



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Hybrid silica membranes with enhanced hydrogen and CO₂ separation properties



Hessel L. Castricum^{a,b}, Hammad F. Qureshi^a, Arian Nijmeijer^a, Louis Winnubst^{a,*}

^a Inorganic Membranes, MESA+ Institute for Nanotechnology, University of Twente, P. O. Box 217, 7500AE Enschede, The Netherlands

^b Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

ARTICLE INFO

Article history:

Received 22 January 2015

Received in revised form

13 March 2015

Accepted 22 March 2015

Available online 20 April 2015

Keywords:

Hybrid silica

Sol-gel processing

In-situ SAXS

Microporous membrane

Gas separation

ABSTRACT

Hybrid silica membranes are of great interest for molecular separation owing to their outstanding hydrothermal stability. Despite good separation properties in liquid applications, the selectivity for gas separations has yet been too low. Here, we report membranes from 1,2-bis(triethoxysilyl)ethane (BTESE) with H₂/N₂ permselectivity between 50 and over 400. The membranes are fabricated from a dip-sol with a H⁺:Si ratio of 0.01 that is applied onto a support system with a controlled low water content (pre-treated at RH < 0.5%). For support systems pre-treated at 90% RH, H₂/N₂ permselectivities ≤ 10 are obtained, indicating larger pores. The pore formation process is studied *in situ* by Small-Angle X-ray Scattering in a dedicated setup. The formation of larger pores can be understood by a higher condensation rate and longer drying times when more water is present. This results in a stronger network that better withstands the compressive forces during drying. By limiting both the water and acid contents in the dipped sol, a dense pore structure is obtained that gives the highest H₂/N₂ and CO₂/CH₄ permselectivities found to date for hybrid silica membranes. Further variation of the water and acid concentration will allow for additional tuning of the separation properties for both gas and liquid separation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The separation and purification of molecular mixtures in the chemical industry consume substantial amounts of energy. To reduce fossil fuel consumption, efficient separation processes are needed to obtain high-grade products in the food and pharmaceutical industries [1,2], high-purity water [3], and to remove or recover toxic or valuable components from industrial effluents [4]. Today, membranes are used on a large scale for the production of potable water, cleaning industrial effluents, recovering valuable constituents in biomass fermentation [5–7], biogas upgrading [8] and for gas and vapor separation [9,10]. Besides, membranes are a key component in energy conservation and -storage systems [11], artificial organs [12] and drug delivery devices [13].

Amorphous silica is an attractive material for the application in microporous inorganic membranes because of its thermal stability and high gas separation selectivity [14]. Through acid catalyzed sol-gel processing of *e.g.* tetraethylorthosilicate (TEOS), it is relatively easy to develop a thin separation layer with a narrow pore size that is applied onto a support that provides mechanical

strength [15]. After thermal consolidation of the dip-coated sol-gel-derived silica network, a homogeneous membrane is formed [16] that allows the selective permeation of small molecules such as helium (kinetic diameter = 0.26 nm) and hydrogen (0.289 nm), while showing little or no permeation of the bigger molecules like nitrogen (0.364 nm) or methane (0.389 nm) [17]. However, the low stability of the silica structure to water severely limits its application in many industrial processes that involve hydrothermal conditions [18]. Modification of the silica network with metal ions [19–22] or the use of silanes with hydrophobicity-inducing pendant alkyl groups [18,23,24] have been reported to improve the hydrothermal stability.

An even more effective way to obtain high hydrothermal stability is by applying silicon alkoxide precursors that contain an organic bridging group between two silicon atoms [25–30], such as 1,2-bis(triethoxysilyl)ethane (BTESE). Acid-catalyzed hydrolysis and condensation of BTESE can be assumed to follow the same S_N2-reaction mechanism as for tetraalkoxysilanes [31–33]. A single dipping procedure allows the formation of an isotropic selective layer with a homogenous pore microstructure, with reported thicknesses down to 90 nm [29]. The resulting ‘hybrid silica’ membrane has shown stability in relevant liquid mixtures with water for several years at 150 °C and higher [25,34]. The exceptional hydrothermal stability of hybrid silica has directly been associated

* Corresponding author. Tel.: +31 53 4892994; fax: +31 53 4892336.

E-mail address: a.j.winnubst@utwente.nl (L. Winnubst).

with the organic bridging group. This provides a higher internal network connectivity of the minimum non-hydrolyzable 'building block', and enhances the mechanical properties, which results in a lower sensitivity of Si–O–Si to hydrolysis, and in a higher fracture resistance [35]. By varying the structure of the organic bridge, different separation properties can be obtained [28]. Short alkylene bridging groups were found to be advantageous for separations based on differences in molecular size, while separation based on differences in the affinity of adsorption in the material were enhanced for membranes with longer (C₈H₁₆) alkylene and aryl bridges. Recently, it was shown that the pore size can be varied independently by applying different acid contents previous to drying [36]. By adding more acid catalyst, larger pores are formed, which gives higher overall permeances and allows the separation of mixtures of larger molecules. At low acid content, the H₂O/butanol pervaporation selectivity was improved. By reducing the H⁺:Si ratio (acid ratio, AR) from 0.1 to 0.01, a tenfold increase of the H₂O separation factor to 7.9 · 10³ was measured. However, lowering AR below 0.1 did not result in a better gas permselectivity. H₂/N₂ and H₂/CH₄ permselectivities were limited to about 25 for BTESE-derived membranes, suggesting a lower limit in the pore size. Values reported by various groups for this type of membrane are all of the same order (Table 1). Computer simulations indicated that the lower permselectivities as compared to those reported for SiO₂ are related to the size of the bridging group [37,38]. This could explain the substantial permeation of molecules of the size of N₂.

Acid-catalyzed sol–gel synthesis of silica results in sols with linear polymeric chains, giving microporous materials after drying and calcination [16]. The smallest pores are produced around the isoelectric point (pH ≈ 2), at which condensation rates are at a minimum. Compressive capillary forces exerted by the receding pore liquid may determine the pore structure formed during drying [36]. With more acid, the compressive forces are balanced by a network strengthened by ongoing condensation reactions, and by the positive charge on the hybrid organosilica. This results in larger pores. We investigate here whether the presence of additional water, which is a reactant in sol–gel hydrolysis and condensation, may similarly give larger pores. Water present in the mesopores of the support system may diffuse into the applied sol. We investigated the role of water by pretreating the membrane supports before the dip-coating process in different atmospheres of controlled humidity. It was anticipated that narrower pores could be formed with a smaller amount of water in the support, giving a higher size selectivity to gas permeation. Membranes were prepared at AR=0.01 and 0.1, and additional experiments were carried out for unsupported systems to study the pore formation process *in situ*. Considering the general complexity of the membrane preparation process, results on the membrane with the highest permselectivity were reproduced multiple times to ensure that the results were not accidental. Because of their high hydrothermal stability, hybrid silica membranes with high and tunable gas separation selectivity could prove of great promise for application, as realistic gas mixtures are usually not strictly devoid of water.

Table 1
Reported highest H₂/N₂ permeation ratios for BTESE-based organosilica membranes, along with the H⁺:Si acid ratios (AR) and consolidation temperatures (T).

AR	T	H ₂ /N ₂ permselectivity	Ref.
0.1	523	27	[36]
0.08	473	15	[45]
0.05	473	10	[27]
0.05	473	20	[46]
0.05	473	34	[47]
0.05	473	40	[48]

2. Experimental

1,2-bis(triethoxysilyl)ethane (BTESE) (purity 97%, ABCR Germany) was used as a hybrid silica precursor. Water was deionized at 18.2 MΩ/cm using a Millipore purification system. A polymeric sol was prepared by drop-wise addition of BTESE to a nitric acid (65 wt%, Aldrich)–water–dry ethanol mixture. Nitric acid has been used for the preparation of many other silica-based sol systems applied for membranes. Addition was done in an ice bath under vigorous stirring to control the reaction rate and thus avoid extensive early-stage hydrolysis. This mixture was subsequently refluxed at 333 K under continuous stirring to produce a hybrid silica sol at H⁺:Si (acid ratio, AR)=0.01 and H₂O:–OC₂H₅ (hydrolysis ratio, HR, with –OC₂H₅ the hydrolysable alkoxy-group in the BTESE precursor)=1. A second sol was prepared with AR=0.1 and HR=1.

Membranes were synthesized by means of coating these sols on porous γ-alumina ceramic membrane support systems. These were prepared by dip-coating a boehmite–PVA sol on α-alumina supports (support thickness of 2.08 ± 0.01 mm and pore diameter of about 100 nm; Pervatech B.V. The Netherlands), followed by subsequent drying and calcination, as described in detail in [15]. The dip-sol was applied twice to create a smooth mesoporous γ-alumina intermediate layer with 3–5 nm pore diameter, as determined with permeometry [39].

For membrane fabrication, the BTESE sol was diluted to a final dip-sol with [Si]=0.6 M. This dip-sol was applied onto the alumina support system by a single dipping procedure (withdrawal rate 1.4 cm/s) in a class 100 flow cupboard situated in a class 1000 cleanroom (controlled at 296–298 K and RH=45–55%), followed by a thermal treatment at 573 K for 3 h in N₂ (99.99% pure) with heating and cooling rates of 0.5 K/min. Prior to coating, the support was either kept in a furnace at 413 K for 24 h (relative humidity, RH < 0.5%) or in a climate chamber at 348 K at RH=90% for 72 h. The thicknesses of the hybrid silica top-layer of the membranes were determined from cross-sectional micrographs acquired with a high-resolution scanning electron microscope HR-SEM (ZEIS 1550) at an accelerating voltage of 1.0 kV. Unsupported xerogels were prepared by drying and a thermal treatment under the same conditions as for the supported membranes.

Particle sizes of freshly prepared hybrid sols were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS at 298 K. The hydrodynamic diameter of the sol particles was determined from the Brownian motion of the particles as defined by the translational diffusion coefficient *D* in the ethanol solvent. The hydrodynamic diameter *d*_{hyd} was obtained by the Stokes–Einstein equation

$$d_{\text{hyd}} = kT/3\pi\eta D \quad (1)$$

in which *k* is Boltzmann's constant, *T* is the temperature, *η* is the solvent viscosity and *D* is the diffusion coefficient in the solvent.

N₂ adsorption/desorption isotherms were obtained for unsupported xerogels on a CE-Instruments Milestone 200 at 77 K after drying (*p* < 10^{−4} mbar at 473 K). Surface areas were determined by the Dubinin method, modified by Kaganer [40,41], as in

$$\log n = \log n_m + D_a (\log p^0/p)^2 \quad (2)$$

with *n* is the gas adsorbed at relative pressure *p/p*⁰, *n*_m is the monolayer capacity of the surface, both expressed in mol per g adsorbent, and *D*_a is an adsorbent-dependent constant. The surface areas *A* were subsequently determined according to

$$A = n_m a_m N_A \quad (3)$$

in which *N*_A is Avogadro's number and *a*_m is the area occupied by a molecule in the completed monolayer, taken as 0.162 nm² for N₂ (ISO 9277). The mean pore diameter *d*_p was calculated from the

Download English Version:

<https://daneshyari.com/en/article/632949>

Download Persian Version:

<https://daneshyari.com/article/632949>

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