Hydrothermal stability of cobalt silica membranes in a water gas shift membrane reactor

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ABSTRACT

Cobalt silica membranes were fabricated using sol–gel techniques for separation of H_2 in a membrane reactor set up for the low temperature (up to 300 °C) water gas shift (WGS) reaction. Single dry gas testing prior to reaction showed He/N_2 and H_2/CO_2 selectivities increasing from 75–400 to 45–160 as the temperature increased from 100 to 250 °C, respectively. During reaction the membrane delivered a H_2 permeation purity of 89–95% at high conversions, with the higher water ratio conversion providing superior membrane operational performance. Characterisation of bulk gels indicated that the cobalt silica was hydrophilic and exposure to steam at 200 °C resulted in the densification of the film matrix. The cobalt doping allowed for the membrane structural microporosity to be maintained as H_2 selectivity was not affected by steam exposure, though the flux decreased due to pore collapse of the film matrix. A total of 8 thermal cycle testing were carried out from room temperature to 300 °C, and the membrane displayed good hydrothermal stability, maintaining a high H_2 selectivity for over 200 h of operation.

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1. Introduction

Hydrogen is utilised in a number of industries today, including fertilisers, oil refining and petrochemical. Most importantly hydrogen has gained significant interest as a future clean energy carrier, with major advantages possible when used with new fuel cell technology. Hydrogen is primarily produced from fossil fuels, such as natural gas and coal through steam reforming/gasification and water gas shift reactions, and these hydrogen production reactions have thermodynamic limits of equilibrium. This limit can be enhanced through the removal of the H_2 reaction product, using H_2 selective membranes to potentially drive the reaction to completion. The application of membrane reactors (MR) to this type of yield enhancement reaction has been well documented [1–5], noting that the membranes' characteristics for H_2 permeance and selectivity over time is a vital consideration to the commercial feasibility of this technology [6].

Microporous silica membranes have found great potential for use in industrial applications, particularly when used in MR arrangements [5,7–8]. These have been shown to provide good permeation and selectivity for H_2 in a variety of temperatures, however

are known to suffer from poor hydrothermal stability [9–11]. This is a large problem as humid atmospheres are more often encountered in industrial applications, especially as steam is a common component in H_2 producing reactions (i.e. steam reformation and water gas shift (WGS)). The WGS (Eq. (1)) is an equilibrium limited, exothermic reaction with high conversion favoured at low temperatures.

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H = -41.2\, kJ\, mol^{-1} \qquad (1)$$
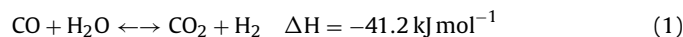
Typically, conventional WGS reactors use excess steam reactant to optimise the equilibrium conversion. However, in a MR this can also be achieved through H_2 removal, allowing excess steam to be minimised. This establishes an interesting balance to the system; excess steam enhances the catalyst efficiency while increasing conversion, but decreases the membrane's separation and can severely limit the membranes operating lifetime [12–13]. While a water to CO ratio of 1 represents the minimum amount of water necessary for potential complete conversion, excess water would still be used for industrial purposes. Therefore it is a requirement for membranes to provide greater hydrothermal stability for maintained selectivity and flux over their operational lifetime.

The major problem with silica-derived membranes is associated with silanol (Si–OH) groups as Iler [14] proposed that hydroxyl groups are the most active sites for water interaction. On the other hand, silanol groups are necessary for the precise tailoring of the

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microporous silica films [15–16]. Early work addressed this problem by heat treatment strategies, thus reducing surface hydroxyl groups [11,17]. Later work showed superior improvements by adding inorganic and organic precursors to the silica matrix [9,18–20]. For instance, the membrane surface gained a degree of hydrophobicity by using a methyl template covalently bonded to the silica, thus reducing the level of adsorbed water [9,21]. However, no work was carried out on the effect of prolonged steam exposure, at high temperature and pressure, on the membranes selectivity.

Giessler et al. [12] investigated the stability of silica membranes using non-covalently bonded short carbon chain surfactants (i.e. as templates) for the WGS reaction on a MR set up. This work compared the hydrostability of the templated silica against conventional silica membranes, noting that over time the templated silica membranes performed better, though initially gas separation was lower. This was attributed to the slightly pore widening effect of the surfactants on the silica micro-structure. Duke et al. [10,22] developed a method to improve hydrostability without decreasing initial selectivity. By carbonising the surfactant template in the silica matrix, it was found that selectivity improved over conventional silica membranes while maintaining high hydrothermal stability. This method differed from the hydrophobic membrane approach as hydrostability was due to structural stabilisation of the silica matrix by the carbonised surfactant, as the membrane proved to be hydrophilic.

Inorganic oxides such as TiO_2, ZrO_2, Al_2O_3, MgO, have also been used to improve the performance of membranes in steam [23–26]. The use of the metal dopants (i.e. NiO and CoO) in silica membranes has led to very high selectivities [27–28] even in the presence of steam [29–30] showing great promise for use in commercial membrane and membrane reactor units [31].

In this work, we investigate the hydrothermal stability of cobalt silica membranes in steam and temperature cycling. Cobalt silica tubular membranes were fabricated using sol–gel techniques and tested under hydrothermal conditions in a MR for the low temperature WGS reaction. Xerogel samples were exposed to steam in autoclaves and the structural changes were analysed using nitrogen and water adsorption. The cobalt silica membranes were tested for a range of water to CO feed ratios, and for temperatures between 150 and 300 °C. The stability and selectivity characteristics were examined by observing the gas permeation characteristics of the cobalt silica membrane before (i.e. dry gas testing) and during reaction (i.e. under steam exposure conditions).

2. Experimental

2.1. Material preparation

Commercial Noritaki alumina tubes (OD-11 mm, Length-120 mm) coated with a top γ-alumina layer were used as the membrane substrate. Cobalt silica sol was prepared through the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in ethanol and H_2O_2 with cobalt nitrate hexahydrate $(Co(NO_3)_26H_2O)$ as described elsewhere [29,31]. This process allowed for the incorporation of cobalt oxides into the silica gel which subsequently undergoes reduction resulting in metal cobalt embedded within the selective silica phase. A solution of 42.2 g TEOS in 600 g ethanol was added to a second solution of 51.8 g cobalt nitrate in 30% (w/w) aqueous H_2O_2 and vigorously stirred for 3 h in an ice-cooled bath. The tubular substrates were then dip-coated onto the outer tube shell. The tube was immersed lengthwise in a beaker of the stable sol using a controlled dipping and removal speed of 2 cm min^{-1} and an immersion time of 1 min. This allowed for a film formation without cracking or forming pin hole defects. The tubes were sequentially coated followed by calcination, with a total of six layers deposited on the tube substrate. Calcination was carried out for

each layer in air at 600 °C for 4 h at a ramp rate of 0.7 °C min^{-1}. Finally the membranes were calcined in H_2 at 500 °C for 15 h to reduce the cobalt oxide within the selective silica layer.

A commercial pelletised low temperature CuZnAl WGS catalyst was used for this work. The catalyst pellets were crushed using mortar and pestle and sieved to a particle size of 250–425 μm. Fused alumina (crushed and sieved to 250–425 μm particle size) was used as a catalyst dilutant to ensure an even distribution of catalyst along the membrane length.

2.2. Characterisation

Water vapour adsorption on silica and cobalt silica gels was characterised using a spring loaded gravimetric adsorption rig. Samples were prepared by degassing overnight under vacuum at 200 °C. Water uptake of the sample was then measured by the displacement of the quartz spring under varying H_2O partial pressures, introduced from an ambient temperature water reservoir and measured using a MKS Baraton type pressure transducer. Hydrothermal testing was conducted using an autoclave batch process. The xerogel bulk samples were placed in an autoclave with liquid water added to make up the steam gas volume composition (25% and 75%, v/v). The autoclaves were sealed gas tight and placed in a box furnace at 200 °C for a set time before being removed and quenched. Hydrothermally treated samples were dried at 50 °C overnight and subsequently degassed at 200 °C and tested for pore volume using N_2 adsorption Quantachrome NOVA. SEM was performed using a JEOL JSM-6400F scanning electron microscope. Membrane cross-sections were made conductive using platinum coating with an EIKO coating apparatus in high purity argon.

2.3. Membrane reactor

In the tubular MR arrangement used in this experiment, the catalyst with diluents were placed in the inner shell of the tube, while the cobalt silica membrane faced the permeate stream in the outer shell. The membrane tube had an effective permeation area of 27.5 cm^2 and a maximum reaction and gas separation length of 80 mm. The tube membrane with catalyst was placed inside a pressure vessel, and Kalrez o'rings were used to seal the membrane. The MR experimental apparatus is shown in Fig. 1. Pressure in the retentate line at 4 bar was controlled via a Swagelok back pressure valve and measured using an MKS Baraton pressure transducer. The permeate flux was maintained at 1 bar, and flow rates were measured using a bubble meter. Nitrogen was used as the sweep gas in the permeate stream for the MR work only, due to reduced H_2 partial pressure in the reaction chamber.

The catalyst was activated prior to experimentation following manufacturer's protocols at 250 °C with 20% H_2 and 20% H_2O in N_2 at 20 ml min^{-1} total flow. After activation, H_2 was switched off and the H_2O/CO reactant flow was fed to the reactor, with all gas flows controlled using high precision Cole Parmer rotameters. Water liquid flow into the MR was controlled by a Bronkhurst liquid mass flow controller, prior to injection into the evaporator. This allowed for a precise injection of water feed ratio into the MR. The temperature of the MR was maintained within a muffle furnace using a Eurotherm PID temperature controller. Dry gas samples were collected from both retentate and permeate streams, after the condenser and were tested in a Shimadzu GC-2014 using a Porapak Q column with TCD and FID detectors to determine gas concentrations. As the WGS is equimolar as per Eq. (1), the conversion of CO was calculated on the basis of the production of H_2 or CO_2. In addition and for comparison purposes, packed bed reactor (PBR) tests were conducted within the same reactor module with catalysts packed within a non-permeable tube of the same dimensions, thus maintaining the same reaction conditions.
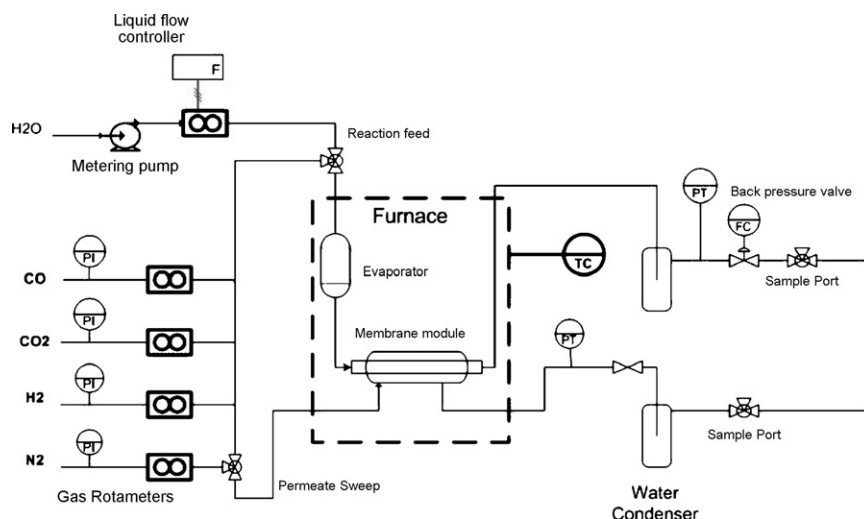
Fig. 1. Membrane reactor rig schematic.

In order to determine the membrane separation and permeation effect prior to the reaction conditions, the membranes were also tested for dry single (He, H_2, CO_2 and N_2) and H_2/CO_2 mixed gas permeation under non-reactive conditions using the same experimental apparatus shown in Fig. 1. These tests were carried out at 100–250 °C at 4 bar feed pressure. In this work the selectivity of single gas was calculated on the basis of the permeation ratio of the faster over the slow diffusing gas. Gas mixture permeance was calculated using the partial pressure difference across the tube, determined by measuring the concentration on the retentate and permeate side of the tube and normalising for the measured flux of each gas in the mixture.

3. Results

3.1. Characterisation

Fig. 2 shows an SEM photo of the cross-section of a cobalt silica membrane. The membrane has a γ-alumina intermediate layer to ensure a smooth defect free surface for coating of the selective layer. The thickness of the top layer, which is responsible for the molecular sieving property of the membrane, was approximately 0.25 μm with uniform coverage. With a total of 6 cobalt silica layers coated, the thickness of each layer was estimated at 43 nm.

Fig. 3 depicts the H_2O adsorption on pure silica and cobalt silica xerogel samples at different temperatures. At low H_2O partial pres-

sures (Po < 5 kPa) the uptake of water corresponds to bonding of the surface silanol (OH) groups with possible siloxane (Si—O—Si) bond breakage [22]. The comparable level of water adsorption between pure silica and cobalt silica samples indicated that the cobalt gels made in this work were hydrophilic instead of hydrophic. The water adsorption decreased with temperature to almost negligible coverage.

In order to examine the effect of steam on the pore structure, xerogel samples were subjected to 2 different levels of steam (25% and 75%) for varying lengths of time and analysed using N_2 adsorption. Fig. 4 shows that steam exposure resulted in the densification of the xerogel matrix. The high content water (correlating to a water ratio of 3:4 in reaction) showed the highest densification of 98% while 90% densification was achieved for the low water content (water ratio of 1:2). The water partial pressure has a large effect on silica degradation as the lower water concentration (25% steam test) gave lower densification with 10% higher pore volume than the higher water concentration. However, the majority of the densification occurred very quickly (0–24 h), with little change in pore volume for both water concentrations after this initial period of time. Fig. 5 shows the N_2 adsorption isotherms of the respective samples after 100 h of treatment in steam. The pure silica xerogel resulted in an increase in mesoporosity (type IV isotherm) after hydrothermal treatment, as the small pores collapsed and large pores opened up. The cobalt silica gel however, maintained
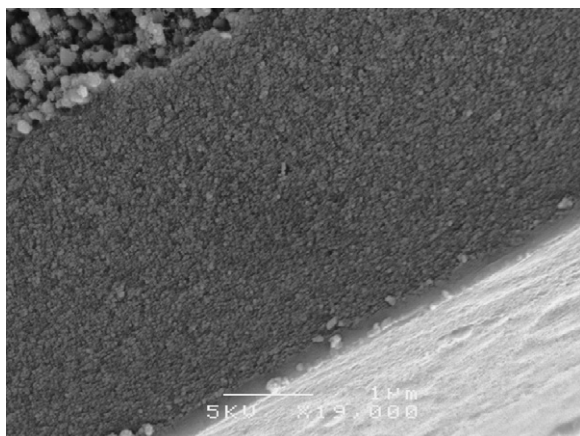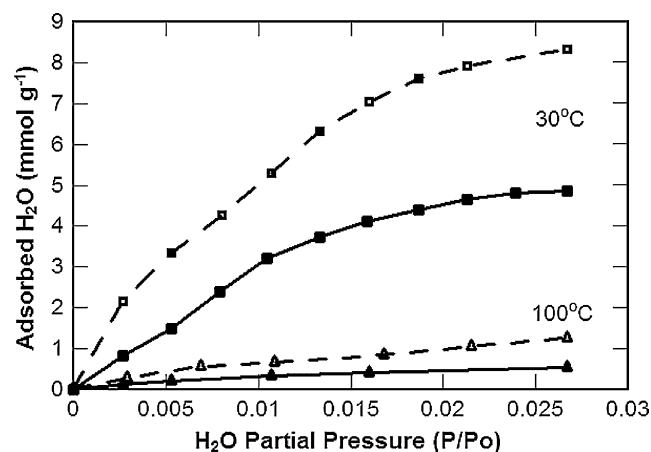

Fig. 2. Cross-section of Co silica membrane.

Fig. 3. H_2O adsorption of cobalt silica (closed symbols) and silica (open symbols) xerogels at 30 and 100 °C.
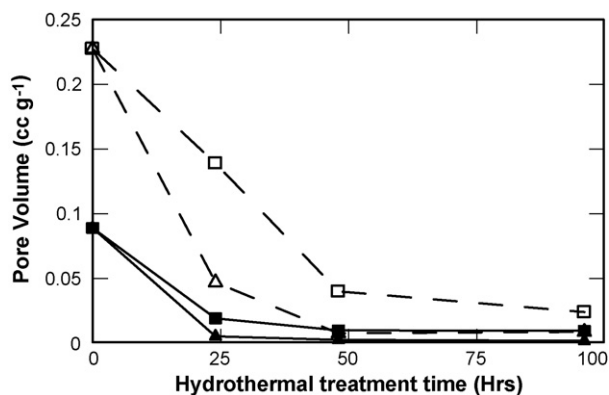
Fig. 4. Pore volume change due to exposure of steam to cobalt silica (open symbol) and pure silica (closed symbol) gel samples.

its microporous structure (type I isotherm) even after densification under hydrothermal treatment conditions, indicating that the cobalt played a vital role in stabilising the membrane's pore structure.

3.2. Permeation, selectivity and reaction

Dry gas permeance of the membranes to He, H_2, N_2 and CO_2 shown in Fig. 6(a) was carried out to determine the separation efficiency of the cobalt silica membrane prior to exposure to steam. The closed symbols show single gas permeation while the open symbols show mixed gas permeation for a 50/50 H_2/CO_2 feed binary mixture. The single gas transport through the membrane resulted in temperature dependency permeation as observed elsewhere [28–32] for cobalt silica membranes, with He and H_2 permeance increasing while N_2 and CO_2 permeation remained constant over the testing temperature range. As a result, the membrane selectivity increased from 75 to 400 (He/N_2) and 45 to 160 (H_2/CO_2) as depicted in Fig. 6(b).

The selectivity of H_2/CO_2 binary gas mixture significantly increased with temperature, from 2 at 100 °C to 50 at 250 °C as shown in Fig. 6b. These values are lower than those for single gas selectivities, though the trend is that both single gas and gas mixture selectivities will be very similar at temperatures in excess of 300 °C. This trend is clearly observed in Fig. 6(a), due to the positive temperature dependency of H_2 permeance, contrary to the CO_2 permeance. Fig. 7 shows that in a single pass the membrane processed a 50% H_2 mixed gas feed to 97% H_2 purity in the permeate stream
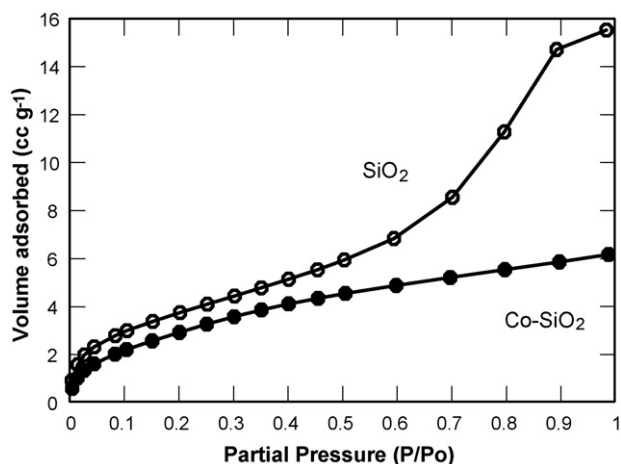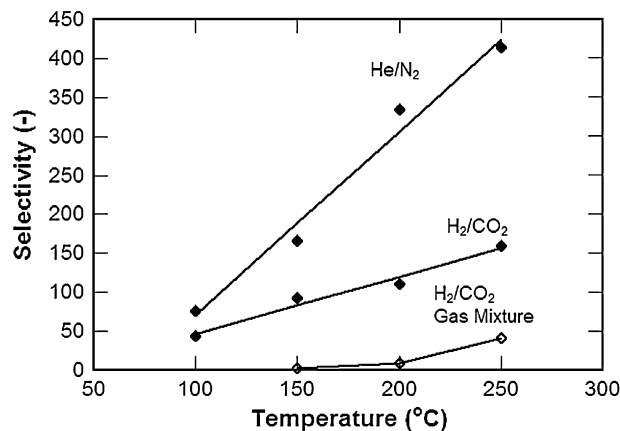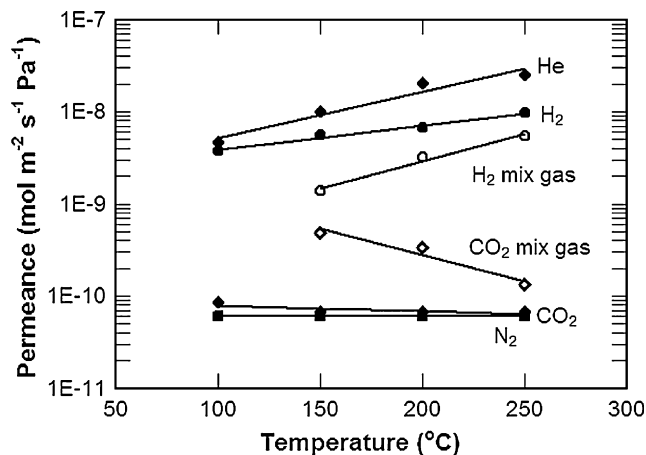

Fig. 6. Temperature dependency of (a) gas permeances (He, H_2, N_2, CO_2) and (b) membrane selectivity before reaction.

at 250 °C. This represents a single pass enhancement of H_2 concentration by 47%, with potential for even higher purity permeate at higher operating temperatures. It is also observed that the cobalt silica membranes showed significant temperature activation with the permeate H_2 concentration increasing 23% over the range of 150–250 °C.

Fig. 8 shows the MR conversion test with varying water contents, also including the PBR conversion for comparison purpose. These results clearly indicate the benefit of MR over PBR when the CO conversion is limited for equimolar feed water to CO ratio of 1:1, providing an extra 7% conversion at 300 °C. In addition, CO conversion increased with temperature, which is expected for the low
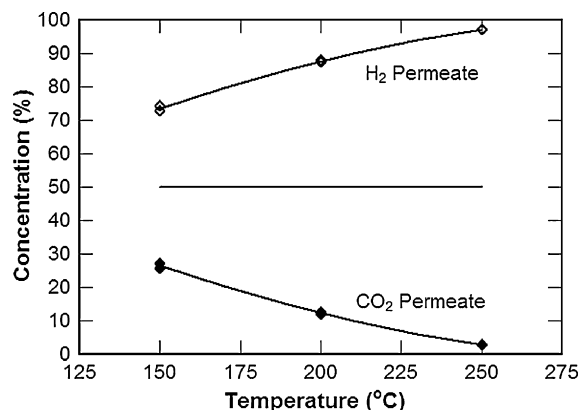

Fig. 5. N_2 adsorption isotherm of hydrothermally treated gels (100 h).
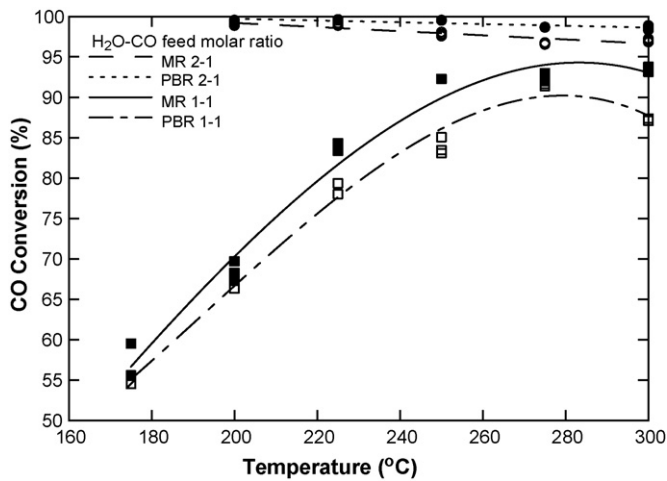

Fig. 7. Mixed gas separation of a 50% H_2/CO_2 feed gas.

Fig. 8. Membrane reactor conversion with increasing water content (Solid–Membrane Reactor, Dashed–Packed Bed Reactor).

Fig. 10. Operational H_2 selectivity of cobalt silica MR during reaction and temperature cycling (dotted line: H_2 permeate concentration, full line: MR temperature cycling).

temperature WGS reaction operating under low water to CO feed ratio. On the other hand, excess reactant or high feed water to CO ratio of 2:1 led both MR and PBR to reach similar conversions. In this case, the reaction went to almost full completion within the tested temperature range.

Fig. 9 shows the permeate concentrations (a) and the normalized gas permeance (b) delivered by the membrane during the MR
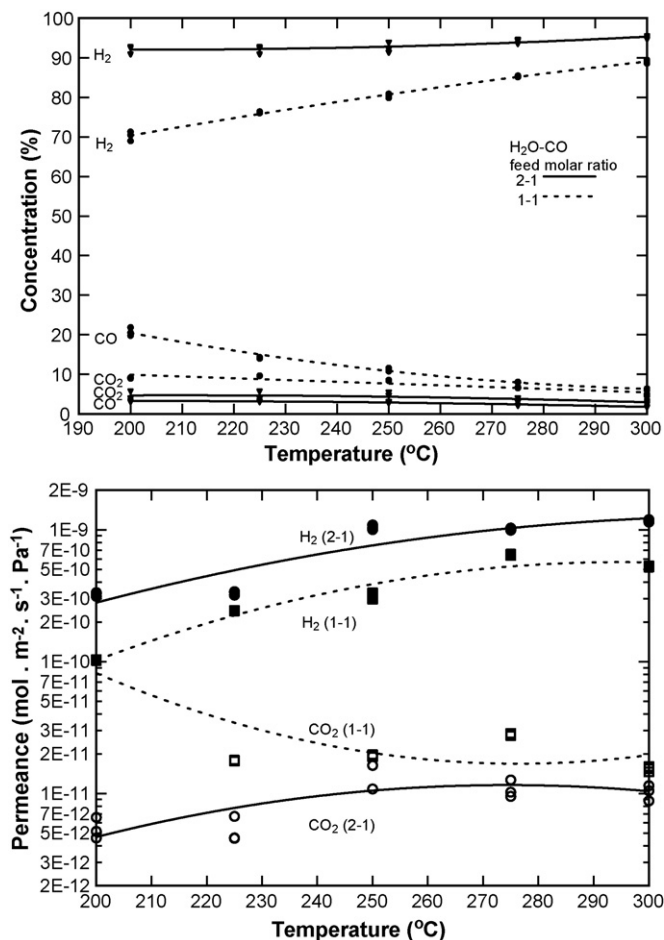

Fig. 9. (a) Permeate gas concentrations for varying H_2O ratios, and (b) permeance. (1:1 or 2:1 are the water to carbon dioxide feed molar ratios in the reaction).
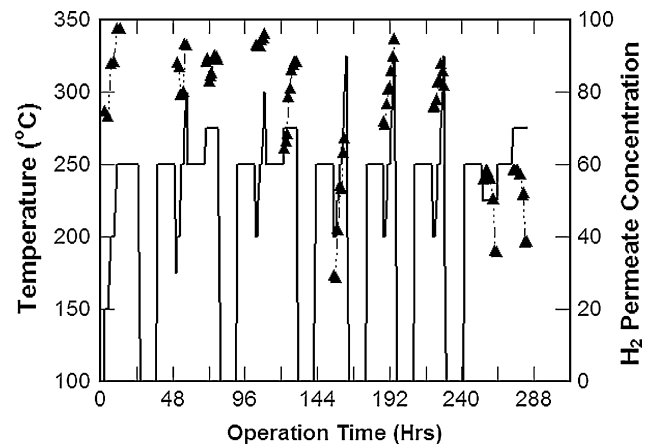
operation. At high temperatures the MR delivered high H_2 purity in the permeate stream for a single pass, with a maximum H_2 purity of 95% and 89% for r-2 and r-1 feed molar ratios, respectively. At the same time, the concentration of CO_2, CO and H_2O were greatly reduced to very low levels as the temperature increased to 300 °C. The separation of H_2 was considerably improved at the higher water ratio 2:1, with a 5–30% improvement in H_2 permeate concentration achieved over the equimolar water ratio 1:1. This difference in H_2 purity in the permeate stream is associate with the changes in reaction conditions from the feed water to CO molar ratio, in addition to changes for H_2 and CO_2 permeation. For instance, at 300 °C the H_2 permeance increased from 1.3×10^{-9} to 5×10^{-9} mol m^{-2} s^{-1} Pa^{-1} while the CO_2 permeance slightly decreased from 1.3×10^{-11} to 1.0×10^{-11} mol m^{-2} s^{-1} Pa^{-1}.

The MR was subjected to a long term temperature hydrothermal testing as shown in Fig. 10, with temperature cycling shown by the solid line and H_2 permeate concentration across the membrane shown by the dotted line. A total of eight heating and cooling cycles ranging from room temperature to 300 °C were carried out totalling 250 h of testing. For each cycle, increasing temperature resulted in high H_2 purity in the permeate stream. At about 150 h, the MR seal failed, but the membrane re-established its separation capability soon after the seals were replaced. At the 6th cycle (over 200 h), the H_2 purity slightly decreased again, thus suggesting seal failure. The seals were again replaced, but the membrane tube cracked during the 7th cycle. Hence, the membranes showed to be robust enough to withstand the hydrothermal cycling test, the limitation being the seals and the substrate mechanical failure.

4. Discussion

The sol gel method employed in this work produced high quality membranes with H_2 permeation of 1×10^{-8} and H_2/CO_2 selectivities as high as 160. The membranes complied with a temperature activated transport for H_2 and He while N_2 and CO_2 showed no activation energy. These results strongly suggest that a precise pore size tailoring with molecular sieving properties was achieved, as the temperature dependency permeance facilitated the transport of the small gas molecules (He and H_2) while hindering the diffusion of the large molecules (N_2 and CO_2). These results suggest that a high quality membrane was synthesised, showing no micro cracks or pin holes on the top cobalt silica layer, as observed by the SEM micrograph. However, the application of a H_2/CO_2 gas mixture indicated different results to the single gas permeation. As compared to H_2 single gas permeance at 250 °C, the H_2 permeance decreased

by 40% to 6.0×10^{-9} mol m^{-2} s^{-1} Pa^{-1} for a 50/50 H$_2$/CO$_2$ mixture, and by one order of magnitude for the WGS reaction at a water to CO molar ratio 2:1.

In the case of gas mixtures, the partial pressure (or concentration) of each gas across the membrane provided a competitive adsorption regime which effectively favoured the lower permeating gas (CO$_2$) at low temperature, thus reducing H$_2$ selectivity. In addition, pore blocking occurred due to adsorption of larger molecules (CO$_2$) on the membrane surface. Though a dynamic process, competitive adsorption added to the reduction of H$_2$ permeation and thus selectivity [32]. As adsorption decreased with temperature this blocking effect was reduced and gas mixture permeation approached the single gas permeation, as shown in Fig. 6(a). At high temperatures, adsorption of gases is generally negligible, thus favouring microporous mobility as evidenced by the high permeance of the small molecules (He and H$_2$).

The effect of gas mixture separation becomes a real issue for industrial applications as it is the case for MR. For the WGS reaction, the reactor needs to remove a significant volume of produced H$_2$ to overcome equilibrium limits. However the improvement in equilibrium is related to the reactant left unconverted. As shown in Fig. 8, for excess water ratios the equilibrium conversion was already above 95%, thus almost reaching full reaction conversion. In this case, a MR can only provide a maximum of 5% improvement over conventional PBR. In contrast to this, for equimolar feed water ratio the MR provided a considerable conversion advantage over the PBR. As the conversion reached the equilibrium limit (300 °C) the MR delivered a 7% conversion improvement over the PBR, while at lower temperatures improvements of 2–5% were observed. At 175–200 °C, no conversion improvement was realised as the catalyst kinetics were the limiting factor on conversion, thus the product separation had little effect on product yield. An equimolar feed water ratio (1:1) represented the minimum water content if full conversion of CO is desired. It is possible at this condition, with high conversion, to almost completely react out all water within the system. The advantage of this is twofold: (i) low water content reduces possible hydrothermal effects on the membrane and (ii) while reducing the need for expensive downstream condensation and recycling of excess water. By the same token, this has an opposite effect on the catalyst efficiency with higher water ratios favouring higher conversions. Nevertheless, there is a PBR conversion difference of 13% at 300 °C between equimolar and excess feed water ratios. In this case, the MR compensated for the lower conversion for equimolar feed water ratio (1:1), as the conversion was improved to only 3% below the PBR conversion for the excess feed water ratio (2:1).

Water also affected the membrane permeance as depicted in Fig. 9(b). There was a decrease in H$_2$ and CO$_2$ gas permeance after exposure to steam in the membrane reactor. The adsorption of water is at low coverage, in particular for temperatures in excess 100 °C as observed in Fig. 8. The reaction temperatures used in this work were in excess of 200 °C, thus in principle water adsorption effect on the transport of H$_2$ across the membrane could be considered as negligible. However, the water effect that was very pronounced was related to the densification of cobalt silica. After hydrothermal treatment (Fig. 3), the reduction of the pore volume occurred over relatively short times (0–24 h). Densification causes collapse of the cobalt silica network [29], thus resulting in the reduction of percolation or pore connectivity. In this MR work, the catalyst was activated in a wet gas stream. Therefore, these results strongly suggest that the membranes had already undergone densification before the reaction and gas permeation tests started. This point can be substantiated by the hydrogen permeation results, which indicates a permeation decrease of 70% after the membranes were exposed to 72 h of WGS reaction (Fig. 9b) from an initial dry gas condition Fig. 6b).

While permeance decreased with densification, the ability of the cobalt silica membranes to selectivity separate H$_2$ was not altered. Fig. 5 shows that the cobalt silica pores maintained a microporous structure after hydrothermal treatment, which compared very favourably to the undesired mesoporosity gained by pure silica. Therefore the densification process did not affect the microporous structure of the cobalt silica membrane. These results differed from conventional thinking on hydrothermal stability, as the cobalt retained the micro structural integrity and fidelity within the silica matrix for gas separation even after densification, contrary to conventional pure silica. Hence, cobalt plays a vital role in stabilising the membrane against hydrothermal degradation. As shown in Fig. 10, the cobalt silica matrix provided stable membrane operation for over 200 h with a stable 90–95% H$_2$ concentration in the permeate. As the WGS reaction in Eq. (1) leads to the production of one mole of CO$_2$ and H$_2$, this means that the concentration of H$_2$ in the reaction chamber is always below 50 vol%. Hence, to achieve 90–95% H$_2$ purity in the permeate stream, the cobalt silica membrane delivered at least a 45% increase in H$_2$ concentration over the reaction chamber in a single pass. As membrane selectivity was not affected by the initial water densification, the membrane operated effectively for a significant time. In this case the membrane selectivity only dropped after sealing issues and mechanical failure of the substrate. The robustness of the cobalt silica top selective layer for thermo cycling and steam exposure was substantiated by 8 thermal cycles over 200 h operation. Sealing problems and mechanical failure of the tube substrates are required to be overcome in order to operate the membrane stably in reaction for longer periods of time, providing a feasible operating lifetime of the MR system.

5. Conclusions

Cobalt silica membranes were synthesized using sol–gel techniques and tested for hydrothermal stability in a MR set up for the low temperature WGS reaction. The membranes dry gas selectivity showed temperature activation with He/N$_2$ selectivity increasing from 75 to 400 while H$_2$/CO$_2$ increased from 45 to 160 at 100 to 250 °C. The membrane showed good operational selectivity, providing a H$_2$ permeation purity of 90–95% at high conversions. While excess water in the reaction was shown to have a positive effect on conversion and H$_2$ separation, it was led to greater densification of the silica structure over time. The MR showed superior performance over conventional conversion at the lower water ratio (r-1), providing an increase in conversion of 7% at high temperatures (300 °C). The membrane delivered good hydrothermal stability, operating under harsh thermal and chemical conditions for over 200 h. This work highlighted the advantage of cobalt silica membranes when used in hydrothermal conditions in particular applications such as the water gas shift reaction.

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