



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Binary gas mixture and hydrothermal stability investigation of cobalt silica membranes



Liang Liu^{a,b}, David K. Wang^a, Dana L. Martens^{a,b}, Simon Smart^{a,b},
João C. Diniz da Costa^{a,b,*}

^a The University of Queensland, FIM²Lab – Functional Interfacial Materials and Membranes Laboratory, School of Chemical Engineering, Brisbane QLD 4072, Australia

^b Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), Australia

ARTICLE INFO

Article history:

Received 31 March 2015

Received in revised form

29 May 2015

Accepted 30 June 2015

Available online 13 July 2015

Keywords:

Cobalt silica membranes

Gas mixture

Gas separation

Hydrothermal stability

ABSTRACT

This work investigates the influence of hydrothermal exposure on the separation performance of sol–gel derived cobalt oxide silica membranes for both single gases (He, H₂, CO₂ and N₂) and binary gas mixtures (He/CO₂). The surface area of the materials slightly decreased after exposed to 25 mol% water vapour at 550 °C for 100 h. The membranes complied with activation transport mechanism before and after hydrothermal treatment (HT), and for both single gas and gas mixture permeation. Best values were achieved for He permeance of $3.3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 500 °C and permselectivity of 479 for He/CO₂. After HT, the permeance of He and H₂ decreased by 28% and 22% at 500 °C, respectively, while the permeance of CO₂ increased and resulting in a lower He/CO₂ permselectivity of 190. For gas mixtures, the He purity in the permeate side increased from 62% to 97% at 200 °C when the He feed molar concentration increased from 10% to 50% before HT. The He permeance remained unchanged with respect to He feed concentrations and was unaffected by the presence of CO₂, although a reduction of He permeance was observed after HT exposure. The He purity in the permeate side was similar before and after HT exposure as a function of the He concentration in the feed side. Hence, the membrane matrix underwent densification though the overall pore size distribution did not broaden after hydrothermal treatment.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Owing to their intrinsic molecular sieving properties and thermal stability, microporous silica membranes have attracted the concerted effort of the research community, particularly for high temperature gas separation. Silica derived membranes have proved to be stable for over 2000 h operating at 500 °C [1] using dry gas mixtures, as well as for H₂/CO₂ separation [2,3], dehydrogenation of propane [4–6] and cyclohexane [7,8], and H₂ separation from syngas generated in the water gas shift reaction [9,10] among several examples. Although pure silica has excellent thermal and chemical stability, they are hydrothermally unstable

in the presence of steam [11,12], which is a major issue for the deployment of silica membranes for industrial applications involving wet gas separation. To address this problem, metal oxide silica membranes have been investigated to improve performance and hydrothermal stability. In this subset of silica membranes, a wide range of metal/metal oxides have been incorporated into silica including alumina [13], titania [14], cobalt [15,16], niobia [17–19], nickel [20–22] and binary metals such as PdCo [23] and FeCo [24].

Cobalt oxide silica membranes have spearheaded the development of hydrothermally stable silica membranes. Uhlmann et al. [25] reported that a cobalt tetroxide silica material was much more stable than a cobalt (i.e. reduced metal) silica material, indicating that the cobalt phase is critical to the final membrane performance. Recently, the hydrothermal stability of cobalt oxide silica materials was shown to be dependent upon the cobalt phase embedded in the silica films. For instance, cobalt oxide silica xerogels were more hydrostable for Co³⁺ coordination (as in Co₃O₄) whilst Co²⁺ coordination led to unstable structures when exposed to steam [26]. Novel work in this area is now focusing on tailoring the cobalt phase using the halide groups of surfactants [27,28] or

Abbreviations: FTIR, Fourier transform infra-red spectroscopy; SEM, Scanning electron microscope; GC, Gas chromatography; FID, Flame ionisation detector; TCD, Thermal conductivity detector; HT, Hydrothermal treatment; CVD, Chemical vapour deposition; E_{act} , Apparent activation energy

* Corresponding author at: The University of Queensland, FIM²Lab – Functional Interfacial Materials and Membranes Laboratory, School of Chemical Engineering, Brisbane QLD 4072, Australia. Fax: +61 7 3365 4199.

E-mail address: j.dacosta@uq.edu.au (J.C. Diniz da Costa).

<http://dx.doi.org/10.1016/j.memsci.2015.06.058>

0376-7388/© 2015 Elsevier B.V. All rights reserved.

by sol–gel conditioning [26].

Generally, a significant amount of literature work has been reported for single gas permeation tests as a starting point. This allows the membrane engineers to calculate the size of unit operations using gas permeances ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) as a production factor and the permselectivity as a quality factor. High performance silica derived membranes are dependent on the substrate quality, microporous film textural properties, geometries and testing procedures. As a rule, H_2 permeance in the order of 10^{-8} – $10^{-6} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ with a H_2/CO_2 (N_2) permselectivity ranged from < 100 to < 5000 have been reported [29–32]. For example, a cobalt oxide silica membrane showed a H_2 permeance of $1.8 \times 10^{-7} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ with H_2/N_2 values of ~ 730 at 500°C [31], whilst a niobia silica membrane delivered $3.8 \times 10^{-8} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ (H_2) and 22 (H_2/CO_2) at 200°C [33]. Single gas permeation is an easy and rapid way to carry out experimental work and to provide fundamental understanding of the performance of membranes, but the results cannot be directly applied to real industrial separation processes due to gas flow effects and changes in driving force [34], and competitive sorption [35] among other reasons. As a consequence, membrane engineers require gas mixture results in order to gain important information on how the membranes would perform in industrial deployment. In industrial applications, the permeate gas purity and flow rate (or flux) are most of interest. It has been reported that both purity and flow rate [36], which translate into membrane production rate and product specification, can be controlled by temperature and feed partial pressure for H_2/CO_2 separation.

Despite the industrial requirements for processing gases, there is only a limited number of reports for gas mixture separation using microporous silica-based membranes, and none of these reports have considered membranes exposed to harsh steam conditions. Therefore, this work investigates the performance of cobalt silica membranes for gas mixtures at high temperatures before and after exposing the membranes to 25 mol% water vapour at 550°C for up to 100 h. To this end, permeation testing was initially carried out for single gases (He , H_2 , CO_2 and N_2) and binary gas mixture of He/CO_2 with different He feed concentrations (10, 30, 50, 70 and 90%) at temperatures between 200 and 500°C . Subsequent to exposing the membranes to harsh steam condition, single and binary gas mixture permeation tests of the hydrothermally treated membrane were again carried out following the same protocol to investigate the influence of harsh hydrothermal exposure on the membrane performance. The textural and chemical properties of membrane material were characterised by N_2 sorption and FTIR spectroscopy, along with the SEM examination into membrane morphology.

2. Experimental

2.1. Sol–gel synthesis and characterisation

Cobalt oxide silica xerogels were synthesised from a sol–gel method as described elsewhere for the preparation of hydrothermal stable silica structures [37]. Briefly, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Sigma-Aldrich) was dissolved in a solution of ethanol, double distilled water and nitric acid under constantly stirring. Then the mixture was cooled down to 0°C using an ice bath. Tetraethoxysilane (TEOS, 99%, Sigma-Aldrich) was added drop-wise and stirred for 3 h to achieve a final sol with the molar ratio of $\text{EtOH}:\text{H}_2\text{O}:\text{TEOS}:\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:\text{HNO}_3 = 255:80:4:1:0.34$. The sol was dried in a temperature controlled oven at 60°C for 96 h. The dried gel was then calcined in an air atmosphere in a furnace at 630°C for 2.5 h with heating/cooling rates of 1°C min^{-1} to produce the xerogel samples. From

hereafter, the sample is named as cobalt oxide silica (CoSi).

Nitrogen sorption was carried out on a Micromeritics TriStar 3020 analyser after degassing under vacuum on a Micromeritics VacPrep061 at 200°C for a minimum of 12 h. The specific surface areas were calculated from the adsorption isotherms via the multi-points BET model at relative pressures of $p/p_0 = 0.05$ – 0.3 . Single point pore volume was calculated at $p/p_0 = 0.96$. Fourier transform infra-red (FTIR) spectra were recorded with a Shimadzu IRAffinity-1 instrument with a Pike MIRacle diamond attenuated total reflectance (ATR) attachment. Spectra were taken over a wavenumber range of 1400 – 600 cm^{-1} .

The calcined xerogels were exposed to 25 mol% vapour at 550°C up to 100 h in a customised rig [37] to investigate the hydrothermal stability of the material. Briefly, the sample was placed inside a quartz tube furnace with an external temperature controller. N_2 was used as carrier gas at a flow rate of 40 ml min^{-1} . The water flow rate was controlled by a Bronkhorst flow controller and was heated to 200°C in a vaporiser prior to entering the furnace.

2.2. Membrane preparation, characterisation and permeation test

The thin film cobalt oxide silica sol was coated on a tubular alumina support (10 mm i.d., 14 mm o.d., 80 mm length) consisting of α -alumina substrate, α - and γ -alumina interlayers with thickness of ~ 3 and $\sim 30 \mu\text{m}$, respectively, purchased from the Energy Research Centre of the Netherlands (ECN). Each layer was coated on the outer shell of the tubular support with the as-synthesised sol using a dip-coater with a dwell time of 1 min and immersion/withdrawal rate of 10 cm min^{-1} . After the coating of each layer, the membrane was calcined at 630°C for 2.5 h with a ramping rate of 1°C min^{-1} for both heating and cooling cycles. The whole coating–calcination process was repeated four times to achieve the final CoSi membrane.

The gas permeation tests were carried out in a customised rig as shown in Fig. 1. The transmembrane pressure was controlled at 500 kPa and the permeate side was under atmospheric pressure for both single gas and gas mixtures. For single gas test, the valve at retentate side was closed, similar to a dead-end set up. The permeate flow rate (ml s^{-1}) of He , H_2 , CO_2 and N_2 in the temperature range of 100 – 500°C was measured by a bubble flow metre and it was converted to permeance ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$). He/CO_2 mixture of various He molar fractions (10, 30, 50, 70 and 90%) was used for gas mixture separation from 200 to 500°C . For gas mixture separation, the back pressure valve at retentate side used to control the total pressure in the membrane module. The feed concentration, retentate concentration and He purity at the permeate side were analysed in a Shimadzu GC-2014 with two columns (Porapak Q and Restek Molesieve) and FID and TCD detectors. N_2 was used as carrier gas and the flow rate was 10 ml min^{-1} . The temperature of the column, TCD and FID detector was set to 140, 140 and 380°C . The GC was calibrated by using a He/CO_2 mixture with different concentrations ranged from

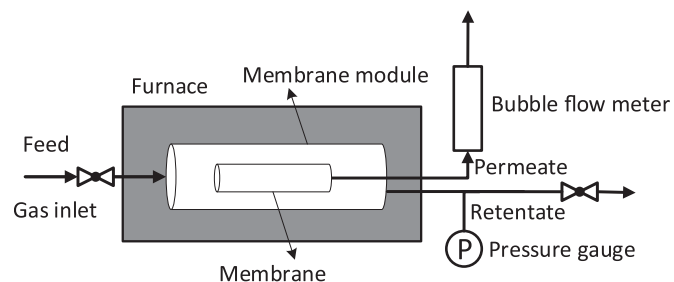


Fig. 1. Gas permeation rig.

Download English Version:

<https://daneshyari.com/en/article/7021109>

Download Persian Version:

<https://daneshyari.com/article/7021109>

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