



# Micro-porous silica–yttria membrane by sol–gel method: Preparation and characterization

Shirin. Khanmohammadi, Ehsan. Taheri-Nassaj\*

*Department of Materials Science and Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran*

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## Abstract

Micro-porous yttria doped silica membrane, fabricated on alpha-alumina substrate and gamma-alumina interlayer, has been prepared via the polymeric sol–gel method. In order to investigate the hydrothermal stability of the membrane, silica sols with different amounts of 5, 15 and 25 wt% yttria were prepared. These sols showed particle size distributions in the range of 0.6–3 nm. It was found that the hydrothermal stability of the unsupported silica–15% yttria membrane heat treated at 500 °C is the highest according to the results of FTIR analysis showing the formation of Si–O–Y bonds. XRD data showed thermal stability up to around 800 °C for the unsupported silica membrane with 15% yttria. N<sub>2</sub> adsorption–desorption isotherm confirmed the existence of micro-porous structure for this membrane as BET surface area and average pore size of the unsupported membrane was 286 m<sup>2</sup>g<sup>−1</sup> and 1.9 nm, respectively. Modified substrate surface reduced average roughness and a layer with similar roughness and pore size was achieved. Cross sectional images by FESEM showed the thickness of 680 nm for the obtained membrane. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** Ceramic membrane; Hydrothermal stability; Roughness; Silica; Sol–gel; Yttria

## 1. Introduction

During recent years ceramic membranes have received considerable attention due to their applications in chemical, petrochemical and drug and food industries, where high temperature and high pressure is needed. The sol–gel method is considered to be the most practical method in fabrication of porous inorganic membranes [1–4]. In the sol–gel method, synthesis of gel is based on hydrolysis and condensation reactions to form oxide network from molecular precursors through making chemical bondings.

Ceramic membrane's physical and chemical structures are determinant factors on various key properties such as permeability, selectivity, thermal, hydrothermal stability and fouling manner. Improving physical structure quality by eliminating imperfections and making defect free membrane surface has great importance, since it can diminish permeability and selectivity due to the inappropriate diffusion through defects

[5,6]. So a minimum roughness of the support surface is needed to produce defect-free membrane layers. The roughness can limit the achievable layer thickness and also determines the maximum size and sharpness of flaws which can act as crack initiators. A smaller roughness can be obtained to some extent by polishing the support surface [7]. Similarly improving chemical structure can be performed by modifying its bondings which takes place by altering experimental conditions like precursors, concentration and temperature.

Among competing membranes, so–gel derived silica-based membranes are the most attractive because of their amorphous structure and pore sizes less than 1 nm and also relatively inexpensive to produce. Gamma-alumina almost exclusively used as an intermediate layer for this membrane layer, because of its high specific properties. Micro-porous SiO<sub>2</sub> membrane is usually used for gas separation involving small gas molecules such as H<sub>2</sub>, He, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> etc. because of excellent selectivity and high gas permeation. Gas separation in many of the applications as coal gasification, steam methane reforming, water–gas shift reaction requires high temperatures and wet gas streams. For example hydrogen is primarily produced from

\*Corresponding author. Tel.: +98 21 82883306; fax: +98 21 82883381.  
E-mail address: [taheri@modares.ac.ir](mailto:taheri@modares.ac.ir) (Ehsan. Taheri-Nassaj).

natural gas through reforming and water–gas shift reactions under humid atmosphere which is usual component of hydrogen producing reactions. So hydrogen separation membrane which can be used under humid condition at high temperature is needed to meet this demand. Micro-porous amorphous silica based membranes are well known for their  $H_2$  permselectivity [8–12] and the only drawback of the silica membrane's application is its poor hydrothermal stability when exposed to water and water vapor at high temperatures [13–15]. As it has been reported previously, at the presence of humid, Si–O–Si linkages are broken upon interaction with water which forms Si–OH hydroxyl groups and creates destruction and reconstruction of Si–O–Si bonds in the silica structure. This mechanism is dominant in micro-porous silica membrane and results in structure densification and deterioration of its micro pores. Metal oxide (MO) doped silica membranes are considered to be stable under hydrothermal conditions due to the incorporation of metal ions into the silica matrix which yields hydrothermally stable M–O–Si bonds. Oxygen forms more stable bonds with transition metals than with silicon. Additionally, because of larger coordination number of transition metals, they tend to have packed structure than pure silica [10]. In order to improve the silica membrane's hydrothermal stability, many oxides and metal ions addition, such as NiO,  $TiO_2$ ,  $ZrO_2$ ,  $Cr_2O_3$ ,  $Co_3O_4$ ,  $Al_2O_3$ ,  $Nb_2O_5$ , etc. have been investigated [16–22].

In this work, an experimental study was made on the synthesis and characterization of a asymmetric ceramic membrane with defect free and smooth silica–yttria toplayer. The objective of yttrium oxide addition was to improve the membrane's hydrothermal stability. Different properties of the membrane were characterized with XRD, FTIR, FESEM, AFM and  $N_2$  adsorption–desorption analysis. It is intended to investigate the performance of yttria–silica membranes for the single gas ( $H_2$ , He,  $CO_2$ ,  $CH_4$  and...) permeation and separation of binary gas mixtures like  $H_2/CO_2$  or  $H_2/CH_4$  in future researches.

## 2. Experimental

Fabricating multilayer membrane in our work involves three stages: (1) making macro-porous support, (2) making meso-porous intermediate layer, and (3) making micro-porous toplayer.

### 2.1. Support preparation

Disk-shaped macro-porous alumina substrates (diameter 4.5 cm, thickness 2 mm, porosity 50%) were prepared by uniaxial pressing of  $\alpha$ -alumina powder with average particle size of 0.3 micron and

8 wt% distilled water. The green disks were dried at room temperature for 24 h, followed by sintering at 1400 °C. After sintering, in order to obtain smooth surface the supports were polished with 400–1200 grade sand papers, washed with deionized water and dried for 24 h at room temperature.

### 2.2. Sols preparation

Meso-porous and micro-porous membrane layers were prepared through the colloidal and the polymeric sol–gel methods, respectively. In order to make gamma-alumina interlayer, boehmite sol was prepared using procedure described by Yoldas [23,24]. Aluminum trisecbutoxide (ATSB, Merck) was added to preheated distilled water (molar ratio of water:ATSB=100) at the temperature of 80 °C. The sol stirred vigorously on a hot plate for an hour to complete alkoxide hydrolysis, then  $HNO_3$  (65%, Merck) was added drop wise to peptize the sol. This solution was stirred for 12 h under reflux condition to ensure complete mixing. Prior to coating, the boehmite sol was mixed with 35  $gL^{-1}$  concentration of PVA (Merck, MW:7200) aqueous solution.

Upon obtaining required membrane layer, three silica sols containing 5, 15 and 25 wt% yttria were prepared. The preparation procedure of silica–15% yttria according to similar procedures in other works [25,26] was as follows: 1.2 g Yttrium nitrate hexahydrate ( $Y(NO_3)_3 \cdot 6H_2O$ ) (99.99%, Dae Jung) was dissolved in 15 mL ethanol, followed by the addition of 8.94 mL tetraethyl orthosilicate (TEOS, 99%, Merck) which was allowed to get mixed on magnetic stirrer. Subsequently, 3 mL water and 0.1 mL nitric acid were added drop wise to complete the hydrolysis and condensation reactions. The resultant sols were dried as xerogel powders (unsupported membrane) and also used for coating on substrate to make supported membranes. Unsupported gels were made by drying the coating sol in petri-dishes.

### 2.3. Membrane coating

Dip-coating process was performed using automatic dip-coating device. Intermediate layer deposited on top of the support with dipping and withdrawal speed of 10  $mm\ min^{-1}$  and holding time of 10 s. The toplayer solution was coated on gamma-alumina layer with dipping and withdrawal speed of 5 and 30  $mm\ min^{-1}$ , respectively and holding time of 50 s. The number of layers and their calcination temperatures for the membrane prepared in this work are listed in Table 1.

### 2.4. Characterization of support and membrane

Atomic Force Microscopy (AFM, CP-Research) and roughness checker (Surtronic 25) were used to quantify and visualize

Table 1  
Membrane's preparation details.

Type	Number of layers	Sol	Calcination temperature (°C)	Calcination time (h)
Intermediate layer	2	Boehmite	600	3
Top layer	3	Yttria doped silica	500	1

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