



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Gas permeation redox effect on binary lanthanum cobalt silica membranes with enhanced silicate formation

Benjamin Ballinger, Julius Motuzas, Simon Smart, João C. Diniz da Costa*

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

ARTICLE INFO

Article history:

Received 14 January 2015

Received in revised form

13 April 2015

Accepted 17 April 2015

Available online 25 April 2015

Keywords:

Silica membranes

Cobalt oxide

Lanthanum silicate

Gas separation

Redox

ABSTRACT

This work investigates the characterisation and performance of binary lanthanum cobalt doped silica membranes. The prepared membranes resulted in temperature dependent gas transport, a characteristic of molecular sieving membranes. Under reduction and oxidation cycles at 500 °C, the maximum steady state permeance of the membranes reached $1.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 500 °C. It was found that the membranes contained both cobalt oxide and lanthanum silicate phases embedded in the silica matrix. The permeance of all tested gases under redox cycling decreased during the 350 h permeation test, though the reduction was slightly more pronounced for larger gas molecules (H_2 , CO_2 and N_2). As a result, He/CO_2 permselectivity increased from ~ 80 at the initial tests to 196 during the redox cycling test, an improvement of 145%. This indicates that the pore sizes $\geq 2.89 \text{ \AA}$ (i.e. kinetic diameter of H_2) preferentially collapsed/closed instead of the smaller pores available for the permeation of the smaller gas He ($d_k = 2.6 \text{ \AA}$). These results are contrary to other silica and metal doped silica membranes which undergo thermal densification and closure of the smaller pore sizes. Therefore, the formation of lanthanum silicates conferred superior structural stability in the silica matrix.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Inorganic membranes have long showed potential for high temperature industrial applications due to their high thermal and chemical stabilities. The production of microporous thin films derived from silica precursors in the early 1990's [1–3] enabled the development of gas selective membranes which achieve separation through a size selective, molecular sieving transport regime [4–7]. The highly versatile sol–gel synthesis of silica precursors, particularly tetraethyl orthosilicate (TEOS), is at the core of the processing of these materials. For instance, reacting TEOS in an acid catalysed solution containing a solvent and sub-stoichiometric quantity of water favours the growth of polymeric silica chains with minimal side branches [8,9]. Consequently, during solvent evaporation (i.e. water and ethanol), the polymeric chains pack densely, which results in the formation of micropores when calcined at high temperatures [10].

Over the past decade, research has primarily focused on the incorporation of single metal nanoparticles into the silica matrix to enhance properties such as the hydrothermal stability and gas permeance [11–14]. The most promising single metal dopant is cobalt oxide, whilst nickel oxide [15] and niobia [16] have also been demonstrated to confer membranes with molecular sieving properties. Of

particular attention, cobalt oxide silica membranes were successfully tested in a large multi-tube module for 2000 h operation and delivering very high permselectivities up to 1000 (He/N_2) [17]. An added benefit of embedding metal oxide particles into silica membranes is directly related to extra functionalities otherwise not available in pure silica membranes. For instance, the phase of the metal nanoparticles has been shown to affect the performance of silica membranes as the oxidised phase promotes hydrothermal stability [18,19], while the metallic phase promotes the selective adsorption and permeation of hydrogen [20].

Recently, further functionalities have been reported by integrating binary metal nanoparticles into silica membranes. This concept was pioneered by Ballinger and co-workers [21] who provided a proof-of-concept of tailored molecular gaps in cobalt palladium silica membranes. It was shown that palladium was selectively reduced to its metallic phase when the membrane was exposed to hydrogen at 500 °C, while cobalt remained in its oxidised state. The molecular gap was a direct consequence of the palladium reduction, resulting in a membrane with different separation properties as compared to the fully oxidised membrane. In a separate study, Darmawan et al. [22] incorporated iron and cobalt oxides in silica and reported that the Fe/Co ratio altered the chemical structure of the resultant silica functional groups. It was interesting to note that Fe/Co ratio of 0.1 provided the best permeance and permselectivities indicating that the molecular sieving structures can be adjusted by varying the metal ratios.

Whilst there is a very limited number of binary metal silica membrane studies, there is a large array of binary metal compositions

* Corresponding author. Tel.: +61 7 3365 6960; fax: +61 7 3365 4199.

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

for consideration. These initial studies open a window of research opportunities to exploit different functionalities related to metal silica, nanoparticle phase and size, pore size distribution among many other important factors in membrane preparation and performance testing. Furthermore, by investigating the different reduction potentials of metal species, the uncoupling of reducing gas/metallic and oxidising gas/metal oxide nanoparticle phase formation can be overcome. To address these points, this study investigates the use of a lanthanide metal (lanthanum) as one of the components of the binary metal oxide, whilst a transition metal (cobalt) is the other component. The key idea to be explored here is the propensity of lanthanum to form silicates [23], an unexplored area in terms of the interactions between metal silicates and transition metal nanoparticles within microporous silica materials and membranes. Furthermore, the separation properties of silica membranes with metal silicate formations will be investigated for the first time.

2. Experimental

2.1. Xerogel preparation and characterisation

The lanthanum cobalt doped silica ($\text{La}_x\text{Co}_{15-x}\text{Si}$) materials were synthesised through the acid catalysed sol-gel processing of tetraethyl orthosilicate (TEOS). Initially lanthanum nitrate hexahydrate and cobalt nitrate hexahydrate were dissolved in hydrogen peroxide. Water and ethanol were then added to the solution, which was subsequently cooled to 0 °C in an ice bath. Finally TEOS was added dropwise and the solution was stirred for 3 h. The final molar ratio of the reagents was 1 TEOS: $x/100$ $\text{La}(\text{NO}_3)_3$: $(15-x)/100$ $\text{Co}(\text{NO}_3)_2$:10.4 H_2O :2.5 H_2O_2 :64 EtOH, with x varied between 0 and 15.

The sol was dried at 60 °C for 7 days under atmospheric conditions. The resultant monoliths were crushed via mortar and pestle and calcined at 630 °C for 2.5 h at a 1 °C min^{-1} ramping rate under ambient air pressure. LaCoSi xerogels were reduced by exposure to 60 mL min^{-1} of hydrogen flowing through a furnace. Re-oxidation was performed by exposure under ambient air pressure. Calcination conditions for reduction and re-oxidation were the same as in the first incidence, except with a maximum calcination temperature of 500 °C to avoid densification of the porous network.

The porous structure of the xerogels were analysed using a Micromeritics Tristar3020 N_2 adsorption apparatus. Samples were degassed in a Micromeritics VacPrep061 under a vacuum of 2 Pa for 12 h. Fourier transform infrared – attenuated total reflectance (FTIR-ATR) characterisation was performed with a Shimadzu IRAffinity-1 with a PIKE MIRacle single-bounce diamond crystal plate accessory. FTIR spectra were recorded between the wavenumber ranges of 700–1300 cm^{-1} . X-ray photoelectron spectroscopy (XPS) was conducted after xerogel powders were re-crushed to minimise any contaminant formed on the surface layer. A Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser was implemented to acquire the data. An Al $K\alpha$ (1486.6 eV) monochromatic X-ray source was used at a 90° takeoff angle with 0.05 eV step size to obtain XP spectra. Charge compensation was performed by setting the adventitious C1s peak to a binding energy of 284.6 eV. Peak deconvolution of the high-resolution data was carried out using CasaXPS software with a Shirley baseline.

2.2. Membrane preparation, testing and characterisation

Lanthanum cobalt silica membranes were synthesised on top of an alpha-alumina support with gamma alumina interlayers purchased from the Energy Research Centre of The Netherlands. Thin films were prepared by dip coating the alumina support in the reacted lanthanum cobalt silica sol. The support was held in solution for 1 min to ensure sufficient soaking into the pores and

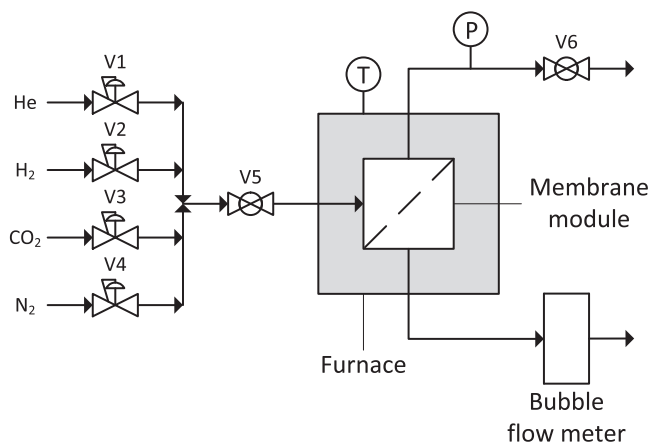


Fig. 1. Membrane permeation rig arrangement.

extracted at a rate of 10 cm min^{-1} . The membrane was then calcined in an air environment. This process was repeated 4 times for each layer to ensure a defect free layer was produced.

Single gas permeation testing was performed using a custom made permeation rig schematically shown in Fig. 1. The temperature of the furnace was controlled with an external PID temperature controller while the pressure in the retentate stream was monitored with a pressure gauge. The permeate stream was kept at atmospheric pressure and its flow rate was measured through a bubble flow meter. Valves 1–4 control the gas pressure throughout the system. For gas permeance testing, valve 5 was opened to allow gas into the system, and valve 6 was closed to keep a constant pressure on the retentate side of the membrane.

Permeation testing was carried out between 100 and 500 °C with a ramping rate of 4 °C min^{-1} . Throughout testing, repeated reduction and oxidation experiments were performed. Membrane reduction occurred by exposing the membrane to hydrogen at 500 °C for a minimum of 10 h, or until permeation reached a steady state. Similarly, oxidation was performed by exposing the membrane to compressed air until equilibrium was reached, using the same criterion as for the membrane reduction.

The silica thin film layer thickness was measured by XPS depth profiling. The depth profiling was performed with a differentially pumped Kratos minibeam III ion gun using 4 keV argon ions at an ion source extractor current of 750 nA and data collected every 1 eV. The order of sputter rates for silicon was in the region of 2.9 nm min^{-1} . The analysed surface area of 0.5 $\text{mm} \times 0.3 \text{ mm}$ was centred in a sputter area of 2 $\text{mm} \times 2 \text{ mm}$. XP spectra were analysed over the binding energy range 1000–0 eV after each 5 min etch cycle.

3. Results

N_2 adsorption isotherms for lanthanum doped and cobalt doped silica xerogels are displayed in Fig. 2a. It can be seen that all xerogels exhibit a type I isotherm, characteristic of microporous materials. Cobalt silica xerogels (i.e. $\text{La}_0\text{Co}_{15}$ to La_5Co_5) demonstrate higher levels of porosity than lanthanum silica xerogels (i.e. La_5Co_0 to $\text{La}_{15}\text{Co}_0$) across all concentrations. Fig. 2b shows similar trends for the binary doped xerogels with a loss in microporous volume with an increase in lanthanum concentration. The loss in microporosity has previously been attributed to the reaction between microporous silica and lanthanum oxide which forms a dense lanthanum silicate [23]. This reaction typically occurs at temperatures above 200 °C for lanthanum [23] and above 850 °C for cobalt [24].

Fig. 3 shows the infrared spectra for lanthanum, cobalt and lanthanum cobalt xerogels. Peaks in the spectra located at 800 and 1080, and the shoulder at 1220 cm^{-1} are attributed to siloxane

Download English Version:

<https://daneshyari.com/en/article/632907>

Download Persian Version:

<https://daneshyari.com/article/632907>

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