



Hydrothermal stability of microporous silica and niobia–silica membranes

V. Boffa¹, D.H.A. Blank, J.E. ten Elshof*

MESA Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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ABSTRACT

The hydrothermal stability of microporous niobia–silica membranes was investigated and compared with silica membranes. The membranes were exposed to hydrothermal conditions at 150 and 200 °C for 70 h. The change of pore structure before and after exposure to steam was probed by single-gas permeation measurements and nanoporometry. The hydrothermal stability of the niobia–silica membrane was found to be higher than that of silica. After hydrothermal treatment at 200 °C, the hydrogen permeance of the niobia–silica top layer had declined by 32%, while the H₂ permeance of the silica top layer was reduced by 73%. The apparent activation energies of the H₂ permeance were 12.2 ± 0.2 and 15.3 ± 0.7 kJ mol⁻¹ for silica and niobia–silica, respectively. Nanoporometry experiments on the silica membrane were in semi-quantitative agreement with the gas permeation data. The data suggest that densification of the top layer occurred predominantly in those areas with the highest convex curvatures, thereby increasing the effective transport path of helium and hydrogen across the membrane.

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1. Introduction

We recently developed a niobia–silica microporous membrane [1] that shows a very low permeability of CO₂. It may find application in enabling technologies for CO₂ sequestration, or in membrane reactors to recover H₂ from hydrogen synthesis processes such as steam reforming [2] and water–gas shift reaction [3]. Industrial application of ceramic membranes requires stability under working conditions for at least several years. Hydrothermally stable supports consisting of La-doped γ -alumina mesoporous layers coated on α -alumina macroporous supports have already been developed [4]. Unfortunately, the long-term durability of gas-selective microporous top layers, which are all based on silica, is limited in the presence of steam [5]. Crystallization of microporous silica hardly occurs below 1100 °C [6], but it undergoes drastic structural changes in the presence of steam below 200 °C [7–11]. Hydrothermal exposure leads to collapse of the porous structure, yielding dense impermeable materials. Microcracks may form as a result of the stresses that develop during these structural rearrangements. Densification occurs mostly in the early stages of exposure to steam, but microcrack forma-

tion is less predictable. Loss of selectivity due to this type of deterioration often occurs after extended periods of exposure to steam.

Himai et al. [7] proposed that Si–O bonds are broken upon interaction with water at high temperature, creating vicinal hydroxyl pairs that are subject to recondensation. This mechanism, consisting of the cyclic destruction and reconstruction of Si–O–Si network bonds, gives some flexibility to the material, so that it can reorganize itself eventually in a more stable and denser state. The hydroxylation of silica finally results in depolymerization [12], because silicic acid dissolves in the thin film of adsorbed water that is covering the material during exposure to steam. The silicic acid can freely migrate through the sorbed water layer until it precipitates and recombines with the silica matrix due to saturation. Dissolution (the depolymerization of silica) occurs fastest in those areas where the convex curvature is largest. This process is dominant in microporous silica, where pores have larger degrees of curvature than in mesoporous silica and are filled by water even at low water partial pressures.

Microporous silica can be stabilized by introducing transition metals in the silica network [13–17]. Oxygen forms more polar and stable bonds with transition metals than with silicon. Furthermore, most transition metals have coordination numbers larger than that of silicon [18]. Thus, they tend to yield more closely packed and crystalline structures than pure silica.

To determine the changes in pore size distributions upon hydrothermal treatment, different monitoring techniques can be

* Corresponding author. Tel.: +31 53 489 2695; fax: +31 53 489 3595.

E-mail address: j.e.tenelshof@utwente.nl (J.E. ten Elshof).

¹ Present address: Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, Corso M.D'Azeglio 48, 10125 Torino, Italy.

employed. One way is to carry out single-gas permeation experiments with a series of gases with different kinetic diameters. Assuming that separation is based on size differences only, a low permeance corresponds to a small number of pores that is accessible for a species with a certain size. The advantage of this approach is that it is not dependent on any theoretical model. The results may nevertheless be affected by differences in interactions between different molecular probes and the membrane pore walls [1].

Another established technique to determine pore size distributions in supported thin films is permoporometry. Its advantage is that all pore sizes are accessed with the same molecular probe, so that pore size distributions are not influenced by probe–wall interactions. On the other hand, estimates of pore size distributions can only be obtained by applying theoretical models and making assumptions regarding the shape of the pores. The permoporometry technique was originally developed in the 1990s for mesoporous membranes [19]. Pore size distributions can be calculated by applying the Knudsen [20] and Kelvin [21] equation. More recently, Tsuru developed the nanopermoporometry technique, which is able to access micropores [22,23]. However, the interpretation of nanopermoporometry data is more complex than conventional permoporometry data. The Knudsen and Kelvin equations are not valid in the microporous regime [22], and simple alternative models are not available in literature. Tsuru et al. defined the average pore size as the Kelvin diameter at which the permeance of the vapor-containing gas was half of the permeance of the dry gas [22]. Here the Kelvin diameter is two times the Kelvin radius (r_K), which is defined by the Kelvin equation:

$$\ln P_r = -\frac{\gamma_s V_{\text{mol}} \cos \theta}{RT} \frac{1}{r_K} \quad (1)$$

where P_r is the relative vapor pressure, γ_s (J m^{-2}) the gas–solid interfacial tension, V_{mol} ($\text{m}^3 \text{mol}^{-1}$) the molar volume, and θ is the contact angle of the condensed phase on the pore wall. The latter value is normally assumed to be zero.

In this work the hydrothermal stability of a niobia–silica microporous membrane was investigated and compared with that of pure silica. Nanopermoporometry and single-gas permeation measurements were employed to probe the change of pore structure of the membrane after exposure to steam at elevated temperatures.

2. Experimental

2.1. Sol synthesis

The niobia-doped silica sol (denoted as NS sol) was prepared by adding 11 ml of tetraethyl orthosilicate (Aldrich, 99.999% pure; denoted as TEOS) to 10.5 ml of ethanol. An aqueous solution of

nitric acid was dropped in the mixture until the final molar ratio (Si)–OC₂H₅:H₂O:HNO₃ was 1:0.5:0.01. We have chosen to express the chemical composition of the sol in this way because alkoxy groups, water and acid are the moieties that participate directly in the reaction. This mixture was heated under reflux at 60 °C for 2 h. A 1-M solution of niobium(V) penta(*n*-butoxide) (Gelest) in *n*-butanol (Aldrich, anhydrous) was added slowly to the mixture. Aqueous nitric acid was dropped into the mixture to restore the initial composition (M)–O–R:H₂O:HNO₃ to 1:0.5:0.01, with M = Si or Nb and R = C₂H₅ or C₄H₉. The sol was refluxed at 60 °C for 5 h. Then it was cooled down to 20 °C and kept at this temperature for several days until it was used for characterization and membrane preparation. Prior to coating membranes, the sol was diluted 11.5 times with ethanol.

The silica sol was prepared by adding 11 ml of 0.73N aqueous nitric acid to 21 ml of tetraethylorthosilicate (TEOS, 98%, Aldrich) dissolved in 21 ml ethanol ($\geq 99.5\%$, Aldrich). The addition was carried out drop by drop under vigorous stirring, while the reaction flask was cooled in an ice bath. The mixture was then refluxed at 60 °C for 3 h. The resulting silica sol was diluted 18 times in ethanol and kept at –5 °C for a few days until it was used for preparation of membranes.

2.2. Preparation of silica membranes

Flat supports were prepared by coating a 6% La-doped boehmite sol on a 2.0-mm thick α -alumina disk (\varnothing 39 mm) as described elsewhere [4]. After calcination at 600 °C a mesoporous 6% La-doped γ -alumina layer with average pore size of 5 nm was formed, as verified by conventional permoporometry [10]. Silica and niobia–silica membranes were prepared by dipping the supports in the sols at an angular speed of 0.06 rad s^{–1}. The membranes were calcined for 3 h in air at 500 °C, with heating and cooling rates of 0.5 °C/min. Since the silica sol yielded an extremely thin layer, the coating and calcination cycle was repeated to increase film thickness and cover any remaining defects or uncoated areas of the membrane. The niobia–silica membrane is further referred to as NS membrane.

2.3. Single-gas permeation experiments

Permeation measurements were carried out using the setup shown in Fig. 1. In the single-gas permeation experiments all valves were closed with the exception of valve number 2, and the setup was used as a dead-end mode permeation setup [24]. In a typical experiment, the membrane was first degassed at 200 °C for 2 days in a flowing helium atmosphere. Then the flows of He, H₂, CO₂, N₂, CH₄ and SF₆ were measured sequentially, employing a pressure of 5 bar on the side of the feed, and atmospheric pressure on the per-

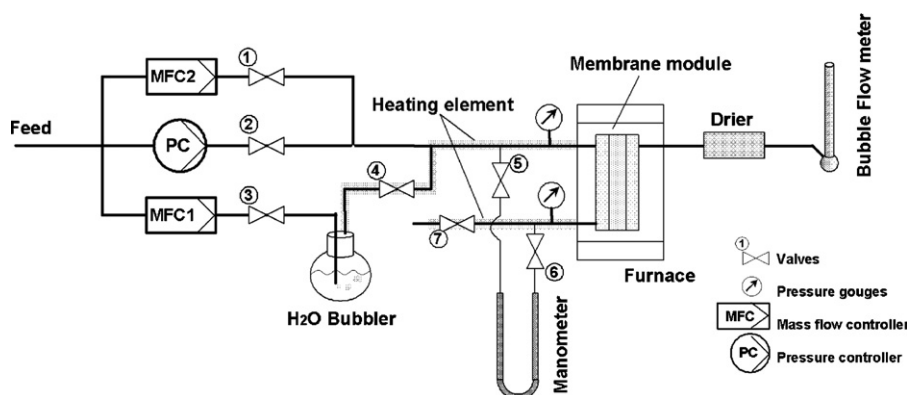


Fig. 1. Schematic diagram of the experimental setup.

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