

Purifying hydrogen with inorganic silica membranes at high temperatures

M. C. Duke, S. Gopalakrishnan, M. Abdel-jawad, M. Macrossan, J. C. Diniz da Costa*

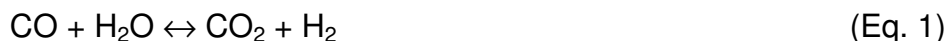
ARC Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane Qld 4072, Australia.

**also Project Leader, Centre for Low Emission Technology (cLET), PO Box 883, Kenmore, Qld 4069, Australia*

Abstract: Development of high quality membranes for industrial applications will lead to cost reductions over traditional separations processes. Silica membranes are a new technology for hydrogen separation that needs R&D specifically to applying them to industrial scales. Past work has shown a carbonised template silica membrane which offered hydrostability. This resulted in better stability under steam and high temperature conditions without compromising the permselectivity for small molecules. In this paper a hydrostable silica membrane was developed for hydrogen separation having a pore cut-off around 3Å. The carbon templates did not compromise the membrane's ability to selectively permeate hydrogen over other major gases coming from a synthesised coal gasifier gas mixture of CO, CO₂ and N₂. The selectivity of H₂ to N₂ was 26, whilst the hydrostable property of the carbonised template membrane was maintained. Computational fluid dynamics (CFD) can be used to develop membrane systems in tandem with these intrinsic improvements. CFD simulation studies were also conducted to gain better insight into the macroscopic flow parameters.

Introduction:

Membrane separation of gas mixtures has always considered as a more energy conservative separation method than the conventional separation processes. Hydrogen permselective silica membranes have attracted preference in the membrane gas separation applications due to the importance of hydrogen as a fuel and an industrial feedstock for the production of various chemicals [1]; especially to derive high purity hydrogen for fuel cell applications [2]. Membrane reactors, which combine separations and reactions in one system, benefit from such membranes which shift the reaction conversion limited by thermodynamic equilibrium to the product side, such as processing syngas in the water gas shift reaction [3]:



By removing H₂ from the reaction system shifts the reaction to the product side deriving increased CO conversion than a conventional catalytic reactor, producing more H₂ while also lowering the operating temperature. This reaction is significant in coal gasification processes which produce syngas, offering significant advantages to cost and size reduction of the operation.

Silica membranes are proven to be thermally and chemically stable offering high permeability and selectivity for hydrogen [4] with much work concentrating on their hydrogen separation property [5]. In silica membranes, the separation is mainly based on a sieving effect through small pores (~3Å) producing reasonably high combined values for flux and selectivity. Based on their mode of formation, silica membranes are mainly divided into sol-gel and chemical vapour deposition (CVD) membranes. Sol-gel membranes are prepared by coating an alkoxide precursor sol atop a porous substrate where the membrane quality is mainly determined by the sol chemistry. CVD membranes are prepared by the decomposition of gas

phase precursors inside the micropores of the substrate, thereby blocking the pore diameter to molecular dimensions. The CVD method results in membranes with lower permeance and higher selectivity. However, the main concern regarding the silica membranes is that they are unstable under hydrothermal conditions. A 50% reduction in H₂ permeance under lean hydrothermal conditions (50% H₂O + 50% N₂; atmospheric pressure) was displayed by silica-sol membranes at 500 °C [6]. This paper reports a novel concept in which carbon molecules were introduced into the system which position themselves between the silica molecules and act as supporting pillars, thus inhibiting the reorganization of silica molecules under hydrothermal conditions. Another key issue for membrane development is the engineering of separator modules. It is of interest to understand the resulting macroscopic flow parameters such as velocity and pressure distributions for tubes composed from this membrane. Computational fluid dynamics (CFD) simulation studies were conducted to gain insight into the macroscopic flow parameters.

Experimental

Asymmetric supported carbonised template molecular sieve silica (CTMSS) membranes were prepared over porous α -alumina substrates (99.8% purity; porosity = 30%; 0.5 -1.0 μ m) by sol-gel dip coating method as described elsewhere [7]. A γ -alumina layer forms the primary layer that brings down the pore size to 4nm, followed by an intermediate layer prepared by dipping a diluted acid catalysed sol-gel solution having methyl triethoxysilane (MTES, Aldrich) precursor leading to a silica with pore sizes in the region 0.35 – 0.45 nm [8]. The final silica layer was prepared by adding a short chained cationic surfactant hexyl triethyl ammonium bromide (Aldrich) to 0.125M of silica sol solution followed by the calcination under vacuum at 500 °C, to preserve the hydrophobic organic pyrolysis products. Samples were characterized using adsorption studies and SEM and further tested for gas permeation between 50–200 °C (2 atm drop). Permeation was measured using dead-end method to evaluate the performance of single gases involved in Reaction 1 (H₂, CO₂, CO and N₂).

CFD calculations were performed using the commercial code CFD-ACE (ESI Software). The code is a compressible finite volume flow solver. Full Navier Stokes solutions were implemented. Calorically perfect gas was used and viscosity was modelled using kinetic theory. The simulations were axisymmetric. Fixed pressure inflow and outlet conditions were prescribed. Isothermal non-catalytic walls were prescribed at temperatures of 100 °C. No chemical reactions were modelled for this set of simulations. Structured grids were used for this simple axisymmetric geometry and these were created using the commercial package CFD-GEOM (ESI Software) which is typically used in conjunction with CFD-ACE. Computational grids for the tubes were generated with clustering near the walls. Grid numbers were minimized as computational resources were limited. The solution was run on a single Pentium IV 3.4 GHz processor. Simulations typically required 16 hours each. The inner tube diameter was 6mm.

Results and discussion

CTMSS membrane permeation through a planar substrate is shown in Figure 1. In general, permeation increases with temperature for all gases except for CO₂. This trend exhibits the classical activated transport mechanism whereby diffusion occurs through micropores, which is in accordance with other high quality silica membranes as reported by other research groups[9, 10]. The CO₂ permeation was essentially unrelated to temperature and decreased with temperature as observed elsewhere [8, 11]. CO₂ has a high heat of adsorption, allowing for a more adsorption based transport. However as the pores become

smaller in high quality membranes, CO₂ transport is mostly restricted by the pore size and will also be activated [12]. In this result, no activation with temperature was observed due to two competing mechanisms. The separation mechanism in these tight pore spaces is by molecular sieving.

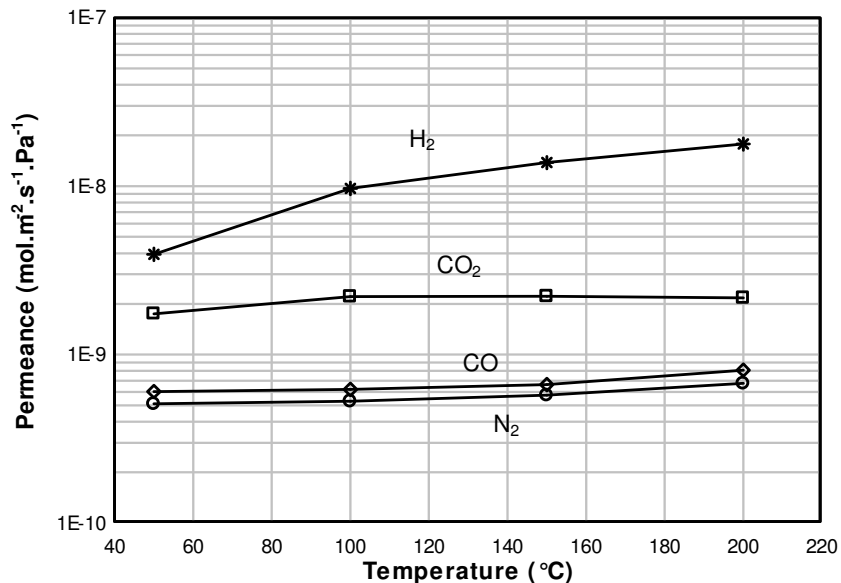


Figure 1: Permeation trend with temperature for planar CTMSS substrate at 2 bar pressure drop.

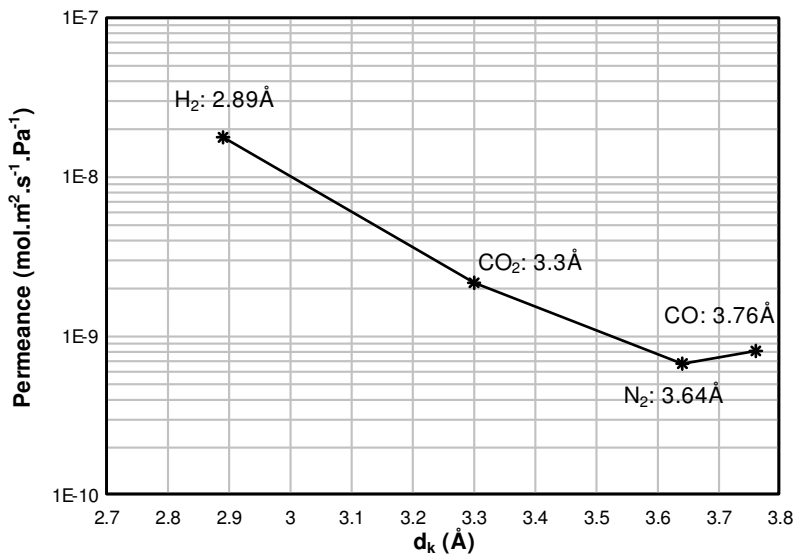


Figure 2: Permeation-molecule size cutoff curve for CTMSS membrane at 200 °C, 2 bar pressure drop.

The kinetic diameter of the molecule pertinent to molecular scale diffusion can be plotted against the experimentally measured permeation as shown in Figure 2. The smaller, more mobile H₂ molecule was more permeable than the larger CO₂, CO and N₂ molecules. As most of the permeation dropped between H₂ (2.89Å) and CO₂ (3.3Å), the average pore size is

around that of H_2 ($\sim 3\text{\AA}$). The permeation of N_2 was lower than CO contrary to the size relationship. Since the permeation of both these gases occurs in the tail of the silica pore size distribution, there is little size selective advantage available. Since CO is a more adsorbing gas than N_2 , its adsorptive property therefore favoured its transport through the membrane. The H_2/N_2 permselectivity of the membrane was 26, well above the ideal Knudsen value of 3.74, is another indicator of the molecular sieving behaviour. CVD membranes has however been reported to have far greater selectivity values >1000 [13,14].

Figure 3 shows the CFD simulation of the non-dimensionalised velocity field and the centre line non-dimensional pressure and velocity curves (bounded by the 2 crosses in the figure). In this simulation the feed side at the top of the figure has a prescribed velocity. Flow passes from the feed side to the permeate side and exits the permeate side at the far right of the permeate region. The figure shows that the boundary layer size is significant and extends the full radius of the tube and that the velocity profile in the tube axially is linear along the centre line of the flow. This is an indication that the model is scalable in length provided that the flow remains subsonic, but that scaling radially would be more effective. Associated with this is the parabolic pressure distribution dropping from the maximum stagnation pressure at the wall to the left of the figure.

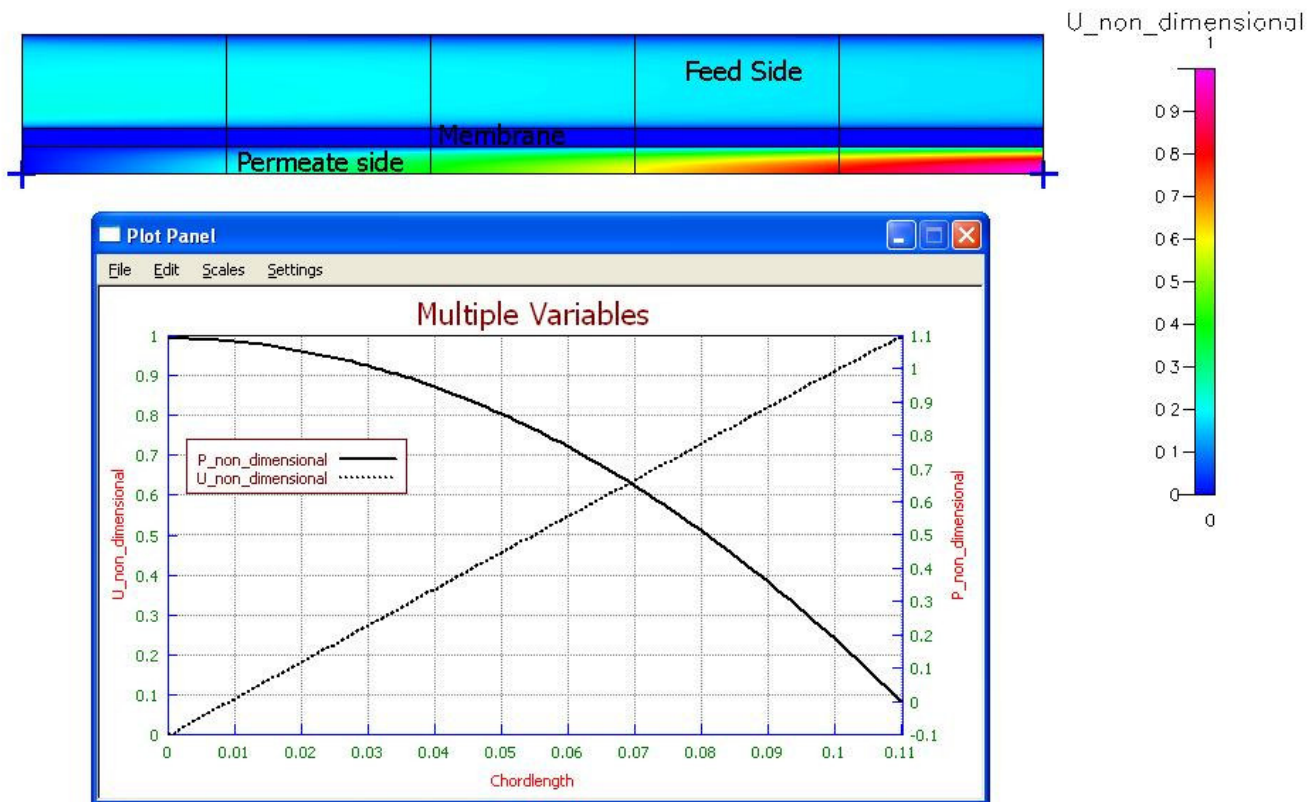


Figure 3 Nondimensional velocity field with centre line nondimensional pressure and velocity plots for flow inside a porous tube.

Conclusion

CTMSS membranes were prepared over asymmetric α -alumina substrates coated with γ -alumina layer. Except CO_2 , all other gases studied displayed activated transport through this membrane, indicating molecular sieving effect through this membrane. H_2/N_2

permselectivity of this membrane was 26 and has in past work been found to be quite stable under hydrothermal conditions. CFD studies revealed that the boundary layer size is quite significant and extends the full radius of the tube, and that the velocity profile in the tube axially is linear along the centre line of the flow.

Acknowledgement

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