



Mesoporous organosilica membranes: Effects of pore geometry and calcination conditions on the membrane distillation performance for desalination



Yen Chua^a, Chun Xiang Cynthia Lin^c, Freddy Kleitz^b, Simon Smart^{a,*}

^a The University of Queensland, School of Chemical Engineering, Brisbane, St Lucia, QLD 4072, Australia

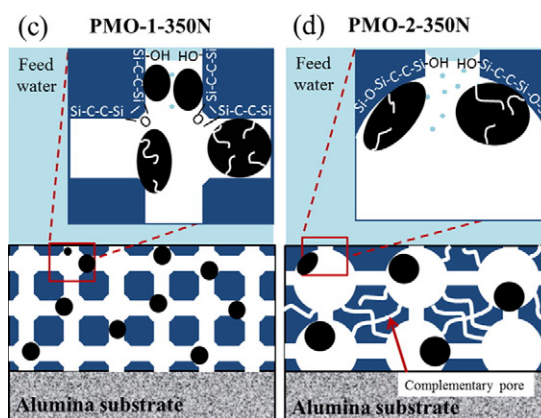
^b Department of Chemistry, 1045 Avenue de la Médecine, Université Laval, Québec G1V 0A6, QC, Canada

^c The University of Queensland, Australian Institute of Bioengineering and Nanotechnology, Brisbane, St Lucia, QLD 4072, Australia

HIGHLIGHTS

- Organosilica membranes with different pore sizes were made via soft-templating.
- Calcination atmospheres influenced surface chemistry but not bulk hydrophobicity.
- F127 templated membranes gave higher fluxes in MD but suffered from pore wetting.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 February 2015

Received in revised form 16 May 2015

Accepted 18 May 2015

Available online 24 May 2015

Keywords:

Periodic organosilica membrane

Pore geometry

Membrane distillation

ABSTRACT

Mesoporous organosilica membranes with different pore geometries and pore sizes (ranging from 2 to 12.9 nm) were synthesized using an evaporation-induced self-assembly (EISA) method and different types of triblock copolymer (Pluronic F68 and F127). The surfactants were removed under different calcination conditions (temperature and air/inert environment) so as to modify the surface chemistry of the final material. The surface chemistry of the organosilica membranes heat treated under different atmospheres was slightly altered, and it was confirmed that calcination in air will inevitably lead to some cleavage of Si–C bonds in the 1, 2-bis(triethoxysilyl) ethane (BTESE) precursor. However, neither heat treatment fully decomposed either surfactant template, leaving some carbonaceous species on the pore wall. For the samples calcined in an inert atmosphere, this in turn increased the tortuosity of the pore channel and decreased membrane flux. Membranes templated with F68 demonstrated lower water fluxes (up to $13.5 \text{ kg m}^{-2} \text{ h}^{-1}$) with excellent stability and salt rejection, whereas F127 templated membranes possessed larger pore sizes which yielded higher fluxes but the cage-like pores, combined with the hydrophilic surface, resulted in pore wetting.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail address: s.smart@uq.edu.au (S. Smart).

1. Introduction

The increasing global water demand, driven by a rapid growing urbanised population and exacerbated by climate change and rising salinity levels, highlights the criticality of producing fresh water by desalination. Whilst much of this need can be met with existing reverse osmosis (RO) and thermal technologies, there is a growing interest and market for non-traditional desalination methods that can tackle unconventional waters. Membrane distillation (MD), is a thermal based separation process driven by a vapour pressure difference across a membrane. As the push for zero-liquid discharge increases there has been a growing interest in MD for desalination due to its simple operational requirements and ability to operate under low temperatures (utilising waste or solar heat) and low pressures [1].

MD membranes are typically porous, hydrophobic polymeric membranes that do not actively contribute to the separation process; rather the transport of vaporized water molecules through the membrane pores is governed by thermodynamics (operating temperature) and kinetic effects (diffusion of the components through the membrane) [2,3]. As a result, most of the reported studies focus on commercially available membrane materials and the effect of membrane surface chemistry (beyond simply increasing hydrophobicity) and water affinity are rarely considered. However, the recognition that MD performance and stability (e.g. pore wetting) must improve to be commercially competitive with RO has seen a new range of membrane materials emerge including ceramics [4,5] and carbon nanotubes [6], as well as different morphologies [7,8]. Of these, ordered organosilica membranes have shown considerable promise [9].

Mesoporous materials [10,11], with well-ordered pore structures of various pore geometries and synthesized from various inorganic precursors (silica, metal oxides, metals, carbon etc.), have been extensively studied over the last decades. The advantages of high porosity, surface area and narrow pore size distribution of these materials have demonstrated success in improving the performances in applications, such as adsorption [12,13], drug delivery and catalysis [14,15] and separation [16,17]. Organosilica materials are hybrid organic and inorganic compounds integrated at the molecular level. They have demonstrated some fascinating properties such as morphological flexibility, versatility for different functionalities, ease of control in sol-gel synthesis and high chemical stability resulting from the inorganic silica framework [18]. Organosilica membranes and thin films are typically prepared by either co-condensation of organic containing precursors (e.g. methyltriethoxy silane, MTES) [19] with silica sources (e.g. tetraethylorthosilicate, TEOS) or by post-grafting of mesoporous silica [20].

Periodic mesoporous organosilica (PMO) is a well-studied subclass that is comprised of covalently-bonded organosilica scaffolds with well-distributed organic moieties within the silica matrix [21,22]. However, there have been very few applications of PMO to membrane distillation. In part this is due to the difficulty of producing a defect free PMO membrane layer, but also arises from the fact that PMO materials appear so radically different for MD membranes compared to their polymeric counterparts. Yet as typical performance requirements include a narrow pore size distribution, low thermal conductivity, low tortuosity, high porosity, good thermal stability, sufficient hydrophobicity and high fouling resistance, PMO materials seem a logical choice. Of these the interplay between the narrow pore size distribution and hydrophobicity is particularly interesting. MD requires the formation of a liquid/vapour interface at or within the pore and that the transmembrane pressure is lower than the liquid entry pressure or pore wetting will result. The liquid entry pressure is a derivation of the Young-Laplace equation [23] and a function of both pore size and hydrophobicity. PMO materials demonstrate some variability in hydrophobicity [24], which is a function of surface roughness (relatively unexplored in the PMO literature) and surface chemistry (dependent on the organic functional groups) [25], among others. Previously, we showed that a PMO membrane synthesized from 1, 2-bis(triethoxysilyl) ethane (BTESE) and the non-ionic

triblock copolymer surfactant Pluronic F68 gave excellent fluxes of up to $13 \text{ L m}^{-2} \text{ h}^{-1}$ across an extreme range of salt concentrations ($10\text{--}150 \text{ g L}^{-1}$ NaCl) at moderate temperatures ($<60 \text{ }^\circ\text{C}$) [9]. In contrast to other MD work with inorganic materials [26,27], no discernible concentration polarisation was evident as salt concentration increased, rather temperature polarisation provided the most significant boundary layer resistance [28]. Importantly, no pore wetting was observed despite apparently possessing a hydrophilic surface, due in large part to the pore size regime used, which has opened further possibilities for PMO as MD membranes [28].

Continuing this work, we have synthesized PMO membranes of different pore sizes and geometries using triblock copolymers Pluronic F68 and F127 and evaluated their performances in vacuum membrane distillation (VMD). In contrast to the previous work we also adopted a new synthesis strategy by heat treating under both oxidising and inert atmospheres in an attempt to elucidate the impact of preserving or otherwise the Si-C bonds within the organosilica matrix.

2. Experimental section

2.1. Materials

Pluronic F68 ($\text{PEO}_{80}\text{PPO}_{30}\text{PEO}_{80}$, $M_{\text{wt}} \sim 8400 \text{ g gmol}^{-1}$), Pluronic F127 ($\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$, $M_{\text{wt}} \sim 12,600 \text{ g gmol}^{-1}$), hydrochloric acid (HCl, 37%) and 1, 2-bis(triethoxysilyl) ethane (BTESE, 96%) were purchased from Sigma Aldrich Co. without any purification prior to use. Sodium chloride (NaCl, 99.9%) was purchased from Ajax Finechem and diluted with double distilled water for the preparation of salty solution of varying concentrations.

2.2. Preparation of periodic mesoporous organosilica membranes

The organosilica hybrid membranes were prepared via the sol-gel method under acidic conditions. First, triblock copolymer surfactant, either 0.28 g of Pluronic F68 ($\text{PEO}_{80}\text{PPO}_{30}\text{PEO}_{80}$, $M_{\text{wt}} \sim 8400 \text{ g gmol}^{-1}$, Aldrich) or 0.43 g Pluronic F127 ($\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$, $M_{\text{wt}} \sim 12,600 \text{ g gmol}^{-1}$, Aldrich), was dissolved in 2.8 ml ethanol and 0.01 M hydrochloric acid (HCl, 37%, Aldrich) at $35 \text{ }^\circ\text{C}$ under stirring for 1 h. Then, 1.0 g of 1, 2-bis(triethoxysilyl) ethane (BTESE, 96%, Aldrich) was added into the mixture and allowed to stir for 2 h, giving the final molar ratio of 1 BTESE:8.7 ethanol:6 H_2O :0.0022 HCl:0.006 surfactant. The organosilica membrane was deposited by dip-coating the prepared sol on (a) glass slides (for TEM analysis) and (b) inner surface of an alumina substrate (PALL, length 100 mm, outer diameter 10 mm, thickness 1.7 mm, for desalination testing) with titania as intermediate layer (average pore size 5 nm as provided by the manufacturer) at a withdrawal speed of 10 cm min^{-1} and holding time of 1 min. After dip-coating, the membrane was dried in air overnight, and then cured at $150 \text{ }^\circ\text{C}$ for 6 h for the complete cross-linking and self-assembly of the organosilica network. The remaining sol was dried on a petri dish to form a thin layer and ground for further characterization analyses. Surfactant removal was then carried out through a 2 hour heat treatment in air at $300 \text{ }^\circ\text{C}$ or nitrogen at $350 \text{ }^\circ\text{C}$ with heating rate of $1 \text{ }^\circ\text{C min}^{-1}$. The organosilica membranes obtained are denoted herein as PMO- x - y , where x is either 1 or 2, for Pluronic F68 and Pluronic F127, respectively, and y corresponds to the calcination conditions ($y = 300\text{A}$ for membranes calcined in air at $300 \text{ }^\circ\text{C}$ and $y = 350\text{N}$ for membranes pyrolysed in nitrogen at $350 \text{ }^\circ\text{C}$).

2.3. Characterization

Transmission electron microscopy (TEM) analysis was performed by JEOL JEM-1010 and JEM-2100 electron microscopes operated at accelerating voltage of 100 kV and 200 kV, respectively. TEM sample was prepared by scraping out the calcined thin films from glass slides, and mixed with ethanol to form a slurry then dropped onto a carbon coated copper grid. Powder X-ray diffraction (PXRD) data were collected on a

Download English Version:

<https://daneshyari.com/en/article/622941>

Download Persian Version:

<https://daneshyari.com/article/622941>

[Daneshyari.com](https://daneshyari.com)