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Fundamental Studies for Sol-Gel Derived Gas-Separation Membranes

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Fundamental Studies for Sol-Gel Derived Gas-Separation Membranes

CONTRACT INFORMATION

Contract Number

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Period of Performance

July 1, 1994 to Sept. 30, 1995

Schedules and Milestones

FY 95 Program Schedule

S O N D J F M A M J J A S

pore size reduction of microporous silica membranes

deposition of titania modified silica membranes

single and two gas transport measurements
of silica and titania modified silica
membranes as a function of temperature

Stability analysis of the membranes

ABSTRACT

We prepared silica membranes using sol-gel techniques and explored the effects of post-deposition sintering, capillary stresses developed during drying, and surface derivatization of the membranes with titanium iso-propoxide. We

observed that both partial sintering of membranes and development of larger capillary stresses during membrane formation lead to consolidation of the membrane structure as evidenced by increased ideal separation factors, e.g. $\alpha_{CO_2/CH_4} > 250$ over the temperature range of 160 to 220 °C. Surface derivatization was also shown to be an effective

tool to reduce the membrane pore size in an angstrom by angstrom fashion, resulting in comparable separation factors. What's more, the altered pore surface chemistry of TiO₂ derivatized membranes may lead to improved stability and impart catalytic properties to the membrane surface.

OBJECTIVES

The primary objective of this study is to prepare supported inorganic membranes suitable for gas separation/gas purification applications in the processing of natural gas. The design criteria for such membranes include: high selectivity and high flux combined with excellent chemical, thermal and mechanical stability.

BACKGROUND INFORMATION

In the processing of natural gas, membranes have been proposed as replacements for more energy intensive purification processes for the removal of H₂O, CO₂, H₂S, and higher hydrocarbons from methane. Due to their inherent thermal, mechanical, and chemical stability, inorganic membranes are attractive for such applications. For practical gas separations, an inorganic membrane must combine high flux J with a high selectivity factor α . The membrane flux for Knudsen transport is proportional to the pore radius r_p divided by the film thickness h :

$$JK(\text{cm/s}) \propto \frac{\epsilon r_p}{\tau^* h} \sqrt{\frac{1}{RT}} \Delta P \quad (1)$$

where ϵ is the porosity, ΔP is the pressure drop across the membrane, and τ^* is the tortuosity. Membrane selectivity is related to pore size and pore size distribution. When the pore size is reduced below the mean free path of a gas molecule, gas transport occurs by Knudsen diffusion, and the separation factor for a binary gas mixture depends on the inverse ratio of the respective molecular weights. For example, the Knudsen selectivity factor α_K for a He/N₂ mixture is 2.65. Much greater separation factors (approaching ∞) are achieved when the pore size is

reduced sufficiently and the pore size distribution is sufficiently narrow to admit and exclude molecules on the basis of size, a mechanism referred to as molecular sieving. Thus to combine high flux with high selectivity it is necessary to prepare extremely thin, porous films with a narrow distribution of extremely small pores ($r_p \sim$ molecule size) and no cracks or other imperfections that would serve as large pores and diminish selectivity.

The traditional approach to the preparation of thin inorganic membranes with controlled pore sizes is to deposit (slip-cast and/or dip-coat) particulate sols with narrow particle size distributions on porous supports.^{1,2,3} If aggregation is avoided, the pore size of the membrane is controlled by the particle size of the sol - smaller particles yield smaller pores. An advantage of this approach is that the porosity of the membrane, which dictates its flux (Eq. 1) is independent of the particle size. So-called Knudsen membranes prepared from particulate sols have been successfully demonstrated by many research groups and are now commercially available.⁴ However due to problems with cracking⁵ and pore size coarsening at elevated temperatures,⁶ it has proven difficult to prepare molecular sieving membranes using this traditional approach.

This paper considers the use of polymeric silicate sols to prepare thin supported membranes, where the distinction between particles and polymers, made on the basis of NMR and SAXS measurements,⁶ is that the polymeric sols contain no regions of fully condensed silica. The idea of this alternative approach is to utilize the fractal properties of polymeric sols to favor polymer interpenetration during membrane deposition. This concept is qualitatively understood on the basis of the following relationship describing the mean number of intersections $M_{1,2}$ of two mass fractal objects of size R placed in the same region of space:⁷

$$M_{1,2} \propto R^{D1+D2-d} \quad (2)$$

where $D1$ and $D2$ are the respective mass fractal dimensions and d is the dimension of space, 3. From Equation 2, we see that if $D1 + D2 < 3$, the probability of intersection decreases indefinitely with R . This suggests that as D is reduced polymers should more easily interpenetrate as they are concentrated during slip-casting/dip-coating. If

compliant, such interpenetrating networks should collapse during drying to create pores of molecular dimensions appropriate for molecular sieving.

As reported in last year's Natural Gas R & D Contractors Review Meeting report, a practical advantage of this polymer approach with respect to the preparation of supported membranes is that the final pore size should be independent of the polymer size. Thus aging can be used to grow the polymers large enough to be trapped on the support surface during membrane deposition (avoiding the creation of thick often imperfect membranes by so-called "pore plugging" (see Figure 1)) without detrimentally increasing the pore size. Also a broadening of the polymer molecular weight distribution should not necessarily be manifested as a broadening of the pore size distribution.

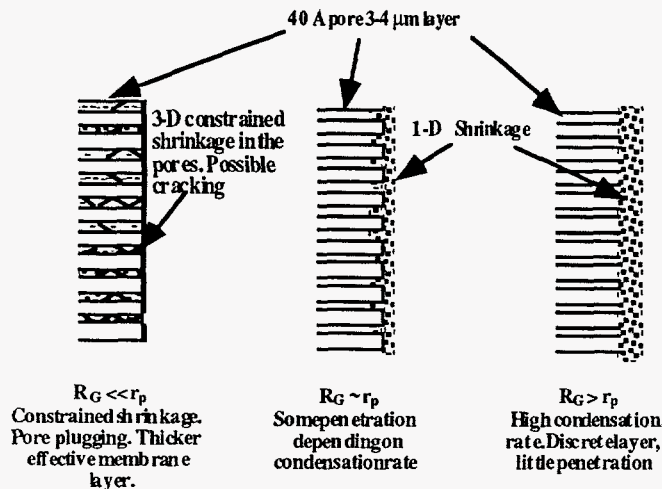


Figure 1. Schematic illustration of the effect of the relative sizes of polymer and support pores on membrane formation

A second advantage of this approach is that polymeric sols generally lead to the formation of amorphous membranes that do not exhibit grain growth or phase transformations during heating (as is often observed for particulate sols). Thus compared to particulate membranes, the pore dimensions of polymeric membranes should exhibit improved thermal stability.

A possible disadvantage of this approach is that small pore sizes are achieved at the expense of pore volume. This limitation may be overcome by the

use of organic molecules or ligands as pore templates.

Last year we reported on the effects of sol-aging conditions and condensation rates on the microstructure and transport behavior of supported silica membranes and demonstrated a template strategy as a means of independently controlling pore size and pore volume. This year we report on the effects of post-deposition sintering, capillary stress during membrane deposition and a derivatization technique designed to develop truly molecular sieving membranes.

Partial Sintering

Partial sintering of an amorphous silica membrane is expected to further collapse the structure at higher sintering temperatures, leading to a narrower pore size distribution and/or smaller pore sizes. The collapse of the structure is accompanied by a large reduction in porosity and a loss of hydroxyl coverage on the silica structure.⁶ The loss of hydroxyl coverage is also expected to make the structure slightly hydrophobic and thus more stable to attack by a humid environment.

Drying Stress

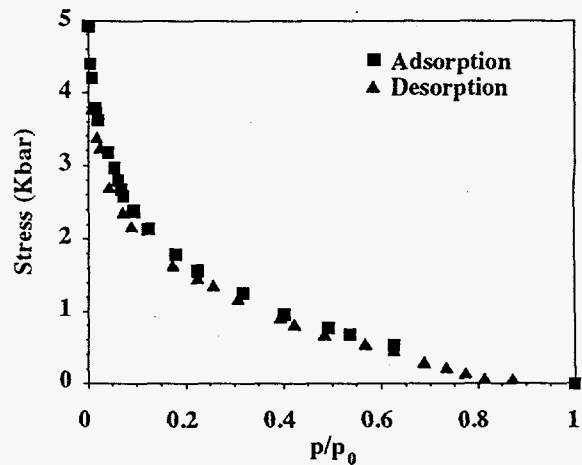


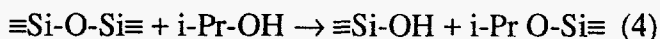
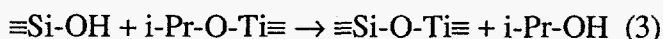
Figure 2. Stress generated in an 'as deposited' A2 film vs relative pressure

Recently Josh Samuel⁸ quantified the capillary stress development in microporous sol-gel derived

silica films. The results shown for an 'as deposited' A2 film in Figure 2 indicate that very large capillary stresses (of the order 5 kbar) are developed at low relative pressures of water in the overlying gas. These pressures are exerted on the solid phase during film deposition causing collapse of the gel network and as we report in the Results section a reduction in pore size and/or narrowing of the pore size distribution leading to enhanced separation factors.

Surface Derivatization

Reaction of a hydroxylated silica surface with a dilute solution of Ti (O i-Pr)₄ can lead to two possible reactions: 1) alcohol condensation between the surface hydroxyl and the alkoxy group (Equation 3) and 2) alcoholysis of the siloxane (Si-O-Si) bonds (Equation 4).



Titanium alkoxides are sufficiently electropositive to undergo reaction 3 even in the absence of a catalyst. Furthermore, the alcoholysis reaction is relatively slow.⁶ As a result, the reaction with Ti(O i-Pr)₄ will presumably lead to the deposition of a Si-O-Ti layer on the silica surface according to Reaction 3.⁹ Apart from the above two reactions some isopropoxide may be adsorbed on the hydrogen bonded surface hydroxyls associated with the silica membranes. These adsorbed molecules can subsequently condense during the calcination stage to form Si-O-Ti bonds similar to Reaction 3 with the hydrogen bonded intermediate step.

According to Srinivasan et. al.⁹ silica surfaces with a larger fraction of hydrogen bonded hydroxyls have a higher loading of titania due to the condensation of adsorbed precursor. The hydrogen bonded surface hydroxyls were found to be the preferred adsorption sites for the precursor as per infrared spectroscopy.

This titania layer has the potential to improve the separation properties and the hydrothermal stability of the membrane.¹⁰ The titania membrane also imparts catalytic properties to the membrane, or alternatively, this membrane can be used as a

high surface area support for other catalysts such as vanadia.⁹ These modified membranes are very good candidates for membrane reactor applications.

PROJECT DESCRIPTION/EXPERIMENTAL DETAILS

Preparation of Coating Solutions

The silica sols were prepared in a two step process referred to as A2**.¹¹ In the first step an A2** stock solution was prepared with TEOS:EtOH:H₂O:HCl ratio of 1:3.8:1.1:5 X 10⁻⁵. and refluxed for 90 min. at 60 °C. Prior to the second step of sol formation, the stock solution was maintained in a freezer at ~ -30 °C. In the second step additional water and acid was added at room temperature, resulting in final molar ratios of TEOS:EtOH:H₂O:HCl of 1.0:3.8:5.1:0.004. The sol was shaken for 15 minutes using a wrist action shaker and aged in a 50 °C oven to determine the gel time. The coating sol was prepared by diluting the A2** sol aged for $t/t_{\text{gel}} = 0.24$ ($t_{\text{gel}} = 99$ hours), with twice the volume of 200 proof ethanol soon after removal from the oven. The coating sols are stable for over 2 months when stored at -30 °C.

The titania modification solution for the silica membranes was prepared by mixing 5 vol. % Ti (O i-Pr)₄ in tetrahydrofuran (THF). Hexane and toluene are used for removal of excess precursor after the titania modification step. The Ti (O i-Pr)₄, THF, hexane and toluene must be freshly distilled to remove any trace amounts of water as the precursor is highly susceptible to hydrolysis.

Membrane Deposition

Membranes were deposited on commercially available Membralox[®] supports (supplied by U. S. Filter in 25 cm lengths). Supports were cut into 5 cm sections, using a diamond wafering saw. Each uncoated support was pre-calcined to 400 °C or 550 °C depending on the final membrane calcination temperature.

Before coating, the supports were cleaned with CO₂ snow using a SNOGUN[™] cleaner. The silica membranes were deposited using a Compumotor[™]

linear translation stage in a glove box, which was continuously backfilled with dry N₂ from a liquid N₂ dewar to maintain a clean and dry environment. Purging time of the dry box was used to control the relative pressure of water. The support was dip-coated at a constant immersion and removal rate of 20 cm/min. The support was held immersed in the sol for 100 seconds prior to removal. After dip-coating the membrane was allowed to dry for 15 minutes in the glove box before calcination in air to 400 °C or 550 °C for 3 hours with a heating and cooling rate of 1 °C/min. After calcination the membranes were always stored in air at 150 °C.

Titania modification was performed on A2** membranes calcined to 550 °C. For the modification experiments the dry box was maintained at < 10 ppm of water. The water content in the box is checked with a TiCl₄ solution by opening the bottle periodically while the box is being purged with dry nitrogen. The chamber has less than 10 ppm water when the TiCl₄ solution no longer fumes when opened. At this stage, the container of the modification solution is opened and the membrane is lowered into the solution. The membrane is allowed to react with the solution for five minutes and then withdrawn. The reaction is followed by repeated hexane and toluene washing.

The membrane was subsequently removed from the dry box and calcined at 400 °C for 3 hours using heating and cooling rates of 1 °C/min.

Characterization

Membranes. The membranes were characterized using a manual or an automated single gas permeability measurement system. The automated system is capable of measuring the permeance of six different gases in succession at various temperatures and pressures. The system is set-up to measure the membrane transport properties over the temperature range 25-220 °C and pressure range of 12 to 92 psia. The series of gases used in the permeability experiments was He, H₂, N₂, C₃H₆, CO₂, CH₄, and SF₆. In case the permeance was below the accurate detection range of the mass flow controllers (MFCs) connected to the system, the flow data was collected by running the system in a semi-automated mode in which gas flux was measured manually with bubble meters.

Adsorption. To obtain the adsorption measurements on bulk silica and modified samples, freshly gelled silica sols were dried in an explosion proof oven at 50 °C. The gel was allowed to dry for approximately 1 day and subsequently calcined to 400 or 550 °C for 3 hours with a heating and cooling rate of 1 °C/min. The calcined xerogels thus obtained were used for N₂ adsorption measurements at 77 K. The bulk gels were modified with titania following the same procedure outlined earlier.

The adsorption data was collected over the relative pressure range of 10⁻⁶ to 1 using a Micromeritics ASAP 2000.

Ellipsometry. Companion coatings to supported membranes were prepared on dense <100> single crystal silicon wafers for ellipsometry analysis. A Gaertner® model L116C ellipsometer, with a He-Ne laser light source, was used to derive the thickness and refractive indices of the silica films. The film porosity was calculated using the Lorentz-Lorenz model⁵ (equation 5) assuming a skeletal refractive index of 1.46 for silica,

$$V_s = \frac{(n_f^2 - 1)(n_s^2 + 2)}{(n_f^2 + 2)(n_s^2 - 1)} \quad (5)$$

where n_f is the film refractive index, V_s is the volume fraction solids, and n_s is the refractive index of the solid skeleton.

RESULTS

Effect of sintering

Sintering was studied as means of reducing pore size and narrowing pore size distribution for bulk, thin film and membrane specimens. Figure 3 plots the adsorption isotherms for bulk A2** xerogels calcined to two different temperatures under similar conditions. The isotherms clearly indicate a sharp decrease in the surface area and volume % porosity for the 550 °C sample compared to the 400 °C sample. The sharper isotherm for the A2** sample calcined to 550 °C also indicates the loss of the larger pores,

consistent with a narrower pore size distribution. Similar results were observed in case of thin A2** films deposited on dense silicon wafers as summarized in Table 1. We see that the film thickness as well as the volume % porosity is reduced with increasing calcination temperature indicative of a more consolidated structure.

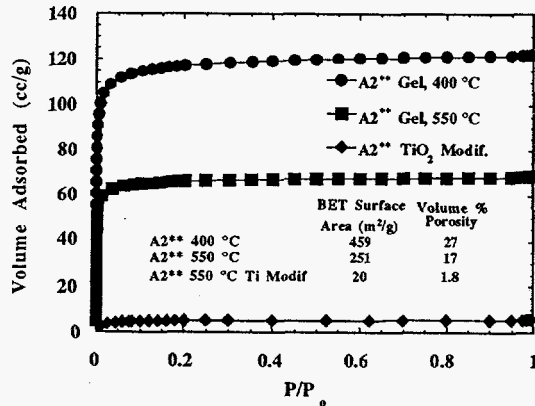


Figure 3. Surface area and porosity comparison, pure silica A2** and modified A2** Gels

Table 1. Film Thickness and Porosity comparison of single coated A2** films Sintered at Different Temperatures

Film Sintering Temperature (°C)	Thickness (Å)	Refractive Index	% Porosity
400	1550	1.375	16.0
550	1300	1.410	9.5

Table 2. Permeability Results on A2** Membranes Sintered at Different Temperatures

	He Perm.	He/N ₂	He/CO ₂	He/CH ₄	He/SF ₆	CO ₂ /CH ₄
Ideal Knudsen	-	2.65	3.31	2.0	6.0	0.6
Single layer membrane, calc. 400 °C	0.0085	2.0	2.4	1.6	4.0	0.66
Double layer membrane, calc. 400 °C	0.0021	6.9	0.74	2.6	11.8	3.5
Single layer membrane, calc. 550 °C	0.0028	9.0	4.4	6.8	16.8	1.6

Single or double layer membranes were prepared using the A2** sol composition and calcined to 400 °C or 550 °C. Table 2 summarizes the permeability results obtained at 25 °C. We can clearly see that the second A2** coating calcined to 400 °C leads to a four fold loss in He permeance accompanied by an increase in gas selectivities above the ideal Knudsen values for the various gas pairs. The second coating presumably acts as a healing layer for the first membrane coating and leads to blockage of the defects or larger pores in the first coating. Instead if a single coating of the A2** sol is calcined to 550 °C we obtain ideal separation factors larger than for the double-layer A2** membrane calcined to 400 °C along with higher permeance.

These observations lead to the following conclusions: 1) Partial sintering is effective in reducing pore size and/or narrowing PSD resulting in greater selectivity and lower flux. 2) Partial sintering enables the achievement of molecular sieving using a single membrane layer, obviating the need of a second layer and resulting in greater flux than observed for double layer membranes.

Effect of Drying Chamber Humidity

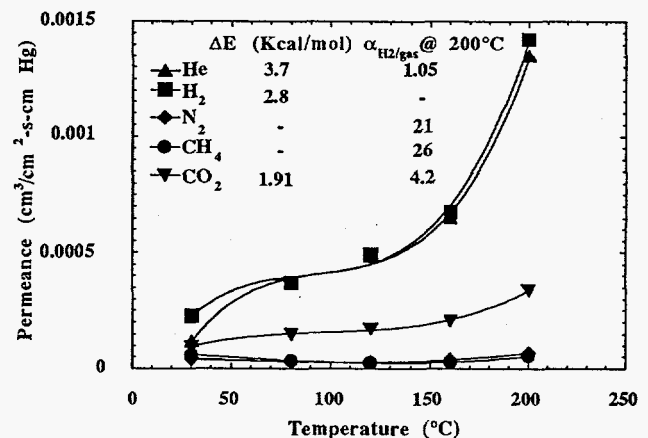


Figure 4. Permeability vs temperature, A2** membrane deposited in drying chamber with > 10 ppm water

Figure 4 plots the typical permeance of the various gases through an A2** membrane calcined to 550 °C versus measurement temperature over the

temperature range, 30 to 220 °C. This membrane was prepared in the dry box with a short purge time causing > 10 ppm of water in the box. The average pressure across the membrane for all the data points is 52 psia with a pressure drop of 80 psi. Ideal separation factors determined at 200 °C are indicated on the plot along with the apparent activation energies for transport. The large activation energies for He and H₂ indicate a very narrow pore size distribution for the membrane. The high separation factors are also an indication of a narrow PSD and suggest that the membrane has a very small fraction of pores larger than the size of a methane molecule. If we can further reduce the pore size and narrow the pore size distribution we expect to achieve membranes that exhibit perfect molecular sieving behavior.

We have discussed earlier that, one of the ways to collapse the silica structure, is by increasing the capillary stress at the time of membrane formation. We have also discussed in Figure 2 that the stress can be increased by reducing the drying chamber humidity.

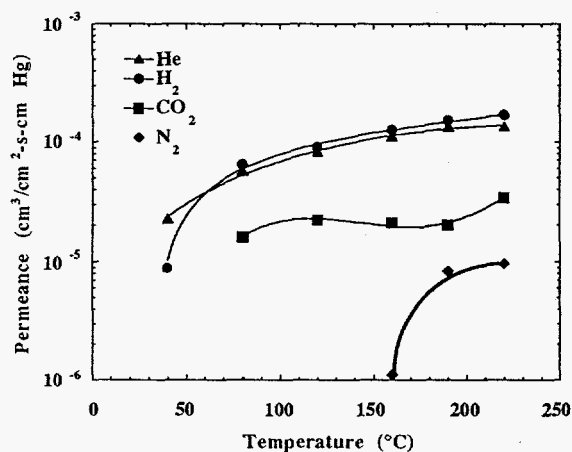


Figure 5. Permeability vs temperature, A2** membrane deposited in drying chamber with < 10 ppm water

Figure 5 and 6 plot the permeance and selectivity results for an A2** membrane prepared when the water content in the coating chamber was reduced below 10 ppm before membrane deposition. The two plots indicate some very significant results. We see that there is no CH₄ flux through the membrane over the complete

temperature range. There is no N₂ flux through the membrane below 180 °C and no CO₂ flux below 80 °C. The flow of these gases was much below the minimum detection limit of the instruments (< ~ 10⁻⁷ cm³/cm²-s-cm Hg). Thus we can easily separate various sets of gases by operating the membrane at selected temperatures and achieve almost perfect selectivity. An order of magnitude

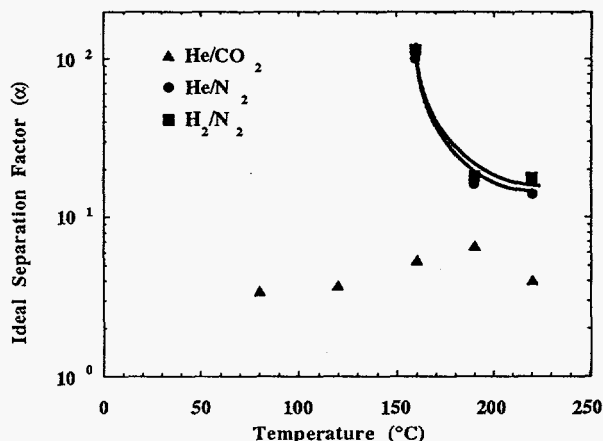


Figure 6. Ideal separation factor vs temperature, A2** membrane deposited in drying chamber with < 10 ppm water

increase in N₂ permeance between 160 and 190 °C indicates that the activation energy for transport is very large over this temperature range. A similar result is seen for the case of H₂ over the temperature range, 40 to 80 °C.

We have therefore been able to prepare membranes in a one step process which have true molecular sieving properties.

A comparison of He flux through this membrane at 40 °C (2×10^{-5} cm³/cm²-s-cm Hg) with the baseline He flux through vitreous silica at 27 °C (7×10^{-9} cm³/cm²-s-cm Hg) indicates that the flux through our membrane is about 4 orders of magnitude greater than the flux through dense silica. This comparison indicates that the fluxes that we are measuring for our membranes must be due to the presence of well defined molecular-sized pores.

Titania Modified Silica Membranes

The comparison of the N_2 adsorption isotherms of an A2** bulk gel and an A2** bulk gel modified with TiO_2 in Figure 3 indicates that the TiO_2 modification step causes a greater reduction in porosity than partial sintering.

Figure 7 shows permeance versus temperature for an A2** membrane deposited at >10 ppm water and modified twice with TiO_2 . For this membrane we have completely excluded CH_4 and N_2 over the temperature range 30 - 220 °C. CO_2 flux is not detectable below 180 °C, and H_2 flux is not detectable below 160 °C.

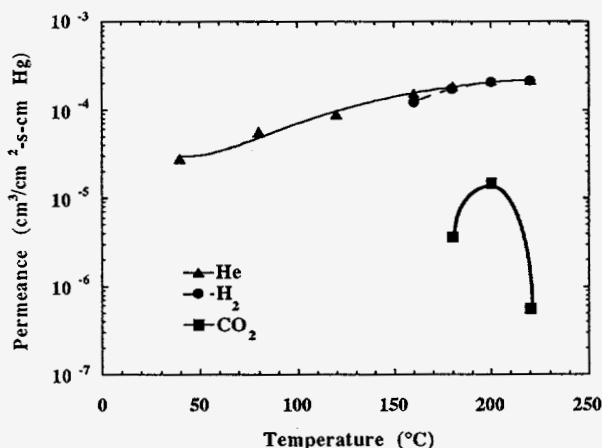


Figure 7. Permeability vs temperature, titania modified A2** membrane, with two TiO_2 modifications

A closer comparison of this membrane with the membrane in Figure 5 indicates that He permeance through the two membranes over the complete temperature range are comparable. The difference is in the flux of the other gases. The titania modified membrane seems to have a smaller number of large pores (we observe a larger N_2 permeance through the pure silica membrane). The activation energies of the gases through these membranes are similar to the activation energies for most zeolites and carbon molecular sieves with pore diameters of the order of 4 to 5 Å.

SUMMARY/FUTURE WORK

Improvements to the membrane deposition process have led to significant increases in membrane performance this year. Through reduction of the relative pressure of water used in the membrane deposition and drying ambient, we have increased the drying stress exerted on the gel network leading to a reduction in pore size and/or a narrowing of the pore size distribution of the resulting membranes. This is evident from the improvements noted in the performance of single-layer membranes processed to 550 °C ($\alpha_{He/N_2} > 250$ below 160 °C compared to 9.0 (last year) and $\alpha_{CO_2/CH_4} > 250$ over the temperature range 80-220 °C compared to $\alpha_{CO_2/CH_4} = 1.54$ (last year) with He permeance $2 \times 10^{-5} \text{ cm}^3/\text{cm}^2\text{-s-cm Hg}$ at 40 °C). We have also demonstrated a surface derivatization technique whereby a hydroxylated silica membrane is reacted with a monomeric titanium alkoxide to reduce the pore size and modify the pore surface chemistry of a thin region of the membrane surface. This approach has resulted in $\alpha_{CO_2/CH_4} > 250$ above 160 °C with He permeance = $3 \times 10^{-5} \text{ cm}^3/\text{cm}^2\text{-s-cm Hg}$ at 40 °C.

The stability of the membranes presented in this paper are currently being studied. The titania modified membranes seem to be a better candidate for membrane application due to the known instability of sol-gel derived ultramicroporous silica structures.

In future we will continue working with the strategies presented in this paper to further optimize the conditions for membrane deposition and improve the permeance of the faster permeating gases.

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