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Hollow fibre microporous silica membranes for gas separation and pervaporation
Synthesis, performance and stability

T.A. Peters[a], J. Fontalvo[a], M.A.G. Vorstman[a], N.E. Benes[a], R.A. van Dam[b], Z.A.E.P. Vroon[b,*], E.L.J. van Soest-Vercammen[c], J.T.F. Keurentjes[a]

[a] *Process Development Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Innovative Materials Group, Department of Models and Processing, TNO TPD, P.O. Box 595, 5600 AN Eindhoven, The Netherlands*
[c] *Department of Chemical Engineering, TNO Environment, Energy and Process Innovation, P.O. Box 342, 7300 AH Apeldoorn, The Netherlands*

Abstract

Thin microporous silica membranes were prepared on the outer surface of hollow fibre ceramic substrates. In principle this enables relatively fast and inexpensive production of large membrane surface area, combined with a low support resistance and a high membrane surface area/module volume ratio ($>1000 \, \text{m}^2 \, \text{m}^{-3}$) compared to tubular membranes. Membranes were analysed using SEM, SNMS, single gas permeance and pervaporation. High He permeance (1.1–$2.9 \times 10^{-6} \, \text{mol} \, \text{m}^{-2} \, \text{s}^{-1} \, \text{Pa}^{-1}$), high He/N_2 permselectivity (~ 100–1000) and Arrhenius type temperature dependence of gas permeance indicate that the membranes are microporous and possess a low number of defects. The contribution of the hollow fibre substrate to the overall mass transport resistance is found to be small, even for fast permeating gases like helium. Hence, the small dimensions of the substrate enable further improvement of the silica layer without the support resistance becoming significant. In the dehydration of *n*-butanol (80 °C, 5 wt.% water) initially a high flux and selectivity were observed ($2.9 \, \text{kg} \, \text{m}^{-2} \, \text{h}^{-1}$ and 1200, respectively). A similar behaviour was found for the dehydration of DMF. For most of the membranes the water permeance finally reaches a steady value of $\sim 1 \, \text{kg} \, \text{m}^{-2} \, \text{h}^{-1} \, \text{bar}^{-1}$ with selectivities between 5 and 25. The good performance of the hollow fibre membranes, combined with their advantages compared to other support geometries, makes them interesting candidates for a variety of applications.
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1. Introduction

Compared to their organic counterparts inorganic membrane materials generally possess superior structural stability, e.g., no swelling and compaction, even in harsh chemical environments and at high temperatures [1–3]. The majority of inorganic membranes are porous and their selective features are often closely related to their pore size. Amorphous silica is an inorganic material containing exceptionally small pores. Membranes based on this material have an asymmetric structure with the actual selective microporous silica positioned on a support structure comprising several α- and γ-alumina layers. Silica membranes were discovered more than a decade ago [4,5] and are still subject of extensive study.

Silica membranes reported in literature have either a flat plate or tubular geometry. The flat plate geometry is

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* Corresponding author.
 E-mail address: zvroon@tno.tpd.nl (Z.A.E.P. Vroon).

advantageous from an academic point of view, but it usually has a small surface area (typically $\sim 10^{-2}$ m^2) due to limitations imposed on the dimensions by the dip-coating technique. The surface area of tubular silica membranes is larger and their geometry is also more compatible with the technology developed in organic membrane science. Consequently, commercially available membranes for pervaporation have a tubular geometry [3]. Drawbacks of this geometry include a relatively low surface area-to-volume ratio (typically <500 m^2 m^{-3}) and high costs associated with tubular ceramic membrane supports.

In this work silica layers are positioned on top of ceramic hollow fibres. In principle this enables the relatively rapid and inexpensive preparation of a large membrane surface area, combined with a high membrane surface area-to-volume ratio (>1000 m^2 m^{-3}). Additionally, pervaporation modules built with externally coated hollow fibres allow for high mass and heat transfer coefficients combined with low liquid pressure drops. The membranes were characterised using SEM, SNMS, single gas permeance and pervaporation.

2. Theory

2.1. Gas permeation

Numerous theories for describing transport in microporous media have been presented in literature [6–8]. These theories become increasingly complex when the microporous medium is less uniform and when more mobile species are present. For our purpose, i.e. the assessment of membrane quality, a simple phenomenological approach is sufficient.

For single gas permeation of permanent gases through amorphous microporous silica membranes, at sufficiently high temperatures and low pressures, transport is activated and permeance is independent of pressure [4,5,9]. Hence, permeance is described by:

$$P \equiv \frac{N}{\Delta p} = (H_0 D_0) \exp\left(\frac{(Q - E_D)}{RT}\right) \tag{1}$$

where N is the molar flux, H_0 and D_0 are pre-exponential factors related to the Henry and diffusion coefficients, respectively, and R and T have their usual meaning. The overall thermally activated nature of transport arises from the simultaneous occurrence of diffusion (E_D) and sorption (Q).

2.2. Pervaporation

For dehydration of solvents by pervaporation the performance of a membrane is usually expressed in terms of water flux, or permeance, and separation factor α. The latter is defined as:

$$\alpha = \frac{y_{H_2O}/x_{H_2O}}{y_j/x_j} \tag{2}$$

where y and x are the molar fractions in the permeate and retentate, respectively. Permeance is defined as the flux divided by the partial pressure difference over the membrane. The equilibrium vapour pressure of component i at the retentate side is related to the mole fraction x and activity coefficient γ in the liquid mixture

$$p_i^* = \gamma_i x_i p_i^0 \tag{3}$$

where p_i^0 is the vapour pressure of the pure component i. When the pressure at the permeate side is small compared to the equilibrium vapour pressure at the retentate side, permeance can be expressed as [2]:

$$P_i = \frac{N_i}{\gamma_i x_i p_i^0} \tag{4}$$

3. Experimental

3.1. Membrane preparation

3.1.1. Support

The ceramic hollow fibres membrane supports (CEPAration, The Netherlands) have a porosity of $\sim$30%, a pore diameter of either 150 or 300 nm, a length in the range of 20–30 cm, and an inner and outer diameter of 2.0 and 3.0 mm, respectively.

3.1.2. γ-Al$_2$O$_3$ intermediate support preparation

On the outer side of the hollow fibre substrates intermediate mesoporous γ-Al$_2$O$_3$ layers were prepared by sequential dip-coating with a boehmite coating solution. The boehmite solution was made by adding aluminium-tri-sec-butoxide (Aldrich) dropwise to water at 90 °C under vigorous stirring, and subsequent boiling for 90 min to remove the 2-butanol produced during the hydrolysis. A white solution was obtained, which was peptised with 1 mol l^{-1} HNO$_3$ (water/alkoxide/acid ratio: 70/1/0.07). The peptisation was accompanied by a change in colour from white to "nano" blue. After refluxing for 16 h the resulting solution had a pH of 3.8. Finally, 120 ml polyvinyl alcohol (PVA) solution was added to 180 ml boehmite solution, followed by stirring at room temperature for 30 min and subsequently stirring at 90 °C for 150 min. The PVA solution was prepared by dissolving 8.75 g PVA (Aldrich, PVA Powder, average M_w 89–98 kD, hydrolysis grade 98%) in 250 ml of 0.05 M HNO$_3$. The dip-coat process was performed at room temperature in a laminar flow cupboard (Interflow, quality class 100) to minimize dust contamination. The substrate speed was 10 mm s^{-1} and the dip-time was 25 s. The membranes were dried in a climate chamber (Espec 100) at 40 °C and 60 RH% for at least 120 min. After drying, the membranes were sintered at 600 °C for 180 min (heating rate 1 °C min^{-1}). The procedure for dipping, drying and sintering was repeated three times in order to obtain defect-free intermediate γ-Al$_2$O$_3$ membranes.