Binary gas mixture and Hydrothermal stability investigation of cobalt silica membranes

Liang Liu, David K. Wang, Dana. L. Martens, Simon Smart, João C. Diniz da Costa

PII: S0376-7388(15)30028-4
DOI: http://dx.doi.org/10.1016/j.memsci.2015.06.058
Reference: MEMSCI13817

To appear in: Journal of Membrane Science

Received date: 31 March 2015
Revised date: 29 May 2015
Accepted date: 30 June 2015

Cite this article as: Liang Liu, David K. Wang, Dana. L. Martens, Simon Smart and João C. Diniz da Costa, Binary gas mixture and Hydrothermal stability investigation of cobalt silica membranes, Journal of Membrane Science, http://dx.doi.org/10.1016/j.memsci.2015.06.058

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Binary gas mixture and hydrothermal stability investigation of cobalt silica membranes

1,2 Liang Liu, 1 David K. Wang, 1,2 Dana. L. Martens, 1,2 Simon Smart, 1,2 João C. Diniz da Costa*

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

2 Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), Australia.

*Corresponding author: Email: j.dacosta@uq.edu.au;
Tel.: +61 7 3365 6960; Fax: +61 7 3365 4199

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.

Keywords: cobalt silica membranes; gas mixture; gas separation; hydrothermal stability.
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 Co₂O₄) 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 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 (mol m⁻² s⁻¹ 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, H₂ permeance in the order of 10⁻⁸ ~ 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with a H₂/CO₂ (N₂) permselectivity ranged from <100 to <5000 have been reported [29-32]. For example, a cobalt oxide silica membrane showed a H₂ permeance of 1.8×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ with a H₂/N₂ values of ~730 at 500 °C [31], whilst a niobia silica membrane delivered 3.8×10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ (H₂) and 22 (H₂/CO₂) 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 H2/CO2 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, H2, CO2 and N2) and binary gas mixture of He/CO2 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 N2 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 (Co(NO3)2·6H2O, 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 EtOH: H2O: TEOS: Co(NO3)2·6H2O: HNO3=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 $\alpha$–alumina substrate, $\alpha$– and $\gamma$–alumina interlayers with thickness of ~3 and ~30µm, 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 meter and it was converted to permeance (mol m$^{-2}$ s$^{-1}$ 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/CO₂ mixture with different concentrations ranged from 0-100% before experimental measurement. The calibration error was less than ±2%.

After the gas permeation tests, the membrane was exposed to 25 mol% vapour at 550 °C for 100 h using the same methodology as described for the xerogels above. Then the membrane was tested again for both single gas and gas mixture permeance to investigate the influence of hydrothermal exposure on the membrane performance. The membrane morphology after the hydrothermal exposure and testing was examined using a FESEM Jeol-7001 field emission scanning electron microscope with an electron gun at an accelerating voltage of 10 kV.

3. Results and discussion

The membrane morphology after the hydrothermal treatment (HT) was investigated by SEM, as depicted in Fig. 2. The membrane consisted of a support containing large α-alumina particles, interlayers of smaller α-alumina particles and γ-alumina particles. The thin top layer had an average thickness of ~30 nm and it conferred the highest resistance to gas transport. The membrane top layer showed no visible defects after exposed to a harsh hydrothermal conditions of 25 mol% steam in N₂ at 550 °C for 100 h. These results strongly suggest that the cobalt oxide silica films were hydrothermally stable under these harsh testing conditions, and their integrity was maintained.
Fig. 2. The SEM image of the membrane after HT.

The influence of hydrothermal treatment (HT) on the membrane material stability in terms of surface area and pore volume was assessed by using N$_2$ sorption techniques on the xerogel samples. As displayed in Fig. 3, the isotherms of the as-synthesised CoSi sample and the HT samples show a strong adsorption at low relative pressures (p/p$_0$<0.3) followed by saturation, which is characteristic of a Type I microporous material. However, after 50 and 100 h of steam exposure, a small reduction in the volume adsorbed was observed. Noticeably, the materials showed indifference in the specific surface area and pore volume (Fig. 3b) upon a further 50 h exposure, suggesting a metastable state has been achieved after hydrothermal exposure. Overall, the surface area decreased from 283 to 249 m$^2$ g$^{-1}$ after 100 h exposure, which is only a 12% reduction, and in good agreement with our previous study [37].
The influence of the hydrothermal treatment (HT) on the chemical structures of the material was investigated by FTIR spectroscopy. Fig. 4 shows the FTIR spectra of the CoSi xerogels as-synthesised and after HT. All samples exhibited typical cobalt oxide silica structures. Vibrational peaks seen at ~800, 1050 and 1220 cm\(^{-1}\) are attributed to different vibration modes of siloxane (Si-O-Si) bridges [38] and at ~950 cm\(^{-1}\) to silanol (Si-OH) groups [39]. The peak at ~660 cm\(^{-1}\) is assigned to the vibration modes of Co(III)-O bonds of Co\(_3\)O\(_4\) [40, 41]. It is clear that the hydrothermal exposure did not affect the chemical composition and structure of CoSi samples significantly. This may be related to the fact that the presence of Co\(_3\)O\(_4\) can confer an improved hydrothermal stability of the silica materials by inhibiting the hydrolysis and condensation reaction of the silica in the pore walls [37].

Single gas permeation tests were carried out to investigate the membrane performance before and after the hydrothermal treatment and the permeances of He (kinetic diameter of 2.60 Å), H\(_2\) (2.89 Å), CO\(_2\) (3.3 Å) and N\(_2\) (3.64 Å). Fig. 5 shows that the as-synthesised membrane complied with temperature-dependent activated transport, which is characteristic of molecular sieving and is commonly reported for microporous silica based membranes [42]. The permeance of He increased from 1.1×10\(^{-7}\) to 3.3×10\(^{-7}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) as the temperature was raised from 100 and 500 °C, whilst the permeance of CO\(_2\) decreased from 1.9×10\(^{-9}\) to 6.8×10\(^{-10}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) at the same given temperatures. After HT, the membrane maintained a similar molecular sieving behaviour, although the permeance of gases with the smaller kinetic diameters (He and H\(_2\)) decreased the
larger kinetic diameters gases (CO$_2$ and N$_2$) increased. For instance, the permeance of He and H$_2$ decreased by 28% and 22%, whereas the permeance of CO$_2$ increased by 18% at 500 °C. Although it is clear that the single gas separation performance was affected by the hydrothermal exposure, it is worthwhile noting that the reductions of permeance of He and H$_2$ gases in this work are relatively lower than those reported for pure silica membranes when exposed to steam. For examples, the H$_2$ permeance reduction was 87% for a chemical vapor deposition (CVD) derived silica membrane when it was exposed to 16 mol% vapour at 600 °C for 100 h [13] and 80% for a sol-gel derived silica membrane when it was exposed to 14 mol% vapour at 200 °C for 70 h [17]. Hence, cobalt oxide silica membrane in this work had much higher resistance to hydrothermal densification, which agreed well with the N$_2$ sorption results (Fig. 3).

Fig. 5. Single gas permeance (±8%) of the membrane as a function of temperature: (a) before and (b) after HT.

Fig. 6: Permselectivity of the membrane as a function of temperature: (a) before and (b) after HT.
The performance of the membrane was further highlighted by calculating the permselectivities of He/CO₂ and H₂/CO₂ as shown in Fig. 6. The permselectivity was also temperature dependent. It is obvious that the influence of temperatures on the permselectivity is more significant for the as-synthesised membrane compared to the HT membrane, evidenced by the slope differences. The permselectivities of H₂/CO₂ and He/CO₂ increased from 8 and 57 at 100 °C to 220 and 479 at 500 °C, respectively, for the as-synthesised membrane (Fig. 6a). After HT exposure, lower increases in H₂/CO₂ and He/CO₂ permselectivity were observed, from 8 and 36 at 100 °C to 134 and 190 at 500 °C, respectively. This represents a loss of H₂/CO₂ and He/CO₂ permselectivities with increasing temperatures of 40 and 60% respectively as measured at 500 °C. However, it is noteworthy that He/CO₂ values remained high (>100) at temperatures in excess of 200 °C. The reduction in permselectivity is attributed to (i) the slight pore widening effect after HT as evidenced by the increase in permeance for CO₂ and N₂ in Fig. 5b, and (ii) by the closure of small pores due to the decrease in the permeation of the gases with the smaller kinetic diameters He and H₂ (Fig. 5b). Therefore, the combined HT effect of pore changes was more pronounced in terms of permselectivity rather than permeance of gases, as permselectivity is the ratio of gas permeance.

The apparent activation energy (E_{act}) was calculated from an Arrhenius plot of the permeance versus temperature data, as shown in Table 1. The positive values for He and H₂ and negative values for CO₂ and N₂ were associated with activated transport behaviour [17, 43]. The E_{act} for H₂ permeance was much higher than that for He permeance. This is attributed to the larger kinetic diameter of H₂ (2.89 Å) than He (2.60 Å) [31, 44]. Hence, the H₂ molecules need more kinetic energy to overcome the potential barrier of small pores than the He molecules. Furthermore, both CO₂ and N₂ gave negative values, suggesting that there is a percolation pathway in the cobalt silica films large enough to allow for the diffusion of these larger molecules. After HT exposure, the E_{act} of He slightly increased indicating a decrease of average pore size for He permeance, which could be associated with the densification of the silica network as evidenced by the N₂ sorption (Fig. 3), as many of these very small pores are accessible by the smaller kinetic He molecule only. However, the E_{act} of H₂ slightly decreased thus suggesting a lower energy level for H₂ permeation. This is attributed to diffusion through slightly larger pores associated with the HT treatment, which is supported by the slightly increase in pore size as the permeation of the larger molecular gases N₂ and CO₂ also increased as observed in Fig. 5b. Nevertheless, it is important to observe that as the permeance experimental variation is ±8%, the E_{act} for H₂ permeance falls within this variation. Hence, the structural changes in the cobalt silica film for H₂ permeance may be very marginal.
Table 1: \( E_{act} \) of gases calculated from single gas permeance results

<table>
<thead>
<tr>
<th>Gas</th>
<th>( E_{act} ) (kJ mol(^{-1})) before HT</th>
<th>( E_{act} ) (kJ mol(^{-1})) after HT</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>6.7</td>
<td>8.0</td>
</tr>
<tr>
<td>H(_2)</td>
<td>13.8</td>
<td>12.8</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>-6.3</td>
<td>-2.1</td>
</tr>
<tr>
<td>N(_2)</td>
<td>-2.3</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

To further investigate the separation performance of the membranes, permeation tests were carried out for He and CO\(_2\) binary gas mixtures ranging from 200 to 500 °C before and after the hydrothermal treatment. Fig. 7 shows the He flux at the permeate side as a function of He feed concentrations at different temperatures. For the as-synthesised membrane, He flux increased significantly from 0.018 to 0.118 mol m\(^{-2}\) s\(^{-1}\) when He feed concentration increased from 30% to 90% at 500 °C. However, this major increase is expected and attributed to the increase of driving force associated with the changes of He partial pressure. Another interesting observation is that He flux was 71% of the value for single gas when He feed concentration decreased from 100% to 90% at all temperature ranges, thus strongly implying that the presence of CO\(_2\) has an influence on the transport of He. Furthermore, the He flux was also temperature dependent at each He concentration, in a similar fashion as in single gas permeation results (Fig. 5). It is worthwhile mentioning that a high feed flow rate was used in this work to maintain a relatively constant driving force along the membrane length. This parameter is crucial in generating a steady state condition of the binary gas testing to reduce any concentration gradient along the membrane module [34]. After HT exposure, the membrane showed similar behaviour compared to the as-synthesised membrane, although a slight reduction of He flux was observed. It is consistent with single gas permeation results, as the membrane had a certain degree of densification after the HT exposure (Fig. 5). Apart from high CO\(_2\) retentate concentration of He/CO\(_2\) (10/90), CO\(_2\) fluxes were generally up to two orders of magnitude lower than that of He for He/CO\(_2\) > 10/90. CO\(_2\) fluxes varied between 0.003 and 0.014 mol m\(^{-2}\) s\(^{-1}\), which are within the experimental error of our setup.
Fig. 7. He flux of the membrane (±8%) at the permeate side as a function of He feed concentration: (a) before and (b) after HT, ΔP=500 kPa.

Fig. 8 shows the He purity at the permeate side as a function of He feed concentration. It noteworthy that the membrane was able to concentrate He to 62% at the permeate side when the feed concentration of He was only 10% at 200 °C and significantly increased to 93% at 30% feed concentration (Fig. 8a). Similar results were observed for the membrane after HT exposure (Fig. 8b) and the differences compared with the as-synthesised membrane are minor and within experimental error. It is interesting to observe that the temperature effect on the purity of gases is marginal only; whilst gas feed concentration becomes more prominent when He feed concentrations are below 30%. These results follow similar trends for gas separation in large membranes modules [1].

Fig. 8. He purity of the membrane (±10%) as a He feed concentration: (a) before and (b) after the hydrothermal treatment (HT), ΔP=500 kPa.
The feed concentration in turn affects the driving force (partial pressure) for He permeation which increased from very small values (~10%), to 73 (~30%), 192 (~50%), 304 (~70%) to 435 kPa (~90%) at 200 °C. The increase in the driving force translated into higher He fluxes as shown in Fig. 7. For instance, the He flux at 10% He concentration was also very small as the driving force was close to zero kPa. However, the driving force effect on the permeate gas purity is not significant for He feed pressures >30%. These results strongly suggest that the molecular sieving structure of the cobalt oxide silica membrane is preferentially allowing the diffusion of He whilst hindering the passage of CO2. Further, it is interesting to observe that although the single gas permselectivity reduced after HT exposure (Fig. 6), this is not the case for the permeate gas purity for gas mixtures in Fig. 8. In principle, these results clearly indicate that very high permselectivity values are not the best engineering parameter for designing unit operations for the separation of industrial gas mixtures. In this case, even as the He/CO2 permselectivity reduced from 158 (before HT) to 78 (after HT) at 200 °C (Fig. 6), the He purity remained very high (>90%) for both cases for He feed concentrations ≥30% (Fig. 8).

The permeance of He was calculated to shed further light on the gas mixture separation performance as shown in Fig. 9. It is clear that the influence of He feed concentration was marginal when He feed concentration ranged from 30% to 90%, and the small variations observed are within experimental error. Note that the He permeance at ~10% could not be calculated correctly as the driving force was very small and close to zero kPa. Interestingly, the He permeance in the gas mixture is slightly lower than that of the single gas results (100% - see Fig. 5). Concentration polarization is generally an issue in gas mixture separation, though the gas to gas diffusion at high temperatures is several orders of magnitude higher than gas diffusion through the membrane [45]. Therefore, concentration polarization in this case was marginal as determined from a computational fluid dynamics simulation [46]. In addition, the adsorptive CO2 was also considered to be negligible as the increase of CO2 feed concentration at high temperatures did not affect He permeance. Last, this slight difference in He permeance from single gas to gas mixture could be attributed to the experimental procedure, which was initially carried out for single gas testing for all temperatures. Hence, it is possible that the cobalt oxide silica matrix underwent minor structural densification, thus resulting in a slight reduction of the He permeance in subsequent gas mixture tests.
Fig. 9. He permeance (±10%) of the membrane as a function of He feed concentration: (a) before and (b) after HT, ΔP=500 kPa.

The apparent activation energies of He permeance at different feed concentrations calculated from the permeance data in Fig. 9 are shown in Fig. 10. The $E_{act}$ values before and after HT exposure are calculated to be approximately 6.1 and 7.8 kJ mol$^{-1}$, respectively, which are in accordance with those of the single gas results (Table 1). It is noteworthy that the $E_{act}$ values were constant for different gas feed concentrations, indicating the presence of CO$_2$ had no influence on thermodynamic properties of gas diffusion through the membrane. In addition, the $E_{act}$ values after HT were consistently higher than before HT. These results suggest that the energy barrier for the transport of He through the porous structure increased after HT. In other words, the average pore sizes for the transport of He decreased after HT, thus requiring more energy for the diffusion of He molecules.

Fig. 10. Apparent activation energy of He as a function of He feed concentration.
4. **Conclusions**

Cobalt oxide silica material with improved hydrothermal stability was synthesised using sol-gel techniques. Xerogel sample resulted in surface area loss of ~12% after exposure to 25 mol% water vapour at 550 °C for 100 h. High quality membranes were prepared delivering a He permeance of $3.3 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 500 °C and permselectivity of 479 for He/CO$_2$. The HT exposure had a moderate influence on the performance of the membranes as the permeance of He and H$_2$ decreased by 28% and 22%, though a large He/CO$_2$ permselectivity reduction (to 190 from 479) occurred at 500 °C.

In the case of binary gas mixture, the He fluxes increased from 0.018 to 0.118 mol m$^{-2}$ s$^{-1}$, as the He feed concentration was raised from 30 to 100%. This increase was expected as the He flux increases as function of the driving force. However, it was noteworthy that for testing at 200 °C the He purity in the permeate stream reached 62% at 10% He feed concentration, and then increased to values >90% at 30% He feed concentration. Very high He purity values of 97% to 99% were measured at 500 °C. Although the He permeance and fluxes reduced after HT, the separation performance of the membrane remained almost the same as before HT. These results suggest HT exposure densified the membrane matrix, but has not broadened the overall pore size distribution, thus proving the hydrostability of the chosen cobalt oxide silica membranes.

He permeation followed a temperature activated transport mechanism for single gas and gas mixtures, both before and after HT. In the case of gas mixtures, the He permeance was constant at different feed concentrations and was not affected by CO$_2$ concentration in the feed side. Likewise, the $E_{act}$ for He permeance as a function of the feed concentration was constant for both single gas and gas mixture permeation. The He $E_{act}$ for He permeance was higher at after HT exposure, thus suggesting a tighter reduction of the overall pore sizes for He permeation.

Finally, the He/CO$_2$ permselectivity reduced from 158 (before HT) to 78 (after HT) at 200 °C, though the He purity remained very high (>90%) and similar for both cases for He feed concentration ≥30%. These results suggest that very high permselectivity values are not the best engineering parameters, whereas the separation of gas mixtures provides a more realistic assessment for designing unit operations for the separation of industrial gases.

**Acknowledgements**

The authors would like to acknowledge financial support provided by the Australian Government through its CRC programme to support this CO2CRC (Cooperative Research Centre for Greenhouse Gas Technologies) research project. L. Liu gratefully thanks the scholarship from the
University of Queensland and CO2CRC. The authors acknowledge the facilities, and the scientific and technical assistance, of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy and Microanalysis, The University of Queensland. The authors would like to thank Dr Julius Motuzas for the SEM analysis. S. Smart would like to acknowledge the support given by the Queensland Government in the Smart Futures Fellowship (ECR). D. K. Wang and J. C. Diniz da Costa gratefully thank the support given by the Australian Research Council via the Discovery Early Career Researcher Award (DE150101687) and Future Fellowship Program (FT130100405), respectively.

List of Acronyms

FTIR: Fourier transform infra-red spectroscopy
SEM: Scanning electron microscope
GC: Gas chromatography
FID: Flame ionization detector
TCD: Thermal conductivity detector
HT: Hydrothermal treatment
CVD: Chemical vapour deposition

E_{act}: Apparent activation energy

References


Graphical abstract.

**Highlights**

- Steam exposure to 25 mol% vapour at 550 °C for 100 h led to 12% surface area loss.
- He/CO₂ permselectivity reduced from 479 to 190 after steam exposure.
- Steam exposure reduced the He flow rate for single and gas mixture separation.
- The purity of He separation from gas mixture was not affected after steam exposure.
- Cobalt silica membranes delivered He purity up to 97% before and after steam.