Molecular Sieve Silica Membranes For H₂/CO Separation

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Efficient separation of fuel gas (H₂) from other gases in reformed gas mixtures is becoming increasingly important in the development of alternative energy systems. A highly efficient and new technology available for these separations is molecular sieve silica (MSS) membranes derived from tetraethyl-orthosilicate (TEOS). A permeation model is developed from an analogous electronic system and compared to transport theory to determine permeation, selectivity and apparent activation of energy based on experimental values. Experimental results for high quality membranes show single gas permselectivity peaking at 57 for H₂/CO at 150°C with a H₂ permeation of 5.14 x 10⁻⁸ mol.m⁻².s⁻¹.Pa⁻¹. Higher permeance was also achieved, but at the expense of selectivity. This is the case for low quality membranes with peak H₂ permeation at 1.78 x 10⁻⁷ mol.m⁻².s⁻¹.Pa⁻¹ at 22°C and H₂/CO permselectivity of 4.5. High quality membranes are characterised with positive apparent activation energy while the low quality membranes have negative values. The model had a good fit of r-squared of 0.99-1.00 using the experimental data.

INTRODUCTION

Membranes have been used for gas separation for quite some time but have seen major growth during the 90’s [1]. For many industrial applications involving gas streams, it is important that membranes resist high temperatures and corrosive environments. As in Table 1, organic membranes are not heat resistant at high temperatures while zeolite membranes have pore sizes too large to separate gases of small kinetic diameters. Out of the technologies listed in Table 1, many research groups [2-8] are developing metallic (palladium) and ceramic (silica based) membranes for H₂ fuel technology. Palladium membranes are expensive but have infinite H₂ selectivity. Hence, palladium membranes are ideal candidates for those applications in which a high purity of H₂ is required. On the other hand, Armor [10] summarised the main features of various membranes and pointed out the following impractical aspects of palladium membranes over silica membranes:

- Specific alloy compositions needed for specific reactions
- Permeability affected by CO, S and other impurities
- Phase changes of Pd cause deterioration of membrane
- High temperature regeneration required

Although silica based membranes have low H₂ permeation, de Vos and Verweij [3] have reported H₂ permeation of 200 x 10⁻⁸ mol.m⁻².s⁻¹.Pa⁻¹, an improvement of one to two orders of magnitude as compared to those results published in the first half of 90’s. As the flux of diffusion molecules is inversely proportional to the film thickness, they produced high quality thin silica films of 30nm in thickness in clean rooms. Silica membranes are reasonably cheap but tend to be hydrophilic because of the high concentration of hydroxyl groups in the silica matrix [2,11]. Table 2 presents H₂ permeances through various silica and palladium membranes reported in the literature [3,12,13]. Although palladium membranes show superior H₂ permeation, the permeation gap is now closing between both technologies. It should be noted that the value for MSS on alumina is for 200°C ΔP = 1bar while the Pd membrane permeances are for 400°C ΔP= 2bar.
Table 1: Some advantages and disadvantages of various types of membrane technologies (adapted from [1,9]).

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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</table>
| Organic                | • Industrial familiarity  
                        • Ease of manufacture and installation  
                        • Controllable pore size distribution, thickness and geometry | • Can’t withstand all solvents and strong acids or bases  
                        • Impractical for high temperature separations. Must generally be less than 200°C |
| Metal                  | • Well established technology                                               | • Expensive  
                        • Poor mechanical stability                                                   |
| Zeolite                | • Separations possible at higher temperatures  
                        • Control of pore sizes                                                    | • Pore sizes general too large for selective CO/H₂ separation               |
| Ceramic (non-silica based) | • Separation in more demanding environments possible  
                        | • Controllable pore size distribution, thickness and geometry  
                        | • Higher temperature resistance                                               | • Low fracture toughness  
                        | • Complicated processing steps  
                        | • Processing techniques not well suited for microporous materials            |
| Ceramic (silica based) | • Processing suitable for microporous materials  
                        • Controllable pore size distribution, thickness and geometry  
                        | • Low H₂ permeability  
                        • Sensitive to H₂O vapour (irreversibly densifies structure)               |

Table 2: H₂ permeance comparison between MSS and Pd membranes

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>H₂ permeance (x 10⁻⁸ mol. Pa⁻¹.m⁻².s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>7</td>
</tr>
<tr>
<td>MSS on alumina</td>
<td>200</td>
</tr>
<tr>
<td>Pd film on alumina</td>
<td>323</td>
</tr>
<tr>
<td>Pd/Ag composite on alumina</td>
<td>467</td>
</tr>
</tbody>
</table>

Many applications for gas separation have been found and are mainly concerned with the separation of H₂, CO₂, He, N₂ and O₂. However, the separation of H₂ and CO reported in the literature is very limited. It is therefore the objective of this paper to explore the separation of these gases, which have application in the alternative energy industry. In this work, MSS membranes are synthesized using an acid catalysis sol-gel process. The membranes are tested to check their performance in terms of H₂ and CO permeation, separation capability and apparent energy of activation. An analogous electronic RC circuit is developed to fit the experimental data.

**EXPERIMENTAL**

MSS membranes were synthesised according to processes described elsewhere [14]. An acid catalysed process was used to prepare silica films derived from sols containing TEOS, absolute ethanol (EtOH), water and nitric acid (1M). Two membranes sets were formed from this process, the first was a standard set based on the exact compositions found in literature. The second was a modified set produced by a reduced water composition. The films were cast on α-AlO₃ supports and calcined. The permeation of the membranes were tested in a dead-end transient mode system.

**PERMEATION MODELLING**

The key assumption for membrane permeation is that the governing mechanism of mass transport is micropore diffusion. Furthermore, adsorption of gases in silica-derived membranes generally comply with
Henry’s regime for temperatures in excess of room temperature. Hence, de Lange et al. [15] showed that the flux \( J \) (mol.m\(^{-2}\).s\(^{-1}\)) through microporous materials is activated transport and increases as a function of temperature:

\[
J \propto J_0 \exp \left( \frac{-E_{\text{act}}}{RT} \right)
\]

(1)

Where \( E_{\text{act}} \) is the apparent activation energy which is the energy required for the transport of the gas from the bulk gas phase on the retentate side to the permeate side. Barrer [16] proposed that this energy is made up of two components. The first is the activation energy within the pore, or the mobility energy \( (E_m) \), which is derived from an Ahrrenius relation. The second is the sorption energy in the micropores, which is equivalent to the isosteric heat of adsorption \( (Q_{st}) \):

\[
E_m = E_{\text{act}} - Q_{st}
\]

(2)

For the transient dead-end permeation test, the flux or permeation can be derived from a simple electronic RC circuit where a capacitor is charged through a resistor. The standard first order form for a charging capacitor under these conditions is given as:

\[
y(t) = B - (B - A) \exp \left( \frac{-t}{\tau} \right)
\]

(3)

where \( y(t) \) is the voltage across the capacitor at time \( t \), \( B \) is the voltage across the capacitor when \( t = \infty \) (maximum voltage), \( A \) is the voltage across the capacitor at \( t = 0 \) and \( \tau \) is the time constant. For a RC circuit, this is \( R \times C \) (resistance times capacitance).

The membrane is a barrier that opposes the flux of gases. Therefore, it can be seen as the resistor in the system and the dead-end volume the capacitor. The driving force for permeation of gases is pressure, which can be related to voltage. In this analogous RC circuit, voltage is synonymous with pressure. Resistance is equal to a resistive constant relative to the material \( (\rho) \), times length of the material in the direction of flow \( (l) \) over the area perpendicular to the flow \( (A) \). As permeation is inversely proportional to resistance, we will arrange the equation into:

\[
R = \frac{l}{P \times A}
\]

(4)

Where \( P \) is the permeation constant of the material.

Capacitance \( (C) \) is the number of coulombs per volt, or similarly, the number of moles \( (dn_{\text{VOL}}) \) per unit pressure \( (dP_{\text{VOL}}) \) across the volume. Using the ideal gas law, capacitance can be shown as:

\[
C = \frac{\text{dn}_{\text{VOL}}}{dP_{\text{VOL}}} = \frac{dP_{\text{VOL}}}{dP_{\text{VOL}}} \frac{V}{RT} = \frac{V}{RT}
\]

(5)

where \( V \) is the dead-end volume (constant), \( R \) is the ideal gas constant and \( T \) is the system temperature. Substituting Equations (4) and (5) into (3), and using the synonymous relations for voltage and pressure we get:

\[
P(t) = P_H - (P_H - P_0) \exp \left( \frac{-t}{\tau} \right)
\]

(6)

where:
\[ \tau = RC = \frac{l}{P ART} \]  

This rearranges to:

\[ \ln \left( \frac{P_{H} - P_0}{P_{H} - P_{(t)}} \right) = \frac{P ART}{l} V^{-1} \]

which is the equation for normalised pressure flux or permeation \((P/l)\) in transient dead end experiments.

**RESULTS AND DISCUSSION**

The results in Figure 1 show different transport mechanisms in the permeance of both H\(_2\) and CO with changing temperature. In Figure 1a, the permeation decreases with temperature indicating that the modified membrane complies with Knudsen or Poiseuille flows. On the other hand, Figure 1b shows that the standard membrane has activated transport as the permeation increases with temperature. These figures also give an indication of the quality of the membranes in terms of selectivity. The membrane with activated transport has a high H\(_2/\)CO selectivity in excess of one order of magnitude while the other membrane has a very low selectivity. Table 4 presents the apparent activation of energy results as a function of the pressure difference across the membrane. The standard membrane shows positive activation energy while the modified membrane has negative values for the permeation of H\(_2\) and CO.

![Figure 1: Permeance trend with temperature for a modified membrane (a) and standard membrane (b)](image)

**Table 3: Activation energies \((E_a)\) for high selective and low selective membrane in kJ/mol**

<table>
<thead>
<tr>
<th>Sol specifications</th>
<th>Pressure drop across membrane</th>
<th>3.0 bar</th>
<th>2.5 bar</th>
<th>2.0 bar</th>
<th>1.5 bar</th>
<th>1.0 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H(_2)</td>
<td>CO</td>
<td>H(_2)</td>
<td>CO</td>
<td>H(_2)</td>
</tr>
<tr>
<td>Standard</td>
<td></td>
<td>2.8</td>
<td>3.6</td>
<td>1.8</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Modified</td>
<td></td>
<td>-5.1</td>
<td>-6.4</td>
<td>-5.3</td>
<td>-6.3</td>
<td>-4.8</td>
</tr>
</tbody>
</table>

The modified membrane has negative activation energy and low H\(_2/\)CO selectivity, a characteristic of low quality membranes. This can be attributed to parallel fluxes in large micropores (5<dp<20Å) or mesopores or some pinhole defects. For average pore size in excess of 5Å, the transport mechanism will comply with Knudsen diffusion or Poiseuille flow resulting in membranes with low separation capabilities and relative high fluxes. Hence, the resistance of the top layer to the flux is small and the pore sizes are large enough to let all molecules to diffuse through the membrane.
On the other hand, the standard membrane has positive activation energy for permeation of H₂ and CO and selectivities ranged between 27 - 57. The standard membrane lets smaller molecules (H₂) to permeate to a larger quantity while the larger molecule (CO) has its permeation reduced by over an order of magnitude. As the difference in kinetic diameter for H₂ (dp=2.9 Å) and CO (dp=3.6 Å), these results indicate that the standard membrane has a narrow pore size distribution.

The difference in membrane performance can be directly attributed to their sol formulation. Membranes are complex systems and support structures and dust in the laboratory environment can cause microcracks and pin hole defects. Having said that, further studies using vibrational spectroscopy and N₂ adsorption technique are required to understand the functional groups and structural differences in the matrix of each sol-gel process. This is a subject of further work.

The transport model developed above and based on an analogous RC circuit relies on experimental data for the determination of permeation values and subsequent calculation of the apparent activation energy. This transport model generally produced an extremely good fitting for the permeation measurements with r-squared values in the region of 0.98-1.00. Whether the transport mechanism is activated or not, the model has a good fit for the transient dead-end experimental data.

**CONCLUSION**

The membrane prepared with the standard sol-gel process resulted in high quality membrane reflected by its positive apparent activation energy and H₂/CO selectivity of 27-57. The modified membrane prepared with a lower water content in a sol-gel process resulted in membrane of low quality (lower selectivity). This cannot entirely be attributed to the sol-gel process, but rather to uncontrollable parameters related to dust deposition on films and support defects. The transport model based on analogous RC circuit fit the experimental data very well for either activated transport or Knudsen or Poiseuille flows.

**REFERENCES**
