# Development of a Hydrogen Selective Ceramic Membrane and Its Application for the Conversion of Greenhouse Gases

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A new membrane with 100% selectivity to hydrogen was developed by chemical vapor deposition of a silica precursor on Vycor glass. Application of the modified membrane to the $CO_2$ reforming of $CH_4$ produced conversion levels above equilibrium.

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In recent years, considerable attention has been directed towards mitigating the adverse effects of greenhouse gases. Two of these, methane and carbon dioxide, can be converted to syngas (a mixture of CO + $H_2$) through the dry reforming reaction $CH_4 + CO_2 \rightleftharpoons 2CO + 2\ H_2$. However, the reversibility of the reaction limits the maximum conversion of the reactants. This limitation can been overcome by the selective removal of $H_2$ with membranes providing a means to effect separation during reaction. Many researchers[1-16] have focused on the development of $H_2$ selective membranes by the modification of ceramic supports using sol-gel, electroless plating, and chemical vapor deposition techniques. Sol-gel and electroless plating processes require great care in preparation, and suffer from lack of reproducibility. Some vapor deposition methods require large capital investment for low pressure equipment and again the use of strict preparation conditions. Also, most studies[1,2,8,9,14] have reported drastic loss of permeability (as high as 50% in the first 12 h) upon exposure to moisture. As will be apparent, these problems are largely overcome in this work.

The membranes developed in this investigation were based on a Vycor glass material (Corning Inc.) with a nominal pore size of about 4 nm. The membranes were used in a concentric shell and tube reactor (O.D. 16 and 10 mm and thickness 1 mm) with the inner tube incorporating a 4 cm porous section. Typically, a quantity of 0.5 g of catalyst (30/120 mesh) was mixed with quartz chips (30/120 mesh) to make up the 4 cm bed on the shell side. A 1 wt% $Rh/Al_2O_3$ catalyst was employed in this study. The feed mixture ($CH_4 = CO_2 = 24\ \mu mol\ s^{-1}$, $Ar = 27\ \mu mol\ s^{-1}$) was fed to the shell side and Ar (7 $\mu mol\ s^{-1}$) was flowed to the tube side. The outlet gases were analyzed using a GC (SRI 8610B). Permeability and reactivity tests are described elsewhere.[18]

Gas permeabilities for the individual components were determined by flowing 20 $\mu mol\ s^{-1}$ of the pure gas at 123 kPa in the shell side and measuring the tube side (at atmospheric pressure) flow rate using a sensitive bubble flow meter. Permeability coefficients ($P_i$) ($cm^3cm^{-2}s^{-1}$ Pa) were obtained from $P_i = Q_i/A\Delta P$, where $Q_i$ is the flow rate on the tube side ($cm^3s^{-1}$), A is the cross sectional area ($cm^2$) of the membrane available for diffusion, and $\Delta P$ is the pressure difference (Pa) between the shell and tube side. For the unmodified Vycor membrane the separation factors obtained were close to those predicted by the Knudsen equation with a temperature coefficient for diffusion of $T^{-0.56}$. The close correspondence to the theoretical results indicates that the mode of transport of hydrogen was molecular.

To overcome the limitations of the porous glass membrane, it was modified by a simple and repeatable method involving the thermal decomposition of a silica precursor. The reactor assembly with a 4 cm porous glass section (no catalyst) was heated to 873 K with Ar flow on both the shell and tube side. Tetraethyl orthosilicate (TEOS, Aldrich, 98%) was introduced through a bubbler (at 298 K) using Ar as the carrier gas. This stream was premixed with the Ar tube stream to make up a TEOS concentration of 0.03 mol $m^{-3}$. The TEOS-Ar stream was allowed to flow for 12 h after which the reactor was cooled in Ar. The decomposition of TEOS in inert streams is known to produce $SiO_2$ without carbon contamination.[17] Our procedure likely resulted in the deposition of a thin layer of silica which formed a barrier to the passage of molecules other than hydrogen. Figure 1 compares the hydrogen permeability of the original porous glass membrane with the modified membrane (termed Nanosil in this study). The permeability of the porous glass membrane declined with increasing temperature as discussed above. However, for the modified membrane, the permeability increased with temperature, indicating an activated diffusion process.

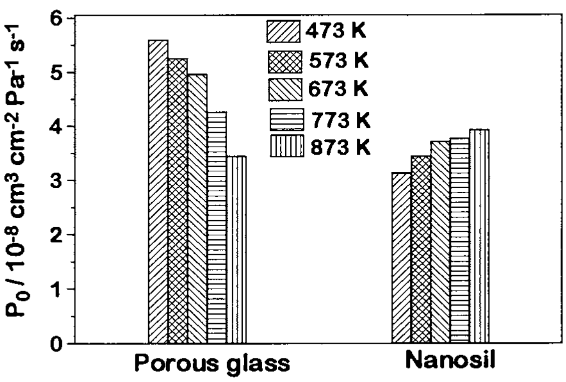

**Figure 1.** Hydrogen permeability coefficients.

Table 1 lists values of separation factors calculated from the ratios of the individual gas permeabilities. The modified membrane showed remarkable separation efficiency with $H_2/CH_4$, $H_2/CO$, and $H_2/CO_2$ separation factors as high as 27000, 87000, and 8200 respectively. Such high separation efficiencies were a result of virtually 100% pure hydrogen separation from the mixture and are limiting values based on the sensitivity of the gas chromatograph for the various gases. Contrary to reports on silica modified membranes by other researchers, this modified membrane did not suffer any significant loss in permeability on exposure to moisture at high temperatures (10% $H_2O$ in Ar at 873 K). Permeability decreased by 4% initially and was stable for > 100 h. The interesting observation is that despite the great

**Table 1.** Selectivity factors for the Nanosil membrane

| T (K) | $H_2/CH_4$ | $H_2/CO$ | $H_2/CO_2$ |
|---|---|---|---|
| 473 | 23000 | 72000 | 6700 |
| 573 | 24000 | 76000 | 7400 |
| 773 | 27000 | 85000 | 8100 |
| 873 | 27000 | 87000 | 8200 |
| 973 | 27000 | 82000 | 7300 |

difference in selectivity, the rate of hydrogen permeation for both the membranes were similar (Figure 1), about $4\times10^{-8}$ $cm^3cm^{-2}s^{-1}Pa^{-1}$ at 873 K. This is comparable to a literature value of $8\times10^{-8}$ $cm^3$ $cm^{-2}s^{-1}Pa^{-1}$ for hydrogen through another sample of Vycor glass.[9]

Isotope exchange experiments[18] indicated that hydrogen dissociatively adsorbs on the modified membrane consistent with a surface diffusion mechanism, and explaining the high selectivity. The dissociation of molecular hydrogen by highly dispersed silica to form surface OH groups has been reported at temperatures as low as 393 –473 K.[19]

The catalytic reforming of methane with carbon dioxide was studied using the Rh catalyst. The catalyst surface area for the fresh and used samples, determined by $N_2$ physisorption was 91 and 74 $m^2$ $g^{-1}$ respectively. The number of active sites for the fresh and used samples, obtained by titration with CO was 60 and 48 μmol $g^{-1}$ respectively. Figure 2 compares the conversion of methane in three different reactor systems, a standard packed bed, and two membrane configurations. The packed bed provided $CH_4$ conversions close to equilibrium levels as indicated by the horizontal dashed line in the bar chart. The reactor with the porous glass membrane gave rise to an improved methane conversion due to a shift in equilibrium by the removal of products from the reaction volume. However, since Knudsen diffusion was the dominant separation mechanism, some loss of reactants to the tube side provided only marginal improvements in conversion. The reactor with the modified porous glass (Nanosil) membrane however, provided even higher conversions of methane than that with the porous glass membrane. This could be attributed to the selective removal of only hydrogen without any loss of other species. In both cases with membranes, conversions above equilibrium were obtained.

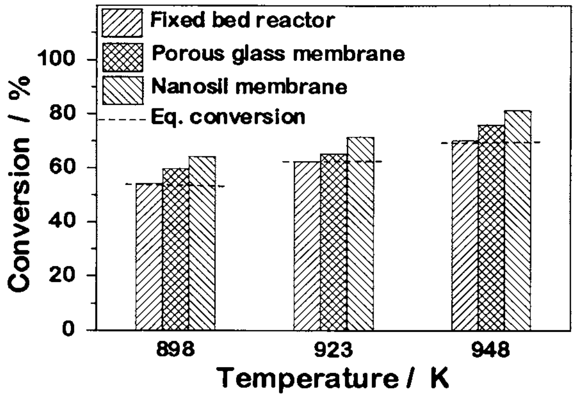

**Figure 2.** $CH_4$ conversion in the three configurations.

In summary, a new modified membrane that has high selectivity for hydrogen has been developed. Application of this membrane to shift equilibrium constraints for the methane reforming reaction provided improved conversions of reactants. The membrane was stable to hydrothermal stresses.

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