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High-Selectivity, High-Flux Silica Membranes for Gas Separation

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Process improvements in silica membrane fabrication, especially the use of clean-room techniques, resulted in silica membranes without detectable mesoscopic defects, resulting in significantly improved transport properties. Supported membranes calcined at 400°C were 30 nanometers in thickness, showed a H_2 permeance at 200°C of 2×10^{-6} moles per square meter per second per Pascal (mol m^{-2} s^{-1} Pa^{-1}), and had a CH_4 permeance more than 500 times smaller. Molecules larger than CH_4 were completely blocked. Silica membranes calcined at 600°C showed no detectable CH_4 flux, with a H_2 permeance of 5×10^{-7} (mol m^{-2} s^{-1} Pa^{-1}) at 200°C. These results signify an important step toward the industrial application of these membranes such as purification of H_2 and natural gas as well as the selective removal of CO_2.

The ability of amorphous microporous silica membranes with pore diameters (Ø) < 2 nm to pass small molecules while blocking larger ones has been known for years (*1*). State-of-the-art microporous silica membranes consist of a thin silica layer on top of a supported mesoporous (2 nm $<$ Ø $<$ 50 nm) γ-Al_2O_3 membrane, which provides mechanical strength. The key problem limiting industrial application of silica membranes is the poor reproducibility of the fabrication process, which results in large fluctuations in performance and often poor separation properties. Improving the membrane properties by lowering the defect size and density is currently one of the greatest challenges in inorganic membrane preparation.

Coherent and strong porous α-Al_2O_3 membrane supports were made from granulated alumina powder (*2*). The supports were uniaxially pressed at 10^5 kPa to shape the disk, followed by isostatic pressing at 4000 kPa to achieve a higher and more uniform "green" density. They were then sintered at 1250°C to a final porosity of 40% with an average Ø = 160 nm. Membranes of γ-Al_2O_3 with Ø = 2.5 nm and a thickness of ~4 μm were prepared by dip-coating the supports in a boehmite sol followed by drying and calcining at 600°C (*3*). Dip-coating was performed by moving one side of the support horizontally through the liquid surface of the sol solution for a few seconds. The whole process of dipping, drying, and calcining was repeated once, to repair any defects in the first γ-alumina layer. These defects could be caused by particle contamination, aggregates, microscopic air bubbles in the sol, and irregularities in the α-Al_2O_3 support surface. The γ-Al_2O_3 membranes, in turn, were used as a substrate for microporous silica membranes, prepared by dip-coating twice in a polymeric silica sol, followed by drying and calcining at 400° or 600°C (referred to as Si400 and Si600 membranes). The silica sol was prepared by acid-catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS) (*4*) in ethanol as follows. A mixture of acid and water was carefully added to a mixture of TEOS and ethanol under vigorous stirring. During the addition of the acid-water mixture, the TEOS-ethanol mixture was placed in an ice bath to avoid premature (partial) hydrolysis. After the addition was complete, the reaction mixture was refluxed for exactly 3 hours at 60°C in a water bath under continuous stirring. The reaction mixture had a final molar TEOS:ethanol:water: acid ratio (based on unreacted components) of 1:3.8:6.4:0.085 (*5*). All processing steps were well controlled, all liquids were filtered with a 0.5-μm filter, and nanoscale-particle processing was done in a clean room with class 1000 conditions. The dipping process was carried out in a flow cupboard in a clean air stream (class 10 conditions).

Well-controlled processing of every membrane fabrication step, clean process liquids, and the use of a clean room were important in membrane preparation. If the membrane preparation was done with extreme care but was not performed in a clean room, large defects and, hence, nonreproducible membranes were essentially inevitable. One defect with Ø $>$ 100 nm per square centimeter of membrane surface led to substantial deterioration of all selectivities, especially those involving CH_4 and CO_2. The use of a clean room reduced the average concentration of particles of $<$0.5 μm in our normal laboratory air from 18 million per cubic meter to less than 100 m^{-3} in the flow cupboard where the membranes are prepared. Without clean-room conditions, the number of defects caused by particles from the air was estimated to be at least five defects of Ø $\approx$ 0.5 μm per square centimeter of membrane surface. This num-

Table 1. Permselectivity (F_α) calculated from observed single-component permeances and selectivities (α) for 50/50 (V/V) gas mixtures for Si400 and Si600 at ΔP = 1 bar and a mean pressure of 1.5 bar.

Mixture	Si400				Si600		
	100°C		200°C		100°C	200°C	300°C
	F_α	α	F_α	α	F_α	F_α	F_α
H_2/CO_2	4.0	3.9	7.5	6.8	36	71	98
H_2/N_2	61		64		>80	>135	>170
H_2/CH_4	770	533	561	321	>2500	>4000	>5000
CO_2/CH_4	194	118	75		>130	>100	>80
O_2/N_2	3.9		3.3		>3	>6	>7

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ber dropped to $\ll 1$ when our clean-room conditions were deployed.

Morphological characterization of the membranes was accomplished by transmission electron microscopy (TEM) of a thin cross section of the membrane. The results for Si400 (Fig. 1) reveal a thin silica layer of ~30 nm on top of the γ-Al_2O_3 support layer. In addition, a boundary between the first and second γ-Al_2O_3 layer ~250 nm from the surface is visible. Membrane single-gas permeance $F = J/\Delta P$ (where J is the single-gas flux and ΔP is the pressure difference) was measured in the pressure-controlled dead-end mode (*6*) for temperatures between 50° to 300°C and pressure differences from 0.5 to 3 bar. Before the permeance measurements, the membranes were dried overnight at 200°C to remove adsorbed moisture from the micropores. Comparison with actual separation measurements shows that the J can be used directly to calculate separation performance (*7*). The latter is expressed as the permselectivity F_α (Table 1), which equals the ratio of single-gas fluxes measured at the same temperature and pressure.

Membrane transport properties were reproducible within 25%, and the membranes could be made in large quantities with rejection ratios of <15%. The permeance of the membranes was in most cases independent of pressure P and showed a slight increase with temperature T, except for CO_2. The CO_2 flux was nearly constant with T and appeared to decrease slightly at higher temperatures. The observations that CH_4, with a kinetic diameter $d_k = 3.8$ Å, had some detectable permeance through Si400 and that SF_6, with $d_k = 5.5$ Å, did not permeate at all (Fig. 2) allowed us to estimate the Si400 membrane pore diameter of 3.8 Å $< \varnothing <$ 5.5 Å. This conclusion is in agreement with the microporous sorption results for unsupported silica material obtained in our lab and elsewhere (*8*). The permeance and F_α values obtained compare favorably with reported results. For the Si400 membranes, the H_2 permeance at 200°C was 2×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with $F_\alpha > 500$ for H_2/CH_4 separation. Previously reported values are 1.6×10^{-6} mol m^{-2} s^{-1} Pa^{-1} and 43, respectively (*9*); a value of $F_\alpha = 235$ for H_2/CH_4 separation at 150°C was reported by Hassan *et al.* (*10*) for a silica hollow-fiber membrane, but no values of single-gas permeance were specified. Commercially available CVI silica membranes made by Media and Process Technology have an $F_\alpha = 27$ for H_2/CO_2 with a H_2 permeance of 1.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 400°C (*11*). The Si400 membranes show promise as air separation membranes with $F_\alpha = 4$ for O_2/N_2. Because of the limitations of the column used in the gas chromatograph, actual air separation experiments were not performed, but deviations of α from $F_\alpha = 4$ are not expected to be significant (*7*).

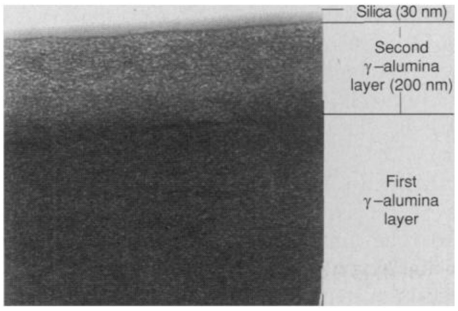

Fig. 1. TEM micrograph of Si400 membrane cross section showing a part of the γ-alumina and silica layers.

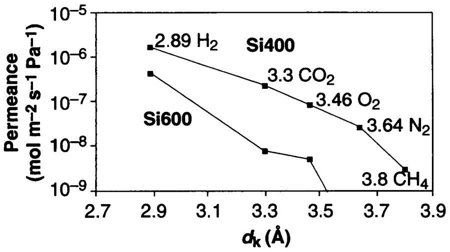

Fig. 2. Kinetic diameter d_k (*13*) versus permeance for Si400 and Si600 membranes at 200°C, ΔP = 1 bar, and a mean pressure of 1.5 bar.

The Si600 membranes had an $F_\alpha = 70$ for H_2/CO_2 with an H_2 permeance of 5×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 200°C. The smaller Si600 permeance was a result of densification of the structure and a smaller pore size. The large increase of F_α for H_2/CO_2 from 7 on Si400 to about 70 can also be attributed to a decrease in the amount of terminal hydroxyl groups at the internal surface of the silica because higher calcination temperatures lead to lower hydroxyl concentrations (*12*). A decrease of the amount of hydroxyls makes the material more hydrophobic, which may result in a lower (surface) occupation and, hence, a lower CO_2 permeance. Methane did not permeate at all through the Si600 membranes, and the N_2 permeance was below the lower limit where we can measure with a reasonable accuracy. Using a sensitive, qualitative soap-solution test, we detected some N_2 flow, but none for CH_4. Estimation of the pore size by means of size exclusion on the basis of kinetic diameters yielded a Si600 pore diameter between 3.6 and 3.8 Å, which is significantly smaller than that estimated for Si400 membranes.

There are several subjects that remain to be addressed. (i) The sensitivity to water needs to be decreased, which might be achieved by making the internal silica membrane surface more hydrophobic through chemical treatment. Our preliminary results are promising. (ii) For the membranes of the present study, support resistance did not impose a serious problem, but if the H_2 permeance can be improved further, measures must be taken, such as increasing porosity and pore size, and making use of multilayered or graded support structures. (iii) Decreasing membrane thickness can also improve performance. If membranes can be made with a thickness of ~1 nm, H_2 permeances of $>5 \times 10^{-5}$ mol m^{-2} s^{-1} Pa^{-1} can be realized, provided no support limitations or surface transfer rate limitations occur. (iv) Improvements in high-temperature resistance can possibly be achieved by doping with polyvalent metal ions or removing silica surface hydroxyl groups. (v) Finally, upscaling of the present silica membrane technology into membrane modules is needed to increase the surface-to-volume ratio for practical applications. The wet-chemical nature of the silica membrane process suggests that production-scale manufacture is possible for membranes on hollow-fiber supports by fast liquid-coating techniques. The present results suggest that application of silica membranes in, for instance, natural gas purification, molecular air filtration, selective CO_2 removal, and industrial H_2 purification are feasible.

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