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Use of Silica Sols in Inorganic Molecular Sieving Membranes

Rakesh Sehgal[1], J. C. Huling[2] and C. J. Brinker[1]
[1]Advanced Matls. Laboratory, 1001 University Blvd. SE, Albuquerque, NM 87106, USA. [2]Los Alamos National Lab., MS E546, Los Alamos, NM 87545, USA.

Abstract

*Polymeric silica sols, were deposited on commercial γ-alumina supports to prepare gas separation membranes. Optimization of the sol fractal dimension and radius of gyration and minimization of condensation rate led to formation of a discrete film with pores of molecular dimensions. Two coatings of this sol (A2**) led to a membrane with ideal separation factor of 7 for helium versus nitrogen after calcination to 400 °C (helium permeance 0.002* cm^3/cm^2*-s-cm Hg). Partial sintering of these membranes resulted in a further reduction in pore size or narrowing of pore size distribution as evidenced by larger separation factors e.g. 9 for helium versus nitrogen (helium permeance 0.0028* cm^3/cm^2*-s-cm Hg) with only one A2** coating. Single gas measurements also showed high ideal separation factors for helium versus methane, propylene, sulfur hexafluoride and carbon dioxide. The deposited A2** membrane was reacted with titanium isopropoxide (*$Ti(O\ i\text{-}Pr)_4$*) to improve both its thermal and chemical stability and modify its pore size. This reaction led to an increase in the membrane selectivity to >300 for He versus* N_2 *below 120 °C, and* CO_2 *versus* CH_4*, when measured below 200 °C. A2** was also used as a host matrix for preparing imogolite composite membranes that showed molecular sieving behavior.*

Introduction

The traditional approach for preparation of supported inorganic membranes is by deposition of particulate sols. Membranes prepared using this approach have high flux values, but thus far can only achieve Knudsen separation characterized by rather

modest separation factors (e.g., α_{He/N_2}=2.65). Attempts to further reduce the pore sizes to achieve molecular sieving have led to problems like cracking, grain growth, and phase transformations at relatively low temperatures. These problems provoked interest in deposition of inorganic polymeric membranes such as silica,[1,2,3] which when thin (<0.2 μm) do not crack and which, due to their amorphous nature, do not suffer grain growth or phase transitions. If complete collapse of the structure is avoided the amorphous structure will have well defined "ultramicropores" to support gas transport, leading to higher fluxes than those achievable by organic membranes.

We have deposited polymeric silica membranes on commercially available alumina supports (U.S. Filter single channel supports with 40 Å pore diameter) by a sol-gel process that combines the features of slip-casting and dip-coating. The sol system is optimized using two variables, aging time and catalyst concentration. Aging time controls the size of the polymer and fractal dimension, and consequently influences the interpenetration of polymer clusters during deposition.[4] Catalyst concentration controls the rate of condensation reactions, that influences both the interpenetration of clusters and the collapse of the polymer network during the final stages of drying.

To evaluate the effect of continuing polymerization during membrane deposition by dip-coating, we previously examined a series of silica sols in which the condensation rate was varied by the concentration of catalyst. We found that minimization of condensation rate allows a greater collapse of the gel network during drying, promoting smaller pore sizes.[4] Aging time was optimized such that the average polymer size is of the order of the average support pore size, leading to the formation of a discrete membrane layer on the support surface. The present study addresses modification of the pore size and pore surface chemistry by partial sintering or alkoxide derivatization. We also consider using polymeric sols to prepare microporous composite membranes.

Partial sintering of an amorphous gel is expected to narrow the pore size distribution while reducing both the volume fraction porosity and the hydroxyl coverage. Adsorption of a partial monolayer of a metal alkoxide is expected to reduce the pore size and volume fraction porosity and alter the surface chemistry according to the choice of metal. Both treatments could lead to improvements in selectivity and thermal/chemical stability.

Polymeric silica coatings can also be utilized as a host matrix in which to embed structurally microporous materials. The matrix serves to "caulk" gaps between the crystalline inclusions avoiding the need for sintering or intergrowth to achieve defect-free layers. We have used imogolite, a hydrated aluminosilicate mineral with a tubular structure, for such coatings. Imogolite tubules have an internal diameter (ID) of 8-10 Å and an outer diameter (OD) of 25 Å. Synthetic imogolite tubules are approximately 1 μm in length.

The total gas flux through a microporous membrane is due to contributions from Knudsen diffusion, surface diffusion and micropore diffusion.[5] Knudsen diffusion is based on a rarefied gas assumption where the separation of two gases is proportional to the inverse square root of the gas molecular weight and temperature. Surface transport is due to the interaction between the membrane pore surface and the gas molecule. Surface transport usually increases the gas flow rate more than the expected Knudsen flow, and it usually decreases with an increase in temperature. Micropore diffusion results from activated transport of a gas molecule at the pore mouth and inside a pore due to surface interactions. Micropore diffusion usually increases with increasing temperature. The net effect of the three transport modes can lead to a net positive or negative "activation energy" for gas transport.

Experimental

Reagents

A polymeric silica sol previously referred to as A2** was prepared from tetraethoxysilane (TEOS) using a two step process[4] with final molar ratios TEOS:EtOH:H_2O:HCl = 1:3.8:5.1:0.0042. The A2** sol when allowed to age at 50 °C, gels in approximately 99 hours (t_{gel}). The sol was aged for $t/t_{gel} = 0.24$ at 50 °C, and diluted 1:2 with ethanol by volume to get the coating solution. The coating solution was very stable when stored at -30 °C. The A2** coating was always applied at room temperature. A mixture of 1 volume of freshly distilled Ti(O i-Pr)$_4$ in 19 volumes of freshly distilled THF, was used for surface derivatization of previously prepared A2** membranes. Freshly distilled hexane and toluene were used to wash off the excess Ti(O i-Pr)$_4$ from the membrane before drying. A 0.1 wt. % dispersion of imogolite in water was prepared as discussed elsewhere.[6]

Procedure

For ease of handling and characterization, commercial Membralox® supports (supplied by U. S. Filter in 25 cm lengths), were cut into 5 cm sections, using a diamond wafering saw. Each uncoated support was pre-calcined to 400 °C or 550 °C according to the final heat treatment of the silica membrane to be deposited.

The supports were characterized in a single gas permeability measurement set-up for helium, nitrogen, methane, carbon dioxide, propylene and sulfur hexafluoride gases with kinetic diameters of 2.65, 3.64, 3.8, 3.3, 4.5 and 5.5 Å respectively. This step is used to test the supports for the presence of cracks or pin holes. Before coating, the supports were cleaned using a CO_2 SNOGUN™ cleaner. The silica membranes were deposited using a Compumotor™ linear translation stage in a glove box, which was continuously backfilled with N_2 to maintain a relatively clean environment (<100 particles/ft^3). 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 dry box, before calcination in air to 400 °C or 550 °C for 3 hours with a heating and cooling rate of 1 °C/min. The membranes were always stored in air at 150 °C.

The titania coating was prepared under N_2 atmosphere, inside a dry box with less than 5 ppm concentration of water and O_2 and water. The process used for surface derivatization of silica membranes is proprietary information and can not be discussed here.

For the composite membranes, 110 cm^3 of the imogolite solution was pressure-filtered through the support to capture the imogolite crystals on the 40Å γ-alumina layer. The imogolite structure is unstable over ~270 °C, thus the membrane was calcined to 250 °C for 3 hours with a heating and cooling rate of 1 °C/min. After the calcination step excess imogolite separated from the support surface in the shape of a tubular shell. The membrane was characterized using the single gas measurement technique prior to application of two coatings of A2** sol according to the dip-coating process discussed above. Maximum calcination temperature was limited to 250 °C.

Characterization

Companion coatings to supported membranes were prepared on dense <100> single crystal silicon wafers and on pieces of the tubular alumina support for ellipsometry and TEM analysis, respectively. A Gaertner® model L116C ellipsometer, with a He-Ne laser light source, was used for the ellipsometry measurements to derive the thickness and refractive indices of the silica films. The film porosity was calculated using the Lorentz-Lorenz model[7] (Equation 1) assuming a skeletal refractive index of 1.46 for silica,

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

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.

TEM was performed to determine thickness, uniformity, presence of defects, and morphology of the membrane layer. The samples on porous supports were mounted on fused silica cylinders such that the membrane layer was adjacent to the fused silica surface. These samples were then sectioned using a diamond wafering saw, ground and polished to a thickness of about 1 µm, and ion milled to a thickness of several hundred angstroms. TEM was performed on a Philips model CM-30 300 KV analytical instrument equipped with a LINK EDS analyzer.

Single gas permeabilities of the support and the deposited membranes were measured using a home-built automated permeability measurement system. The system supports six different gases at a time and also controls a Lindberg model 51794 box furnace with a communications package as a part of the program. The automated system allows permeability measurements at the user specified flow and temperature conditions for all six gases without interruption. For the experiments described below the pressure range was 0-90 psi across the membrane, and the temperature range was room temperature to 200 °C. Viton was used as the gasket material to seal the membrane ends for permeability measurements.

N_2 adsorption isotherms for A2** bulk gels after drying and calcination to various temperatures were acquired at 77 K, using a Micromeritics ASAP 2000 micropore analyzer. Isotherms were measured over a relative pressure range of 10^{-7} - 0.995 to determine the microporosity, pore volume, and surface area of the samples.

Results and Discussions

The optimization of two-step acid-catalyzed silica sols to minimize the condensation rate,[4] and to prepare a sol with a radius of gyration on the order of the support pore size was previously described.[8] However membranes prepared from single coatings of this A2** sol, when calcined to 400 °C, usually did not show separation factors exceeding ideal Knudsen values. A second A2** coating calcined to 400 °C was necessary to consistently achieve molecular sieving behavior, as evidenced by larger than ideal Knudsen separation factors for He versus N_2 (table 1).

Table 1: Comparison of permeance (cm^3/cm^2-s-cm Hg) and gas separation factors ($\alpha_{1/2}$= Flux of gas 1/Flux of gas 2) at 25 °C for membranes sintered at 400 °C or 550 °C

	He Permeance	α for He/N_2	α for He/CH_4	α for He/CO_2	α for He/C_3H_6	α for He/SF_6
Ideal Knudsen separation factors	-	2.65	2.0	3.31	3.24	6.0
1 layer A2** membrane calcined at 400 °C	0.00850	2.0	1.8	2.4	1.6	4.0
2 layers A2** membrane calcined at 400 °C	0.00208	6.9	2.6	0.74	4.7	11.8
1 layer A2** membrane calcined at 550 °C	0.00280	9.0	5.2	4.4	6.8	16.8

Cross-sectional TEM results[4] showed that the first coating of A2** sol leads to the formation of a discrete silica membrane layer. The function of the second layer was proposed to be as a healing layer for any large pores/defects created in the first layer (which presumably prevented achievement of molecular sieving characteristics).[4]

Rather than apply a second coating we have now employed partial sintering at 550 °C as a means of narrowing the pore size distribution and reducing the size of larger pores and defects. Table 2 compares film thickness and refractive index values of "companion" silica films deposited on dense silicon supports and heated to 400 or 550 °C. Clearly, both the film thickness and film porosity decrease as the calcination temperature increases from 400 °C to 550 °C. This behavior is due to the partial sintering of the silica film at higher temperatures.[7]

Table 2: Effect of calcination on the thickness and porosity of a single layer silica film on a silicon substrate.

Calcination temperature	Film thickness (Å)	Refr. Index	porosity %
400 °C	1550	1.375	16.0
550 °C	1300	1.410	9.5

The corresponding nitrogen isotherms of bulk A2** silica gels after calcination to 400 °C or 550 °C are plotted in Figure 1. The sharp type I isotherms indicate that the silica gels are highly microporous. The bulk gels show a large reduction in surface area and volume fraction porosity after heating to 550 °C, indicating that calcination leads to a consolidation of the structure, consistent with the ellipsometry results obtained for films. Adsorption measurements on an A2 thin film deposited on a SAW device indicated that the film is non-porous to N_2. This discrepancy is attributed to the smaller pore size of films (compared to bulk samples) and the slow kinetics of N_2 adsorption at 77 K.[3,8]

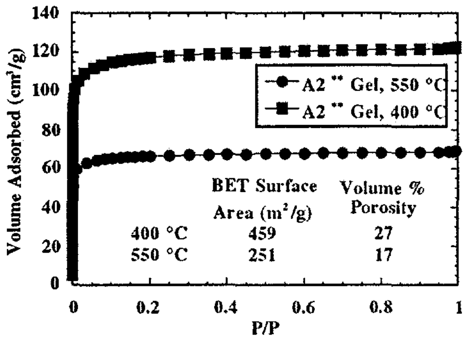

Figure 1: N_2 adsorption isotherms for A2 gels calcined to 400 °C and 550 °C.**

The single gas permeability results at 25 °C for a membrane coated with A2** sol and calcined to 550 °C are also presented in Table 1. A comparison of the permeance and separation factors of the two membranes with a single A2** coating, lead to the following conclusions: 1) Calcination of a silica membrane leads to sintering and densification, with concomitant loss of membrane permeance. 2) Sintering is accompanied by a reduction in the number of larger pores and perhaps in the average pore size of the membrane, as shown by an increase in separation factors.

Seven different membranes with the A2** sol were prepared using two different sol preparations. Consistently high separation factors were obtained in each case, after calcination to 550 °C. Figure 2 plots the permeance results for one such membrane as a function of measurement temperature. In the temperature range of 30 - 200°C, the activation energies (in Kcal/mol) calculated for the various gases from an Arrhenius plot are He 1.33, CO_2 0.08, N_2 -0.19, CH_4 -0.52, and C_3H_6 -1.26. The ideal separation factor (single gas separation factor) for He vs N_2 increases from 4 to

10, and that for He vs C_3H_6 increases from 1.5 to 8 over the temperature range. These results appear to contradict the results for zeolites[9] where the activation energies increase with increasing size of the gas molecule. The decreasing activation energies with increasing molecule size may be linked to a pore size distribution in the silica membranes, in contrast to a discrete pore size for zeolites. As discussed earlier in the introduction section, negative values for activation energies are due to the contributions from surface transport and Knudsen diffusion. The negative activation energy for surface diffusion is due to a loss of surface coverage at higher temperature. Based on the observed trends with temperature, the membrane can be used at different temperatures to get different separations and fluxes. We are in the process of constructing a system that will allow gas permeability measurements to be performed at temperatures higher than 200 °C.

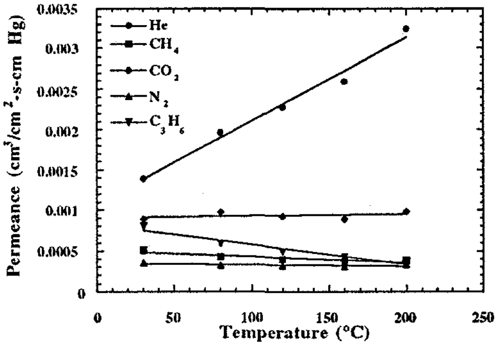

Figure 2: Single gas permeability results for a membrane with one coating of A2 sol and calcination to 550 °C.**

A second coating of A2** sol on a membrane precalcined to 550 °C, did not have an effect on the permeation and separation properties of the membrane. The apparent inert behavior of the membrane to A2** sol may be due to a much lower surface hydroxyl concentration of the membrane, allowing fewer reaction sites.

Titanium Alkoxide Derivatization

One means of simultaneously reducing pore size and altering pore surface chemistry is to react the pore surfaces with a metal alkoxide. Reaction of a hydroxylated silica surface with a solution of $Ti(O\ i\text{-}Pr)_4$ can lead to two possible reactions: 1) alcohol condensation between the surface hydroxyl and the alkoxy group (equation 2) and 2) alcoholysis of the siloxane (Si-O-Si) bonds (equation 3) (obviously silanols created by reaction 3 could subsequently participate in reaction 2).

$$\equiv\text{Si-OH} + \text{i-Pr-O-Ti}\equiv \rightarrow \equiv\text{Si-O-Ti}\equiv + \text{i-Pr-OH} \qquad (2)$$

$$\equiv\text{Si-O-Si}\equiv + \text{i-Pr-OH} \rightarrow \equiv\text{Si-OH} + \text{i-Pr-O-Si}\equiv \qquad (3)$$

Titanium alkoxides are sufficiently electropositive to undergo reaction 2 even in the absence of a catalyst. Furthermore, the alcoholysis reaction is relatively slow.[7] As a result, the reaction with $Ti(O\ i\text{-}Pr)_4$ will presumably lead to the deposition of a Si-O-Ti layer on the silica surface according to reaction 2.[10] The reaction is performed by bringing the $Ti(O\ i\text{-}Pr)_4$ solution in contact with a dry A2** membrane. High capillary pressure forces the solution into the pores. The relative rates of reaction and flow into the pores dictate the amount of titanium penetrating the membrane pores.

The permeance versus temperature results of an A2** membrane reacted with Ti(O i-Pr)$_4$ are presented in Figure 3. Isobutane (i-C_4H_{10}) was used as a larger probe molecule (5 Å kinetic diameter) for these measurements. He and H_2 show a strong temperature dependence with activation energies of 4.9 and 5.6 Kcal/mol respectively. The flux for CH_4 and N_2 drop below the resolution of our test equipment (< 10^{-7} cm^3/cm^2-s-cm Hg) below 220 °C and 120 °C respectively. The corresponding He/N_2, H_2/N_2 and CO_2/CH_4 separation factors are > 300. The higher activation energies for He and H_2, are similar to the activation energies for 4Å zeolite indicative of a narrow size distribution of micropores.[9] The high separation factors coupled with the high fluxes for the various gases make our membranes excellent gas separators. The best reported organic membranes have separation factors at least an order of magnitude lower and fluxes several orders of magnitude lower than our membranes. The best reported organic CO_2/CH_4 separator (a polyimide membrane) has a separation factor of ~ 80 at a CO_2 permeance of 2 X 10^{-7} cm^3/cm^2-s-cm Hg. A comparative plot of such membranes against our membrane is presented elsewhere.[11]

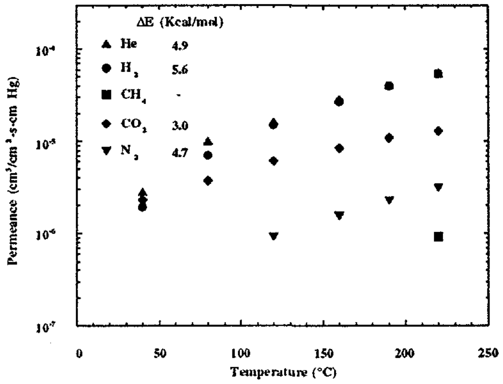

Figure 3: Permeability results of an A2 membrane modified with Ti(O i-Pr)$_4$.**

Microporous Composite Membranes

Figure 4 plots the permeance versus pressure data for an imogolite composite membrane. The membrane has a very atypical reduction in permeance with increasing pressure differential. This pressure dependence results in an increase of the He/SF_6 separation factor from 15 at 20 psi differential to 33 at 80 psi differential. The He/N_2 separation factor remained around 5 throughout the pressure range. The unusual pressure dependence was reproducible on remeasurement of the membrane.

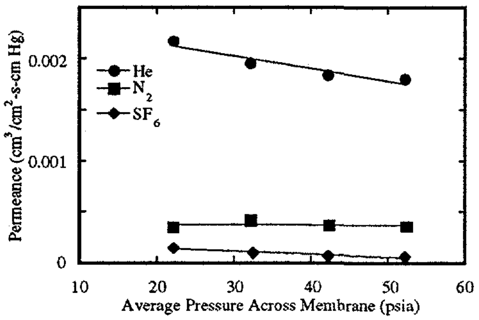

Figure 4: Permeability results for one coating imogolite followed by 2 coatings A2 sol, measured at room temperature.**

When analyzed using the hindered diffusion model through a straight capillary tube, developed by Fain,[12] the separation factors at 80 psi differential pressure yield an average pore diameter of 9.3 Å. This value approximates the internal diameter of the imogolite tube, indicating that the imogolite may actually control the gas flow through the membrane.

Summary and Conclusions

Three different approaches for the preparation of ultramicroporous sol-gel derived ceramic membranes were presented. Sintering of a pure silica membrane at 550 °C resulted in partial consolidation of the structure, resulting in membranes with pores of molecular dimensions, as evidenced by separation factors exceeding ideal Knudsen. Ti(O i-Pr)$_4$ was reacted with an A2** membrane to prepare a Ti-O-Si layer that led to membranes with molecular sized pores with had fluxes and gas separation factors exceeding those reported for the best organic membranes. Use of polymeric silica as a host matrix to prepare structurally microporous composite membranes was demonstrated for the first time.

Acknowledgments

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