MXene nanosheets to realize ordered stacking structures, followed by introducing interfacial polymerization of TMC with PEI to seal possible defects (Fig. 18) [169]. Two kinds of MXene, Ti\(_3\)CT\(_2\) and Ti\(_3\)CT\(_3\), were compared for the membrane fabrication and separation performance. The interlayer height of Ti\(_3\)CT\(_2\) membrane is smaller than that of Ti\(_3\)CT\(_3\) membrane (0.44 nm vs. 0.55 nm). Moreover, Ti\(_3\)CT\(_2\) membrane showed higher water sorption capacity than Ti\(_3\)CT\(_3\) membrane. The Ti\(_3\)CT\(_3\) membrane with stronger size discrimination ability and hydrophilicity was more favorable for selective permeation of water (0.29 nm) from isopropanol (0.47 nm). Defect-free Ti\(_3\)CT\(_2\) membrane with thickness of ~100 nm could efficiently dehydrate 90 wt% isopropanol/water mixtures at 50 °C with total flux of 1.07 kg/m\(^2\)-h and water content in the permeate side of more than 99 wt%.

Until now, the pervaporation performance of MXene membranes requires much more enhancement by precisely controlling the nanochannel size and defect elimination [174]. Additional attention should...
be paid to the chemical stability of MXene. Ti$_3$C$_2$T$_x$ MXene is stable under inert gas until 800 °C with a minimal level of oxidation at around 500 °C (yielding anatase TiO$_2$). However, in the presence of oxygen, surface-exposed metal atoms of MXene are more prone to oxidation, which might lead to spontaneous oxidation [175]. It is reported that Ti$_3$C$_2$T$_x$ MXene solution was completely degraded in open vials after 15 days, while can be well preserved in oxygen-free container at low temperature [176]. In addition, MXene are much more stable in dry form (free-standing or mixed-matrix membrane) or after annealing under hydrogen atmosphere [177].

Besides, LDH consisting of positively charged brucite-like laminates with charge compensating anions located in interlayer galleries offers an opportunity to form a 2D-material membrane with unique vertical transport channels. An orderly CoAl-LDH membrane with an interlayer height of 0.28 nm was in-situ hydrothermally grown on a ceramic substrate [178]. The vertically aligned interlayer galleries of the LDH membrane offered fast transport pathways for water while size-excluded solvent molecules. As increasing the water content in the feed from 10 wt% to 50 wt% at 75 °C, the permeate flux of the CoAl-LDH membrane was increased from 1132 to 5780 g/m$^2$h and the water content in the permeate is increased from 99.13 wt% to 99.99 wt%. Despite of great potential, it remains challenging to precise tune the orientation and size of the interlayer galleries in LDH membrane.

5. Mixed-matrix membranes

In addition to the above-mentioned pervaporation membranes made by a single type of material, mixed-matrix membranes (MMMs), prepared by incorporating fillers into polymeric matrix, have received increasing attention since the 1990s [179]. The permeability-selectivity upper-bound for polymeric membranes can be transcended with incorporation of high performing fillers in polymer matrix [4]. Meanwhile, the fabrication of MMMs adopts the general methods for polymeric membranes, showing an advantage in cost-effective and scalable production compared with inorganic membranes [18]. Molecular transport in MMMs follows the solution-diffusion model. Thus, the filler enhanced transport property of polymeric membrane can be resulted from the enhancement in adsorption and/or diffusion coefficients and selectivity. As for MMMs applied in pervaporation process, hydrophilic or hydrophobic fillers are selected and incorporated into polymeric membranes to enhance the membrane preferential adsorption towards water or organic molecules [20]. The preferential diffusion through the membrane can be promoted with the more permeable and/or selective transport channels of the fillers than the polymer matrix, which relies on homogenous dispersion of fillers in polymer matrix without interfacial voids.

The separation performance of MMMs is mainly dependent on the physicochemical properties of fillers. Indeed, the development of MMMs always keeps in step with the advance of nanomaterials that can be used for fillers. The first generation MMMs intensively studied during the 1990s–2010s are based on purely inorganic fillers (e.g., zeolites, silica). High performance was not often obtained in these MMMs due to the challenges in achieving uniform filler dispersion and inhibition of interfacial voids [180]. The discovery of novel nanomaterials (e.g., MOFs [181], 2D materials [182]) with diverse functionalities and pore structures promotes the emergence of second generation MMMs since the 2010s. Compared with purely inorganic fillers, these nanomaterials with tunable organic groups show much better compatibility with polymers, leading to the highly improved dispersion and interfacial morphology in MMMs [15].

5.1. Zeolite MMMs

The pioneer work of MMMs for pervaporation was incorporating hydrophobic MFI zeolites into PDMS membrane, leading to higher flux and separation factor for ethanol/water separation [89,183]. This is due to the MFI zeolite fillers with high hydrophobicity and well-defined transport channels enhanced the sorption and diffusion of ethanol over water. Uniform particle dispersion, high zeolite loading and particle size, which are mainly related to particle agglomeration, were identified as three key parameters of determining the separation performance of MFI/PDMS MMMs [184]. Surface modification of zeolites was proven to be favorable of achieving uniform filler dispersion at higher loading. Based on the surface Si–OH or Al–OH groups, zeolites can be facilely modified with silane coupling agents, attaching organic linkages to form covalent bonding [185] or other strong molecular interations [186] with PDMS chains. The surface silylation of zeolites could enhance its compatibility and interaction with polymer, improving the zeolite dispersion in polymeric matrix [180]. Excellent ethanol/water separation factor up to 59 was achieved with the

Fig. 19. 2D COF membrane: vapor-liquid interfacial synthesis, SEM images and transport of water and butanol molecules through the membrane [166].
silicalite-1 zeolite loading up to 77 wt% in the PDMS MMMs [12]. As shown in Fig. 20, increasing the zeolite loading in the PDMS matrix could gradually enhance the separation factor, which is attributed to the hydrophobic silicalite-1 zeolite pores promote the ethanol permeation and meanwhile inhibit the water transport through the membrane. However, earlier PDMS MMMs were very thick, with thickness up to 100 μm, resulting in a low permeation flux (<0.2 kg/m²h for 5 wt% ethanol/water at 50 °C) that is unattractive for practical application.

To achieve a thinner MMM layer, smaller sized fillers are needed to reduce the membrane thickness without introducing non-selective defects. By reducing the filler size from 1-3 μm to 0.1-0.2 μm, the membrane thickness of silicalite-1/PDMS MMMs was reduced from 300 μm to 19 μm, resulting in 7-fold enhancement in permeation flux (0.6 kg/m²h) and equivalent separation factor (93) for pervaporation recovery of n-butanol from its 1 wt% aqueous solution at 70 °C [187]. The thickness of MMMs can also be controlled by tuning the fabrication conditions. As for PDMS MMMs, reducing the viscosity of casting solution could obtain thinner membrane layer, but more easily cause filler sedimentation due to the higher density difference between filler and casting solution. A recent study [188] demonstrated that silicalite-1 (particle size < 500 nm with vinyltriethoxysilane surface modification) filled PDMS solution with a suitable viscosity controlled by pre-polymerization of PDMS can be casted into 5 μm-thick MMMs with 67 wt% loading. The thin-film silicalite-1/PDMS MMM exhibited outstanding flux of 5.52 kg/m²h and good separation factor of 15.5 for 5 wt% ethanol/water mixtures at 50 °C.

MMMs based on hydrophilic zeolites and polymers were explored for pervaporation dehydration. Besides of enhanced preferential adsorption property in hydrophobic MMMs, the incorporated zeolite can introduce additional molecular sieving property into the hydrophilic membrane as the organic molecules are larger than the pore size of the zeolite. Hydrophilic zeolites with variable pore sizes were used as fillers for hydrophilic MMMs, which mostly are commercial A-type zeolites: 3A (pore size: 0.3 nm), 4A (pore size: 0.4 nm), 5A (pore size: 0.45 nm) and 13X (pore size: 0.74 nm). Generally, incorporating hydrophilic zeolites with larger pore size led to more enhancement in flux, while zeolite fillers with smaller pore size gained higher separation factor for pervaporation dehydration of organics. This effect was also indicated by the sorption measurement. For instance, P84 PI filled with 20 wt% 5A zeolite exhibited lower sorption capacity but higher water/isopropanol sorption selectivity compared with that filled with 20 wt% 13X zeolite [189]. Considering the enhancement in preferential water sorption, incorporating zeolites with same pore size but higher hydrophilicity (e.g., NaX vs NaY) obtained more water selectivity although both boosted permeances for water and ethanol of PVA membrane [190].

Hydrophilic polymers such as PVA and PI are often glassy polymers. The rigid polymer chains undergo strong shrinkage stress during the solvent evaporation process, leading to poor adhesion with zeolite fillers and decreasing the selectivity of MMM. Moreover, the polymer chains might be rigidified by the filler at the interface, or partially block the zeolite pores, resulting in reduced permeability while higher selectivity. The filler/polymer interface can be improved by enhancing the molecular interactions between filler and polymer. It was found that 13X zeolite/P84 PI MMMs after annealing at 250 °C could form charge transfer complexes between the Na⁺ in 13X zeolite framework and the electron acceptor groups of P84 PI [189]. The molecular interactions generated a stronger interfacial adhesion, but also chain rigidification as indicated by higher T_g of the MMMs. Compared with rubbery polymers, an ideal filler/polymer interface is more challenging for zeolite/glassy polymer MMMs. This may account for an observation that the optimal zeolite loading in glassy PVA or PI membranes to achieve defect-free interface is usually less than 30 wt%, which is only half of that in rubbery PDMS membrane.

Until now, the performance combination between polymeric membranes and zeolite membranes was not so successful in zeolite/polymer MMMs for pervaporation. Reasons include the trade-off between uniform filler dispersion and high filler loading, or between interfacial defect and chain rigidification. As for the MMMs with high separation factor, how to effectivity reduce the membrane thickness requests more efforts. Future attention can be paid to novel synthesis approaches for zeolite nanoparticles and create favorable interactions with polymer matrix.

5.2. Silica MMMs

Silica is a common filler of polymer to produce nanocomposites with dramatically improved bulk properties. Following this idea, silica nanoparticles, although nonporous mostly, were introduced as fillers to tune physical and/or chemical structures of polymer membranes. Two main functions are considered by using silica fillers in MMMs: enhancing hydrophilicity and regulating chain conformation. The sol-gel synthesis of silica nanoparticles can be facilely processed in the aqueous polymer solution. Thus, a unique feature of silica for MMMs is that it can be in-situ formed in polymer matrix, providing a promising solution to inhibit filler agglomeration and interfacial void. Owing to the hydrophilic nature, silica was incorporated into hydrophilic polymers to develop pervaporation MMMs for dehydration of organics.

γ-glycidoxypropyltrimethoxysilane (GPTMS) was regarded as an

Fig. 20. MFI/PDMS MMM: cross-sectional SEM image and ethanol/water separation factor [184].
appropriate precursor for in-situ incorporation of silica into PVA [191] or CS [192] membrane. The trimethoxy groups of GPTMS is hydrolyzed in the presence of acid catalyst to form silanol groups for the following condensation reaction to generate the Si–O–Si linkage of silica fillers (Fig. 21). Meanwhile, under acidic conditions the epoxy of GPTMS will open and react with the hydroxyl groups of PVA to form C–O–C, or with the amino groups of CS to form C–N covalent bonding. Also, the crosslinking will occur between hydroxyl groups of PVA and silanol groups of silica. A uniform distribution of silica with size of 20–50 nm was observed in the PVA membrane. Positron annihilation lifetime spectroscopy revealed that the in-situ incorporated silica affected the packing of PVA chains, thereby increasing the size and number of both network pores (radius from 0.22 to 0.3 nm) and aggregate pores (radius from 0.31 to 0.41 nm) of the membrane. These silica-enlarged free volume cavities are in favor of enhancing the selective permeation of benzene (radius: 0.263 nm) from its mixtures with cyclohexane (radius: 0.303 nm). As a result, the permeation flux of PVA membrane was increased from 20.3 to 137.1 g/m²h and separation was increased from 9.6 to 46.9 for pervaporation separation of 50 wt% benzene/cyclohexane at 50 °C [191]. In addition, the crosslinking effect of silica on CS endowed silica/CS MMMs with an excellent stability (140 days) during pervaporation dehydration of 70 wt% isopropanol/water at 70 °C [192].

Polyhedral oligomeric silsesquioxanes (POSS) is a kind of silica nanoparticles with particle size as small as 1–3 nm. It has an organic-inorganic structure, consisting of Si–O cage and functional groups attached to the corner Si atoms. The ultra-fine particle size and functional groups enabled POSS as a promising filler to develop MMMs with molecular-level dispersion [193,194]. With the intermolecular interactions or even covalent bonding between POSS and polymer, the resulting MMM dense films with loading up to 20 wt% were still transparent, as POSS filler is too small to scatter the visible light. Nevertheless, optimal loading for POSS MMMs was often low (<5 wt%) in terms of obtaining both higher permeability and selectivity [193,194]. This might be due to that the excessive intermolecular interactions increased the transport resistance, and aggregation of POSS at molecular level created non-selective interfacial voids. On the other hand, the molecular interactions between POSS filler and polymer matrix were found to be useful for controlling the conformation of polymer chains [195]. Interestingly, the incorporation of POSS fillers reduced the size of network pores (radius from 0.202 to 0.167 nm) while increased the size of aggregate pores (radius from 0.373 to 0.392 nm) of PDMS membrane. The feature of tunable free volumes achieved in the POSS/PDMS MMMs was beneficial for the selective permeation of large-sized molecules (e.g., butanol with radius of 0.250 nm) over small-sized molecules (e.g., water with radius of 0.145 nm).

MMMs with in-situ formed silica nanofillers can easily achieve uniform dispersion and intact interface, in which however the nonporous silica could not essentially provide fast transport channels. Mesoporous silicas are widely available, which would show great potential in MMMs for pervaporation if post-treatment approaches are developed to reduce the silica pore size to sub-nanometer. On the other hand, it is meaningful to extend the in-situ formation approach from silica to other porous filler in MMMs.

5.3. MOF MMMs

MOF is a new family of crystalline porous fillers for MMMs. Compared with zeolites, the advantages of MOF filler include better compatibility with polymer due to the organic linkers, diverse pore structures, smaller particle size obtained at mild synthesis conditions. Although a larger number of MOFs have been discovered, only a few of them was used as filler of MMMs for pervaporation, such as ZIF-8, ZIF-7, ZIF-71 and UiO-66. As discussed in Section 3.3, the main reason could be the stability of MOF in liquids especially in water. Assuming the MOFs are liquid stable, there are two criteria for selecting MOFs to develop MMMs for pervaporation: affinity and pore size, which is similar to the development of crystalline membranes. Hydrophilicity is often the primary condition to determine a MOF filler suitable for hydrophilic or hydrophobic MMMs. Sometimes the interplay between affinity enhanced sorption and pore size enhanced diffusion on the pervaporation performance is complicated. This explains that a MOF (e.g., ZIF-8) can be either incorporated into a hydrophobic (e.g., PDMS) or hydrophilic (e.g., PVA) polymer to achieve higher separation performance in the resulting MMMs. The first and also the most studied MOF fillers for pervaporation membranes is ZIF-8, which can be easily synthesized at room temperature with high yield and nanosized particles. The framework of ZIF-8 is hydrophobic due to the methylimidazole linkers and the coordinative saturation of metal sites [196], and has aperture size of 0.34 nm while with a certain flexibility. Initial attempt [44] incorporated ZIF-8 nanoparticles with size of ~40 nm into hydrophobic silicone rubber,
polymethylphenylsiloxane (PMPS), towards recovery of alcohols from aqueous solution. Both C<sub>2</sub>-C<sub>4</sub> alcohol permeability and alcohol/water separation factor of PMPS membrane were highly enhanced with incorporation of ZIF-8. The most significant enhancement is for pervaporation separation of 1 wt% i-butanol/water mixtures at 80 °C. The ZIF-8/PMPS MMM with optimal loading of 13 wt% and thickness of ~2.5 μm exhibited total flux of 6.4 kg/m²·h and separation factor of 40.1. The permeation cut-off between C<sub>3</sub> and C<sub>4</sub> alcohols observed in PMPS membrane filled with ZIF-8 even though with smaller aperture size (0.55 nm vs 0.34 nm), suggesting the flexibility of ZIF-8 framework. Moreover, incorporating ZIF-7, another hydrophobic MOF with smaller aperture size (0.30 nm) and more rigid framework, showed lower enhancement in i-butanol permeance and separation factor compared with ZIF-8. The above results demonstrated that the hydrophobic and relatively flexible channels of ZIF-8 offered the membrane highly enhanced selective permeation of alcohol over water molecules.

Inspired by the above stimulating results, later studies were followed to optimize the fabrication of hydrophobic ZIF-8 MMMs. A simultaneous spray self-assembly of a ZIF-8/PDMS prepolymer suspension and a cross-linker/catalyst solution was proposed to achieve higher filler loading (40 wt%) in a submicron MMM layer (~800 nm) [197]. As increasing the ZIF-8 loading in the membrane up to 40 wt%, both the flux (or butanol permeability) and separation factor (or butanol/water selectivity) were significantly enhanced, which was attributed to the stronger affinity of n-butanol over water with a uniform ZIF-8 distribution in the PDMS matrix. Much higher separation factor (81.6) was obtained in the high-loading ZIF-8/PDMS MMM with outstanding flux (4.85 kg/m²·h) as pervaporation separation of 1 wt% n-butanol/water at 80 °C. Recently, ZIF-8 nanofillers were in-situ formed in PDMS matrix via interfacial synthesis in which the Zn<sup>2+</sup> was dissolved in water phase and ligand was dissolved with PDMS in alcohol/heptane mixed organic phase [198]. The ZIF-8@PDMS MMM with thickness of ~1.2 μm showed total flux of 1.78 kg/m²·h and separation factor of 12.1 for pervaporation recovery of ethanol from its 5 wt% aqueous solution at 40 °C.

Besides of ZIF-8, other hydrophobic ZIFs were employed to fabricate MMMs for pervaporation recovery for organic compounds from aqueous solution. ZIF-71 with aperture size of 0.48 nm exhibited equilibrium uptake of 250 mg/g for n-butanol whereas nearly no uptake for water at 40 °C [57], which are comparable to the i-butanol uptake of 350 mg/g and negligible water uptake in ZIF-8 [44]. Compared with highly hydrophobic silicalite-1 zeolite, the butanol uptakes are 3–4 times higher and the same ultra-low water uptake in ZIF-8 and ZIF-71 although with smaller aperture size. Thus, incorporating ZIF-71 with particle size of ~1 μm with loading up to 20 wt%, the flux and separation factor of Pebax 2533 membrane were simultaneously enhanced [57]. The ZIF-71/Pebax MMM showed stable performance during 100-h pervaporation separation of fermentation broth containing 2 wt% n-butanol, acetone and ethanol. The selective permeation of C<sub>4</sub>-C<sub>6</sub> alcohols through PDMS membrane were also enhanced by incorporating ZIF-71 fillers [199].

Interestingly, these hydrophobic ZIFs with molecular sieving properties were also used as fillers in hydrophilic polymers. Four-fold water flux with almost no decrease in separation factor were obtained by incorporating 34 wt% ZIF-8 nanoparticles into PBI membrane for n-butanol dehydration [200]. Similar result was observed in 5 wt% ZIF-7/CS MMM for ethanol dehydration [201]. Analysis on solubility and diffusivity of the MMMs revealed that ZIF-8 fillers enhanced the water diffusivity. The diffusion selectivity was also increased based on the size exclusion of ZIF-8 aperture, which however was offset by the reduction in water sorption selectivity due to the hydrophobic nature of ZIF-8. By attaching –NH<sub>2</sub> groups onto the surface of ZIF-8 filler to increase the hydrophilicity, the resulting MMMs exhibited both higher separation factor and flux than pristine PVA membrane for ethanol dehydration [202].

In comparison, intrinsically hydrophilic and water stable Zr-MOFs, such as UiO-66 and MOF-801, are more suitable fillers for hydrophilic MMMs. The water uptake in MOF-801 was as high as 350 cm<sup>3</sup>/g [203], while ethanol uptake is only 30 cm<sup>3</sup>/g, confirming the hydrophilic framework. By incorporating 5 wt% MOF-801 (particle size: 400 nm) into CS, both the flux and separation factor were increased to

![Fig. 22. ZIF-8/PDMS MMMs: SEM images and butanol/water separation performance [197], inset of SEM is the butanol adsorption site in ZIF-8 framework [44].](image-url)
1.94 kg/m²h and 2456 for dehydration of 90 wt% ethanol/water at 70 °C [203]. With the same loading and separation factor, CS filled with MOF-801 showed much higher flux than ZIF-7 [201], which can be attributed to the higher hydrophilicity and larger aperture size (0.6 nm vs 0.3 nm). UiO-66 with particle size of 100 nm was uniformly dispersed in 6FDA-HAB/DABA PI matrix up to 30 wt% loading, increasing the number and size of free volume cavities [204]. Thus, the incorporation of UiO-66 enhanced the performance of PI membrane for C2–C4 alcohols dehydration. It was further demonstrated that attaching hydrophilic –NH2 (UiO-66-NH2) or hydrophobic –F4 (UiO-66-F4) onto the linkers of UiO-66 fillers could tune the sorption properties of water and alcohol and thus the alcohol dehydration performance of the MMMs [205]. Recently, UiO-66-NH2 with particle size of 80–90 nm was incorporated into cellulose triacetate matrix and spun into dual-layer hollow fiber using Ultem as substrate layer (Fig. 23) [206]. The UiO-66-NH2 MMM hollow fiber exhibited high flux of 2.67 kg/m²h and separation factor of 170 during 200-h continuous dehydration of 85 wt % ethanol/water at 50 °C.

As expected, compared with zeolite MMMs, MOF MMMs exhibited distinct advantages in synthesis of nanofillers, uniform filler dispersion in polymer matrix without interfacial voids, and much thinner membrane layer. It is interesting to notice that ZIF-8, although did not succeed in crystalline pervaporation membranes, have shown excellent pervaporation performance by using as fillers in hydrophobic polymeric membranes. More attention should be paid to the long-term stability of ZIF-8 MMMs due to the known water stability challenge of ZIF-8 crystalline membranes. Up to date, only a small number of MOFs were demonstrated for pervaporation separation. More water-stable MOFs with appropriate aperture size should be identified to extend the spectrum of promising MOF MMMs.

5.4. COF MMMs

COFs possessing purely organic compositions and well-defined crystalline pore structure are ideal porous fillers for MMMs. Compared with MOFs, COFs possess higher chemical stability while lower molecular sieving property due to larger pore size (0.5–4.7 nm) [132]. Thus, incorporating COF fillers with preferential adsorption property and fast diffusion channels can enhance the pervaporation performance of polymeric membranes. Additionally, COFs that remain challenges in fabrication of integrated crystalline membranes can be introduced as fillers in MMMs. Like MOF MMMs, development of COF MMMs is mainly dependent on the affinity of COFs. The –OH, –COOH and –NH2 of linkers endowed COFs with hydrophilicity, meanwhile the aromatic rings and polar bonds of COFs show affinity towards aromatics.

Hydrophilic COFs such as TpHz (pore size: 0.8 nm) and SNW-1 (pore size: 0.5 nm) were employed as nanofillers to enhance the water flux and separation factor of polymeric membranes. A gradient distribution of COFs nanosheets in the polymer matrix can be obtained by controlling the COF addition and phase separation of polymer. Owing to the low density of COF fillers, COF fillers are more prone to be enriched on the surface of MMM (Fig. 24). The resulting SNW-1/S MM [207] or TpHz/PES MMM [208] exhibited outstanding dehydration performance: permeation flux of 2.4–2.5 kg/m²h and separation factor of 1293–1430 during 250–320 h continuous test in 90 wt% ethanol/water at 76 °C. It was envisioned that the surface enriched COFs mainly enhanced the surface hydrophilicity and water preferential sorption, and the minority of COFs entraped in polymer matrix provided additional transport channels for water molecules.

Hydrophilic polymers including PDMS and Pebax were filled with COFs for selective permeation of organics from aqueous solution or organic mixtures. It was demonstrated that hydrazone-linked COF-42 incorporated PDMS membrane with only 1 wt% loading achieved high separation factor of 85.2 with total flux of 1.58 kg/m²h for 1 wt% n-butanol/water at 80 °C [209]. By replacing the ethyl groups of COF-42 framework with n-butyl, n-propyl and 2-propyl, the pore size was reduced from original 2.3 nm–1.77 nm, 1.85 nm and 1.96 nm, respectively, and the local hydrophobicity was also tuned. Highest separation factor was obtained in the 2-propyl modified COF-42 filled PDMS MMM, indicating that hydrophobic regions promoted the transport of butanol molecules while inhibited the transport of water molecules. Another study assumed that imine bonds of COF-300 could form hydrogen bonding with water that may hinder water transport through the channel, while the aromatic structure provides high affinity for organics. This was partially supported by the high furfural uptake in COF-300 (525.3 mg/g) at 80 °C. Pervaporation test showed that incorporating COF-300 enhanced the permeation of organics such as furfural, aniline, butanol, ethanol and phenol but inhibited water transport through PDMS membrane [210]. Another hydrazone-linked COF, COF-LZU8, was modified with Ag+ and then incorporated into Pebax 2533 for pervaporation separation of aromatic/aliphatic mixtures [211]. It was found that the synergistic effect of d-π and π-π conjugation interaction of COF with benzene ring facilitated the selective permeation of benzene (or toluene) over cyclohexane (or n-heptane) in the 50/50 (w/w) mixtures.

The emerging COF fillers have shown great potential in both hydrophilic and hydrophobic membranes, significantly enhancing the pervaporation performance of polymeric membranes with low loading. Assuming little molecular sieving effect of the large intrinsic pores of COFs, the specific function of COF fillers on the enhancement of transport properties is vague as yet. Advanced characterizations of the physicochemical properties of COF MMMs would be helpful to further understand the transport mechanism behind the excellent pervaporation performance.

5.5. 2D-material MMMs

The unique structure of 2D materials motivated researchers to explore them as fillers in MMMs. Besides of the functional groups of 2D fillers, the in-plane pores, edge-to-edge slits and plane-to-plane channels provide versatile molecular transport pathways in MMMs. GO is the most studied 2D materials for MMMs because it can be easily synthesized with single-layer nanosheets, and its abundant oxygen-containing groups offer good solution dispersion and polymer compatibility, as well as preferential adsorption sites. The majority of GO MMMs for pervaporation utilized the intrinsic hydrophilicity and 2D channels of GO nanosheets to enhance the organics dehydration performance.
Alternatively, GO was functionalized with hydrophobic groups and used as fillers for hydrophobic 2D-material MMMs that can be applied in organic recovery from aqueous solution and organic-organic separation.

Sodium alginate (SA) MMMs incorporated with pristine GO or reduced GO nanosheets showed enhanced dehydration performance for ethanol/water mixtures [212]. It was found that reduced GO with smaller nanosheet size, more structural defects and non-oxide regions was more favorable for the selective water transport through the GO/SA MMM. Water transport channels introduced in the MMM were considered as a result of the structural defects, edge-to-edge slits, and non-oxide regions of GO nanosheets. Another study modified GO with zwitterionic groups and incorporated into SA membrane, achieving 1.5–2.5 times of flux and separation factor obtained in unmodified GO/SA MMM [213]. Besides of the GO-introduced channels, the zwitterionic groups on GO electrostatically created a hydration layer that have high water affinity and ethanol repellency. To create molecular interactions with SA matrix, the zwitterionic groups on GO electrostatically created a hydration layer that have high water affinity and ethanol repellency. To create molecular interactions with SA matrix, GO nanosheets were functionalized with calcium lignosulfonate (CaLS) [214]. The Ca\(^{2+}\) could form cationic interactions with GO and crosslink the SA chains. Meanwhile, the anionic lignosulfonate acid groups provided additional hydrophilic sites for the transport of water molecules. The resulting CaLS-GO/SA MMM exhibited 200-h stable permeation flux larger than 2.5 kg/m\(^2\)h and separation factor of 2991 for 90 wt% ethanol/water at 70 °C. Moreover, for hydrophilic polymers with high \(T_g\) (e.g., polyimide), the functionalized GO nanosheets could be bonded with rigid polymer chains to avoid possible interfacial voids and enhance the structural stability of GO MMM [215].

Hydrophobic MMMs often require translating the hydrophilic groups of GO filler into organophilic groups before incorporation in order to enhance the compatibility with hydrophobic polymers and affinity towards organic permeate. To realize hydrophobic surface, GO nanosheets were functionalized with two alkylamines of different lengths, octylamine and octadecylamine, and reduced in hydrazine monohydrate [216]. The incorporation of alkyl-functionalized GO enhanced the flux and butanol/water separation factor of PIM-1 membrane. The octyl-functionalized GO with nanometer lateral size was favorable for inhibition of interfacial voids and membrane swelling, leading to a maximum enhancement in the organophilic separation. By selecting proper monomers, 1-(2-aminoethyl) piperazine and N,N′-methylenebisacrylamide, GO nanosheets were pre-mixed with the monomers via electrostatic interaction between amino and carboxyl groups, and in-situ polymerized to form hyperbranched poly(methylene bisacryl amide amino ethyl piperazine) (HPMA) MMM with uniform GO dispersion and intact GO-polymer interface (Fig. 25) [217]. With benefits from the affinity to methanol and a high specific surface area of GO fillers, the GO MMM exhibited a high separation factor of 1700–2400

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**Fig. 24.** COF/SA MMM: schematic of the membrane structure and transport of water and ethanol [207].

**Fig. 25.** In-situ polymerized HPMA and GO/HPMA MMM: Schematic synthesis and membrane morphology [217].
and flux of 0.2–0.4 kg/m²h for 10 wt% MTBE/methanol at 40 °C. It is clear that incorporating 2D-materials, mostly GO, can significantly enhance the alcohol dehydration performance of polymeric membranes. Despite of excellent molecular transport properties, the transport channels within the 2D-material MMMs are not clear until now. Due to the nonporous or very-low-density porous structure of GO nanosheet, enhanced molecular transport is supposed to mainly occur in edge-to-edge slits and plane-to-plane channels of GO fillers, which however is lack of evidence. Owing to the unique 2D structure of the filler, creating vertical 2D interlayer channels with the aid of polymer matrix and external field if needed, could highly promote the molecular diffusion rate and size sieving effect of the MMMs.

6. Conclusions and perspectives

This article critically reviewed the recent development of materials for pervaporation membranes. The design strategy, fabrication approach, physicochemical properties, pore structures, separation performance and transport mechanism of pervaporation membrane materials have been discussed. Three typical pervaporation separation systems have been employed to study the performance of these membrane materials: dehydration of organic-water mixtures, organic recovery from aqueous solution, separation of organic-organic mixtures. Key achievements and challenges of each kind of materials are concluded as below:

**Polymeric membranes**: Low-cost and highly scalable polymers are still the dominant membrane materials for pervaporation application. Owing to the commercialized precursor and easy fabrication, the benchmarked polymers for hydrophilic membranes (PVA) and hydrophobic membranes (PDMS) did not change. How to stabilize the membrane structure with minimum productivity decline, and to reduce the thickness of defect-free separation layer are the first pursue of these polymeric membranes in recent years. Influences of substrate and interface on the membrane separation performance and stability have been recognized with increasing attention. Processable polyelectrolyte complex and polyamides that can be interfacially polymerized are promising to fabricate submicron thin pervaporation membranes, while their long-term stability still needs further evaluation. Although the demand on organic-organic separations is huge, the performance of state-of-the-arts polymers are unattactive due to the challenges in lack of discrimination ability and structural stability. Polyimides, with rigid and stiff chains, can withstand more aggressive solvents and harsh operating conditions, but showed low permeation flux. Their wider pervaporation application relies on being translated into thin-skinned asymmetric membranes via hollow fiber spinning for instance.

**Inorganic membranes**: Highly porous and relatively rigid structure of inorganic materials endow pervaporation membranes with fairly higher permeance and selectivity than polymers. Zeolite is the most intensively studied inorganic membranes, and also exhibited the best comprehensive performance among the membrane materials for pervaporation. As the first commercial zeolite membrane, NaA membranes achieved very high organic dehydration performance by using hollow fiber substrate and optimizing the seeding method. Acid stability is the main deficiency of NaA membrane, which have been well addressed by developing membranes based on CHA zeolite with properly higher Si/Al ratio. MFI is still the primary hydrophobic zeolite, showing record high selectivity for ethanol recovery from aqueous solution, and xylene isomers separation based on pore size discrimination. The MFI membrane performance can be highly enhanced by growing b-oriented or nano-sheet seeded zeolite layer. The hydrothermal stability of silica membranes was addressed by organic-inorganic hybrid approach. Molecularly designing the silica network to precisely tune the pore structure would be the key to improve the moderate selectivity for organic dehydration. Development of crystalline membranes derived from MOFs and COFs for pervaporation is still in an early stage. Only water-stable UiO-66 MOF membrane showed potential in organic dehydration and organic-organic separation so far. A few emerging COF membranes, by carefully shrinking the excessively large pores during or after synthesis, could separate water from large-sized alcohol (e.g., butanol) as efficient as zeolite membranes.

**2D-material membranes**: GO laminar membrane is the first and most representative 2D-material membranes for pervaporation, in which the selective water permeation is based on preferential adsorption and fast diffusion through the interlayer channels. Crosslinking is effective to tune the interlayer sieving property and stabilize the lamellar structure of GO membranes, meanwhile imparting water capture sites either on the surface or within interlayer could promote the water transport. The butanol dehydration performance achieved in optimal GO membranes are comparable to inorganic membranes. In recent a few years, 2D-material membranes assembled by COF nanosheets with partial pore blockage, could perform even higher flux than GO laminar membranes for butanol dehydration, owing to the lower transport resistance of the well-defined in-plane pores and ultra-thin membrane layer. Until now, there is lack of rational approaches to precisely tune the intrinsic pores of COFs. A common pursue for 2D GO and COF membranes is the specific transport pathway for water and other molecules. The relationship between in-plane pores (defects)/plane-to-plane slits/interlayer channels and pervaporation performance in the 2D-material membranes should be clearly identified. On the other aspect, towards practical application, the observed outstanding organic dehydration performance in the 2D-material membranes should be further checked in long-term operation under realistic conditions (e.g., low pH, high water content). In addition, there are very limited reports on 2D-material membranes for selective permeation of organic from aqueous solution or organic mixtures, probably due to the hydrophilic nature of most 2D materials. In principle, the transport channels with tunable sub-nanometer size and well-established functionalization approaches (e.g., hydrophobic modification) would endow 2D-material membranes with great potential in organic separations.

**Mixed-matrix membranes**: The development of MMMs generally follows the discovery of filler. The first generation MMMs are based on purely inorganic fillers mainly including zeolite and silica. Hydrophobic zeolite MMMs are much more successful in performance enhancement than hydrophilic zeolite MMMs, due to the fact that interfacial voids and chain rigidification are more easily formed between zeolite and (glassy) hydrophilic polymer rather than (rubbery) hydrophobic polymer. Although high separation factor can be obtained in hydrophobic zeolite MMMs with loading higher than 50 wt%, the flux was still unattactive due to the micrometer thick MMM layer ensuring no defects. As an alternative, silica MMMs achieved uniform dispersion and intact interface via in-situ filler formation, while hardly took the usage of incorporated transport channels due to the nonporous nature of silica. The second generation MMMs derived from MOFs, COFs and 2D-materials, overcome the challenges of nanoparticles synthesis, uniform dispersion, interfacial voids and thick membrane layer involved in zeolite MMMs. ZIF-8, used as filler, led great success in enhancing the butanol recovery performance of hydrophobic membranes. Emerging COF fillers with versatile pore structures and crystalline polymer nature achieved remarkable performance enhancement both for hydrophilic and hydrophobic polymers. GO nanosheets, a typical 2D filler, were incorporated into polymeric membrane with enhanced alcohol dehydration property. Considering the multiple transport channels introduced by COF or 2D fillers, the specific function of these fillers on the enhancement of transport properties is yet to be explored.

The past decades witness that the advance of materials plays a critical role in promoting the development of pervaporation membranes and processes (Fig. 26). Polymers and inorganic materials are complementary for pervaporation membranes in terms of separation performance and scalable fabrication. The property of 2D-material membranes, possessing ordered transport channels with tunable sub-nanometer size, is more like inorganic membranes with well-defined pores. Indeed, the organic dehydration performance of 2D-material
membranes are comparable to inorganic membranes. Mixed-matrix membranes, once achieving uniform filler dispersion and ideal interface, can obtain balanced performance between polymers and inorganic or 2D fillers. This explains comparable folds enhancement of organic dehydration property was produced in MOF, COF or 2D-material MMMs.

Non-ideal morphologies include filler aggregation, interfacial voids, chain rigidification and filler pore blockage would complicate the transport channels and separation performance of MMMs. With introduction of in-plane pores (defects), plane-to-plane silts and interlayer channels, membranes involved with 2D materials have more complex molecular transport pathways compared with conventional polymeric membranes and inorganic membranes. Atomic-level characterizations and theoretical calculations of the physicochemical properties of building blocks and membranes would be helpful to further understand the transport mechanism behind the pervaporation separation performance. Novel molecular transport model that applies for the confined sub-nanosized spaces needs to be developed to explain or even predict the unprecedented permeance and selectivity achieved by pervaporation membrane materials with new chemistry and/or physical structure.

Towards practical pervaporation application, long-term stability test under realistic operating conditions must be carried out for the membrane materials, particularly for the emerging MOF, COF, 2D-material and mixed-matrix membranes. After passing this, scalable fabrication approaches should be developed to translate the membrane material into a thin, robust, defect-free separation membrane. Currently, organic dehydration is still the majority of pervaporation applications. A large number of membrane materials including conventional and emerging ones can serve this purpose. By contrast, the pervaporation applications in recovery of organics and organic-organic separations largely involved in chemical and food industries are rather less. Up to date, there are very limited membrane materials possessing desirable hydrophobicity, sub-nanosized pores and organic stability at the same time. This situation should be paid more attention and is believed to be highly improved by applying the recent discoveries in new membrane materials (e.g., MOFs, COFs) and novel pore structures (e.g., in-plane pores, interlayer channels) for pervaporation.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgements**

The authors would like to acknowledge the financial support provided by the National Key Basic Research Program (2020YFC1807202) and the National Natural Science Foundation of China (21922805, 22038006, 21776125).

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>$A$</td>
<td>membrane area ($m^2$)</td>
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<tr>
<td>$D$</td>
<td>diffusion coefficient ($10^{-8}$ cm$^2$/s)</td>
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<tr>
<td>$E$</td>
<td>enrichment factor</td>
</tr>
<tr>
<td>$J$</td>
<td>permeation flux (g/m$^2$.h)</td>
</tr>
<tr>
<td>$l$</td>
<td>membrane thickness ($\mu m$)</td>
</tr>
<tr>
<td>$P$</td>
<td>permeability (g/m$^2$.h kPa)</td>
</tr>
<tr>
<td>$P/l$</td>
<td>permeance (g/m$^2$.h kPa)</td>
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<tr>
<td>$S$</td>
<td>sorption coefficient (cm$^3$(STP)/cm$^3$ atm)</td>
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<tr>
<td>$t$</td>
<td>test period (h)</td>
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<tr>
<td>$W$</td>
<td>weight of permeate (g)</td>
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<tr>
<td>$x$</td>
<td>weight percent of components in the feed</td>
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<td>$y$</td>
<td>weight percent of components in the permeate</td>
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**Greek Letter**

<table>
<thead>
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<th>Symbol</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>selectivity</td>
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<td>$\beta$</td>
<td>separation factor</td>
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<td>$\delta$</td>
<td>solubility parameter (MPa$^{1/2}$)</td>
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**Subscript**

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<tr>
<th>Symbol</th>
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<tr>
<td>$i$</td>
<td>component $i$ at feed or permeate</td>
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<tr>
<td>$j$</td>
<td>component $j$ at feed or permeate</td>
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**Abbreviations**

| 2D | two-dimensional |
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.119557.

References

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