



Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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



Influence of the intermediate layer on the hydrothermal stability of sol-gel derived hybrid silica membranes

Marcel ten Hove, Mieke W.J. Luiten-Olieman*, Cindy Huiskes, Arian Nijmeijer, Louis Winnubst

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

ARTICLE INFO

Article history:

Received 12 January 2017
Received in revised form 17 March 2017
Accepted 19 March 2017
Available online xxx

Keywords:

Hydrothermal stability
Hybrid silica
Gas separation
Microporous membrane
Monoaluminumphosphate coating

ABSTRACT

The hydrothermal stability of microporous silica hybrid sol-gel derived membranes is often only tested for either the mesoporous intermediate membrane layer or the microporous separation layer. In this work an investigation is done on the interaction between the intermediate γ -alumina layer and the hybrid (BTESE-derived) silica separation layer during hydrothermal treatment. Although bare γ -alumina is degraded during a hydrothermal treatment, a coating of hydrophobic BTESE on γ -alumina retains its gas separation performance, albeit with a lower mechanical adhesion between the hybrid silica separation layer and the γ -alumina intermediate layer. Applying a monoaluminumphosphate (MAP) coating between the α -alumina support and the γ -alumina layer stabilizes the γ -alumina membrane. A BTESE coating on a MAP modified γ -alumina membrane did not show any signs of delamination after hydrothermal testing. Moreover, a significant increase in the H_2/N_2 (perm)selectivity, factor 3, was observed for these membranes.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The global energy consumption rapidly increases every year, resulting in a fast depletion of the energy resources. Several strategies are being developed to generate alternative, environmental friendly ways to produce and store energy. Using hydrogen as a fuel is one of them. Hydrogen can be produced via water electrolysis, steam methane reforming, coal gasification and water gas shift reaction [1]. One essential, critical step in the production of hydrogen is gas separation. Highly selective inorganic membranes are ideal candidates to perform this separation as they are able to operate at high temperatures, although the hydrothermal stability of these membranes is debated.

For the above mentioned applications sol-gel derived microporous ceramic membranes are frequently studied. These gas separation membranes are often made as a multi-graded system. A macroporous support provides the system its mechanical strength; a mesoporous layer provides a smooth surface and a pore size of several nanometers for the application of a defect free microporous separation layer with a pore size of less than 1 nm. The mesoporous layer is already a membrane by itself that can be used for

nanofiltration. A typical pore diameter for these mesoporous layer is around 5 nm. Commonly used materials as intermediate layer are γ -alumina [2,3], yttria stabilized zirconia [4] or silica-zirconia [5]. These mesoporous membranes provide a very well defined surface for the deposition of a sol-gel derived microporous top layer, which can have a thickness of only 100 nm or less and hence needs a very smooth surface as a basis.

The material that is widely used as mesoporous intermediate layer is γ -alumina due to the relatively easy way of fabrication and its high surface quality [6]. The hydrothermal stability of such γ -alumina layers is however rather poor. Gallaher et al. [7] showed for commercial γ -alumina membranes (Membralox[®], US Filter) that pore growth occurs, from 4.0 to 6.5 nm, after a hydrothermal treatment at 640 °C with 90% steam. Nijmeijer et al. [8] observed for pure γ -alumina, calcined at 825 °C, a pore growth from 4.2 to 6.2 nm after a hydrothermal treatment at 600 °C (100 h, $H_2O/CH_4 = 3/1$ (by volume) at 2.5 MPa total pressure). They showed that doping γ -alumina with 6% lanthanum could prevent this pore growth. Zahir et al. [9] also observed pore growth in undoped γ -alumina, calcined at 600 °C, after hydrothermal treatment at 500 °C. However, in their work it was found that, opposite to the findings of Nijmeijer et al., the addition of 6% lanthanum could not stop pore growth. Zahir et al. showed that only a mixture of 6% Lanthanum and 30% gallium in γ -alumina could prevent the pore growth during hydrothermal treatments. The reason for the difference between the results of

* Corresponding author.

E-mail address: m.w.j.luiten@utwente.nl (M.W.J. Luiten-Olieman).

Nijmeijer et al. and Zahir et al. might be the difference in calcination temperature used. The stabilization effects of lanthanum are due to the formation of lanthanum aluminate (LaAlO_3), which is only formed above 700°C [10]. After calcination at 600°C , as used by Zahir et al. [9], only lanthanum oxide is formed, which apparently does not contribute to the hydrothermal stability, while Nijmeijer et al. [8] used a calcination temperature of 825°C .

Nagano et al. [11] doped nickel to γ -alumina to prevent pore growth in order to increase the hydrothermal stability. They found that the addition of 5% nickel was sufficient to prevent pore growth during hydrothermal treatments. Larger amounts of nickel led to the formation of nickel oxide and did not contribute to the hydrothermal stability of the membranes.

Nijmeijer et al. [8] have also shown that hydrothermal treatments of α -alumina supported γ -alumina membranes can lead to detachment of the γ -alumina layer from the support. They were successfully able to prevent this delamination by applying a monoaluminumphosphate (MAP) coating between the α -alumina support and the γ -alumina layer. The idea was that the chemical bonding between the support and γ -alumina by MAP is able to overcome the stresses induced by phase transformations and sintering of γ -alumina. Gishti et al. [12] showed that phosphorus doping stabilizes the γ -alumina phase to higher temperatures. Phosphorus doping is often achieved by impregnation [13,14] or addition in the gel-phase [14,15] in the form of phosphoric acid or ammonium phosphate. After calcination the phosphorus is present as a phosphate at the grain boundaries of the alumina, retarding phase transformations.

Although several investigations have been done on the hydrothermal stability of pure and doped γ -alumina intermediate layers, only few long-term stability tests have been performed with membrane separation layers coated on pure (non-modified) γ -alumina. For long-term pervaporation tests Casticum et al. used non-modified γ -alumina as an intermediate layer for their hybrid sol-gel derived separation layers, based on 1,2-bis(triethoxysilyl)ethane (BTESE) [16]. These membranes were used in butanol dehydration at 95°C and performed well for over more than one year. Also cobalt-silica membranes, prepared by the group of Da Costa are coated on non-modified γ -alumina and subjected to hydrothermal treatments without significant degradation [17,18]. This raises the question whether or not the stability of the intermediate layer plays a big role in the stability of such silica-derived membranes.

Investigations on the hydrothermal stability of sol-gel derived membranes often focus on the separation layers, not on the interplay between the different layers. In this work a systematic investigation is performed to comprehend the impact of water or water vapor on the hydrothermal stability of the complete membrane. By using a straightforward hydrothermal treatment test, γ -alumina and MAP-modified γ -alumina membranes were tested. Hydrothermal stability was monitored by performing permeometry measurements on as-calcined membranes and hydrothermally treated membranes. The hydrothermal stability of the membranes coated with a BTESE separation layer was further evaluated by single gas permeation measurements on as-calcined as well as on hydrothermally treated membranes.

2. Experimental

2.1. Membrane preparation

As starting material for the γ -alumina layer a boehmite sol was used, prepared by the procedure as described elsewhere [2]. In short, aluminum-tri-sec-butoxide was precipitated in water of 90°C and peptized by HNO_3 to obtain a boehmite sol with a par-

ticle size of around 50 nm. Prior to coating, the boehmite sol was mixed with a PVA solution, which acts as a binder and drying aid.

Disc shaped, porous α -alumina supports (pore size 80 nm, porosity 35%) with a diameter of 39 mm and a thickness of 2 mm (Pervatech B.V. the Netherlands) were coated under cleanroom conditions with a boehmite sol followed by a calcination at 650°C (heating- and cooling rate of $1^\circ\text{C}/\text{min}$, dwell time of 3 h.) This procedure was repeated once. Monoaluminumphosphate (MAP) modification was performed by coating the α -alumina supports with a 5 wt% MAP (Fluka) water solution. After MAP coating, the supports were calcined at 300°C with a heating and cooling rate of $1^\circ\text{C}/\text{min}$ and a dwell time of 3 h prior to coating the boehmite sol.

BTESE sols were prepared by the following procedure: 1.04 mL of a 1.77 mol/L HNO_3 solution was added to 5.53 mL ethanol and placed in an ice bath. Subsequently 3.33 mL of BTESE (1,2-bis(triethoxysilyl)ethane) was added drop-wise to the mixture under vigorous stirring to obtain a final molar ratio of BTESE:EtOH: HNO_3 : H_2O of 1:10.8:0.2:6. The mixture was allowed to react at 60°C for 90 min and put in an ice bath to quench the reaction. Ethanol was added to the solution to dilute the sol for dip coating to a final silicon concentration of 0.3 mol/L. Further details are given in [19]. This BTESE “dip sol” was coated once on the γ -alumina as well as on the MAP modified γ -alumina membranes under cleanroom conditions. The membranes were fired under nitrogen at 400°C with a heating rate of $0.5^\circ\text{C}/\text{min}$ and a dwell time of 3 h.

2.2. Hydrothermal treatment

The hydrothermal treatment was performed in a reflux setup at ambient pressure. The membrane was placed in a holder with the separation layer facing upwards, and placed 2 cm above the water level in the reflux setup. The water was heated by an oil bath with a temperature of 110°C to ensure a steam temperature of 100°C , resulting in a relative humidity (RH) of 100% around the membrane. The test was continued for 72 h, after which the membrane was removed from the setup and dried in air at room temperature.

2.3. Characterization

Permporometry was performed in a home-made equipment to determine the pore size of the mesoporous layer. The pore-size of the membrane was determined using cyclohexane as the condensable gas, nitrogen as a carrier gas and oxygen for measuring the diffusional flux through the membrane as function of the vapor pressure of the condensable gas. The desorption mode was used to determine the actual pore-size of the membrane, using the Kelvin equation, which relates partial pressure of the condensable gas to a pore size. Full details about the equipment and the calculation method used can be found in the paper by Cao et al. [20].

High resolution scanning electron microscopy (SEM) was performed with a Zeiss Merlin FESEM on membrane cross-sections to study the thickness and morphology of the layers. The cross sections were placed on a sample holder and partly covered with aluminum tape to prevent sample charging. No further pretreatment was done on the samples and images were acquired at an accelerating voltage of 1 kV. For EDX the accelerating voltage was increased to 10 kV to make sure all the elements were detectable.

The membrane performance was characterized by means of single gas permeation. The membranes were measured in a “dead-end” mode. A feed pressure of 3 bara was applied to the membrane, while the permeate pressure was kept at atmospheric pressure. The pressure difference over the membrane was measured by a differential pressure sensor (GE Druck STX2100). The flow through the membrane was determined by a Bronkhorst EL-FLOW mass flow meter. The membranes were pretreated by heating to 200°C under

Download English Version:

<https://daneshyari.com/en/article/5440287>

Download Persian Version:

<https://daneshyari.com/article/5440287>

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