

**CERAMIC MEMBRANES FOR
HYDROGEN PRODUCTION FROM COAL**

FINAL REPORT

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ABSTRACT

The preparation and performance of membranes for application to hydrogen separation from coal-derived gas is described. The membrane material investigated was dense amorphous silica deposited on a suitable support by chemical vapor deposition (CVD). Two types of support materials were pursued. One type consisted of a two-layer composite, zeolite silicalite/ α - Al_2O_3 , in the form of tubes approximately 0.7 cm in diameter. The other type was porous glass tubes of diameter below 0.2 cm. The first type of support was prepared starting from α - Al_2O_3 tubes of 1 μm mean pore diameter and growing by hydrothermal reaction a zeolite silicalite layer inside the pores of the alumina at the OD side. After calcination to remove the organic template used in the hydrothermal reaction, CVD was carried out to deposit the final silica layer. CVD was carried out by alternating exposure of the surface with silicon tetrachloride and water vapor. SEM and N_2 adsorption measurements were employed to characterize the membranes at several stages during their preparation. Permeation measurements of several gases yielded $\text{H}_2:\text{N}_2$ ideal selectivity of 150-200 at room temperature declining to 110 at 250°C. The second type of support pursued was porous glass tubes prepared by a novel extrusion technique. A thick suspension of borosilicate glass powder in a polyethersulfone solution was extruded through a spinneret and after gelation the glass-polymer tube was heat treated to obtain a gas-tight glass tube. Leaching of the glass tube in hot water yielded connected pores with diameter on the order of 100 nm. CVD of the final silica layer was not carried out on these tubes on account of their large pore size.

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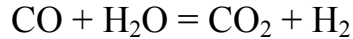
INTRODUCTION

Membrane Separation in Hydrogen Production

Hydrogen production is a major option in the utilization of fossil fuels for power generation, transportation, and chemicals production. A major potential use of hydrogen is fuel cell power generation. Utility power generation by highly efficient solid oxide (SO) fuel cells can use reformat gas directly, but prior separation of H₂ and CO₂ would raise fuel cell efficiency and help sequestration of CO₂. Hydrogen-rich fuel gas can also be used in combined cycle power generation to reduce CO₂ emissions. Polymer electrolyte membrane (PEM) fuel cells under active development for transportation require very pure hydrogen that needs to be generated on board by steam reforming of liquid fuels. Chemical use in hydrotreating of heavy oil or coal liquids, or in ammonia and other chemical synthesis is yet another use of hydrogen.

The first step in the production of hydrogen for any of the above applications is the generation of synthesis gas or fuel gas from coal or liquid hydrocarbons by reaction with steam, oxygen (or air), or steam-oxygen mixtures. The fuel gas is subsequently reacted with additional steam in a catalytic water gas shift (WGS) reactor to increase its hydrogen content with a corresponding reduction of the carbon monoxide content. A second, lower-temperature, water gas shift stage is some times added to further increase CO conversion. The final step is application dependent. For PEM fuel cells, CO needs to be reduced to ppm levels by selective oxidation. High-temperature stationary fuel cells do not require prior removal of carbon oxides but a hydrogen-rich fuel gas would provide better efficiency and allow the possibility of carbon dioxide sequestration. Current technology for separation of CO₂ from synthesis gas after steam-reforming is solvent absorption, however, hydrogen separation by ceramic membranes integrated with the catalytic water gas shift reactor holds the promise of higher overall efficiency.

A schematic of a hydrogen selective membrane integrated with a water gas shift (WGS) reactor is illustrated in Figure 1. As the hydrogen produced in the WGS reaction permeates through the membrane, the equilibrium of the reaction



is driven to the right, and the CO at fixed feed H₂O:CO ratio is increased. Alternatively, the feed H₂O:CO can be reduced at fixed CO conversion. The product hydrogen will not require further purification if the membrane has adequate hydrogen selectivity with respect to H₂S and COS. For example if the gas in the feed side of WGS membrane reactor has 50 ppm H₂S and 50% H₂, the permeate gas obtained using a membrane with a H₂:H₂S selectivity of 100 will have about 1 ppm H₂S. Higher purification is obviously possible with a more selective membrane. Hydrogen of that purity would be suitable as a fuel for power generation in a combined cycle or high temperature fuel cell, or for refinery hydrotreating processes.

The retentate gas containing primarily CO₂ with smaller quantities of hydrogen would be treated for CO₂ sequestration or burned directly for additional power.

Use of the membrane in the WGS process would offer the following advantages relative to fuel cell power generation:

- (i) Reduced excess steam used in the conventional WGS reactor to attain high CO conversion
- (ii) Elimination of the second, low temperature shift reactor also used to reduce the product CO content
- (iii) elimination of the CO₂ and N₂ diluents in the gas fed to the fuel cell stack resulting in higher cell EMF.

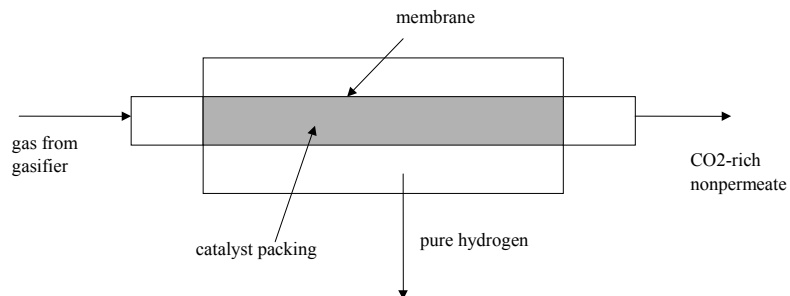


Figure 1. Schematic of a membrane reactor for hydrogen production

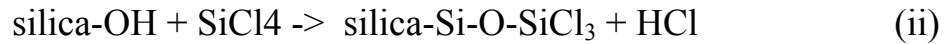
Two types of high temperature membranes are known to have high selectivity for H₂ separation: metallic membranes (e.g. palladium alloy-based), and dense silica membranes. In Pd-alloy membranes, H₂ dissociates to atomic hydrogen that dissolves into and diffuses through the bulk Pd-alloy layer with complete selectivity, in the absence of defects. In dense silica membranes, H₂ permeation takes place in molecular form much faster than that of larger molecules like CO, CO₂, H₂S and N₂.

Previous Work in the PI's Laboratory on Silica Membranes

In previous research in the PI's laboratory techniques have been developed for making silica membranes suitable for hydrogen separation from synthesis gas at temperatures 400-800°C [1-3]. The membranes were formed by chemical vapor deposition (CVD) of a thin, dense, silica layer within the pores of Vycor glass tubes by the overall reaction



This CVD reaction was carried at about 600°C by simultaneous or alternating flows of SiCl₄ and steam and involves the two half-reactions



where the silica in Eq. (iii) has appropriated one SiO₂ from the gaseous precursor.

The silica membranes prepared previously in the PI's laboratory yielded H₂:N₂ selectivity of 300-1000 and H₂ permeance (flux divided by the transmembrane partial pressure difference) 2-3 x10⁻⁸ mol/m²-s-Pa (0.27-0.4 ml/cm²-min-atm) at 600°C.

The membrane selectivities achieved in the previous work exceed the requirements of the application discussed earlier. However, the hydrogen permeance needs to be increased to improve the process economics, given that the membrane cost is roughly inversely proportional to the permeance. The H₂ permeance is controlled partly by the thickness of the dense CVD separation layer and partly by the in-series resistance of the support. The support used in our earlier study was commercially available porous Vycor glass tubes of 1 mm wall thickness and hydrogen permeance about 3.7 MPU (MPU=10⁻⁸ mol/m²-s-Pa). Thinner-walled Vycor tubes of sufficient mechanical strength were not commercially available. By increasing the permeance of the support by a factor of 5, it is estimated that the H₂ permeance can be increased to 5-10 MPU with a corresponding reduction of the membrane cost.

Basic Concept

To increase the permeance we considered two approaches:

(A) Develop “asymmetric” membranes consisting of a thin dense silica layer providing the separation deposited by CVD on a highly permeable support providing the mechanical strength. When using CVD to deposit silica it is essential that the pores of the support are below 5 or so nm diameter, otherwise larger pores

would take a very long time to seal and the resulting silica layer would be very thick. For example, α -alumina is highly permeable but unsuitable as a support because its pore size is in excess of 60 nm. To solve this problem we proposed to modify the α -alumina support by applying an intermediate 5-10 μm layer of pore size 1-5 nm. Thus, the final membrane would consist of three layers. The middle layer could be made of a phase-separated glass (Vycor) or a zeolite such as ZSM-5 (or silicalite).

In a previous project we investigated the coating of porous α -alumina with a thin layer of mesoporous Vycor glass. For that purpose the alumina was coated with a layer of sodium borosilicate glass particles which was sintered to a dense layer and then leached in acid solution to generate the mesoporosity. During sintering, however, the borosilicate glass reacted with the alumina support resulting in drastic compositional change so that upon leaching the desired mesoporosity was not attained.

In the present project we chose to coat the α -alumina with a silicalite layer. Silicalite is the pure silicon variety of the zeolite ZSM-5 and has uniform pores, or channels, of 0.55 nm diameter, therefore in principle it would be possible to seal with a very thin silica layer.

Production of the final layer by silica CVD can be carried out using different precursors and reaction conditions. One such process, the high-temperature alternating half reactions with SiCl_4 and H_2O was employed in earlier work at the PI's laboratory as mentioned earlier.

(B) The second approach to making higher permeance membranes was to prepare symmetric but thinner Vycor glass tubes. One of our coworkers had previously developed an extrusion technique suitable for making ceramic tubes as small as 1 mm OD with 0.7 mm ID, and wall thickness of as low as 0.15 mm. The work in

this part of the project focused on applying this extrusion technique to the preparation of thin Vycor tubes.

The main body of this report consists of Chapters 1 and 2 describing the work done following approach A , and Chapter 3 describing the work done following approach B. The report ends with a short chapter containing the overall conclusions.

EXECUTIVE SUMMARY

The objective of this project was to develop membranes permselective to hydrogen at elevated temperatures, suitable for integration with the water gas shift reaction for applications to hydrogen production from coal gas. Previously developed silica Vycor-supported membranes had high selectivity but low permeance on account of the low permeance of the support. In this project two high permeance supports were investigated. One was composite zeolite silicalite/ α -Al₂O₃ tubes, the other was thin-walled porous glass tubes. These supports were to be coated with a dense silica layer providing the hydrogen separation function. Coating was to be carried out using chemical vapor deposition.

The silicalite/ α -Al₂O₃ supports were prepared starting with α -Al₂O₃ tubes of 0.7 cm OD, and 1 μ m mean pore diameter. The tubes were seeded by dipcoating in a suspension of silicalite crystallites (0.1-0.2 μ m size) and then heated at 100°C in a silicalite growth solution of molar composition 1 TEOS : 0.1 TPABr : 0.2 NaOH : 98 H₂O at 100°C for 16-23 hours. Under these conditions the bulk of silicalite was formed inside the pores of alumina at a depth of approximately 100 μ m below the OD surface. The growth period was repeated once or twice to completely plug the pores near the surface and thus eliminate nonzeolitic pathways through the composite support. Calcination to remove the TPA template was conducted in air at 500°C, and the calcined supports were examined by scanning electron microscopy (SEM), N₂ adsorption porosimetry, and gas permeation measurements. The porosimetry and the gas adsorption measurements showed that the zeolite layer had a certain number of defects on the order of 100 nm size resulting formed during calcination.

Chemical vapor deposition of silica on the silicalite/ α -Al₂O₃ supports was conducted by a series of alternating reactions with silicon tetrachloride (SiCl₄) and water vapor at 450°C. In a limited number of experiments, the larger molecule Cl₃SiOSiCl₂OSiCl₃ was used in place of SiCl₄. Before and after silica deposition the membranes were examined by NMR and nitrogen adsorption porosimetry. Permeation experiments with H₂, CO₂, N₂, CH₄, n-CH₄, and i-C₄ were carried out in the temperature range 25-250°C. At 150°C, after 20 alternating reaction cycles, the H₂ permeance was about 10⁻⁷ mol/m²-s-Pa (1.34 ml/cm²-min-atm) and the H₂:N₂ ideal (single gas) selectivity was 150-200 below 150°C and declined to 110 at 250°C. The H₂:CO₂ selectivity was about 20 and increased with increasing temperature. Examination of the gas adsorption and gas permeation results lead to the conclusion that, during CVD, SiCl₄ penetrates and narrows down the zeolitic channels without forming a dense layer on top of the support. CVD with the larger molecule Cl₃SiOSiCl₂OSiCl₃ produces a silica layer outside of the channels. In

both cases, however, CVD is not sufficient to eliminate the larger defects of the support. In view of the declining $H_2:N_2$ selectivity with temperature, the use of these membranes would be limited to about 250°C.

The second type of materials examined as hydrogen membrane supports were thin, porous glass tubes prepared exploiting the well known phase separation property of BSG. In departure from the standard Vycor process, the tubes were prepared by extruding from a suspension rather than from the melt. A thick suspension was made by mixing a borosilicate glass (BSG) powder (9.1 Na₂O-29.7 B₂O₃-61.2 SiO₂, wt%) with a solution of polyethersulfone (PESf) in N-methyl-2-pyrrolidone at a 8:1 wt ratio of glass to polymer. The suspension was extruded through a tube-in-orifice spinneret and the extruded glass-polymer tubes were immersed in water to gel and achieve mechanical strength. After drying, the glass-polymer tubes were slowly heated in air to a temperature in the range 800-930°C and kept at that temperature for several hours to remove the polymer decomposition products and sinter the glass particles to a gas-tight glass tube. After cooling, the glass tubes were leached in boiling water to generate connected porosity. Gas permeation measurements showed that these glass tubes had pores of 50 nm or larger. Pores of that size cannot be sealed by CVD using the reactions with SiCl₄ and water vapor. The formation of these large pores is attributed to the large particle size in the starting glass powder and to facile phase separation during cooling. Certain modifications of the glass composition and use of finer particles in the starting glass powder are suggested for achieving pore size about 5 nm as needed for silica CVD.

CHAPTER 1. Preparation of Silicalite/ α -Al₂O₃ Supports

As discussed in the Introduction, silicalite/ α -Al₂O₃ tubes were chosen as supports for the deposition of hydrogen permselective silica layers. The main feature of these supports is the small and uniform channel size (0.55nm) of the zeolite, although the inevitable presence of intercrystallite defects compromises somewhat this ideal structure. In the present chapter the silicalite/alumina composites which will serve as supports will also occasionally be referred to as membranes because they are selective in a number of separations such as the separation of hydrocarbons. But they do not have selectivity for hydrogen, therefore, their main interest in this project was as supports for the deposition of hydrogen selective silica films described in chapter 2.

Virtually all zeolite layers grown on alumina supports contain zeolite inside as well as outside of the pores. One report [4] described ZSM-5 membranes prepared by two techniques, one resulting in an external layer with very small pore infiltration, the other resulting in a patchy external layer and a deep internal layer. Other membranes reported in the literature contained a dense, continuous external layer (at SEM resolution) and an internal layer extending as far as 150 μ m from the support surface. [5, 6]. The pore volume fraction occupied by the reaction product (crystalline or amorphous) generally declined with distance from the support surface on account of pore diffusion limitations during the hydrothermal reaction. Good selectivities were observed only when the external layer was fully developed and continuous [7], but this observation does not necessarily imply that separation is localized at the external layer. It may simply signify that by the time the external layer becomes fully continuous (as observed by SEM) the internal layer is also sufficiently developed to provide the separation function either by itself, or in combination with the external layer.

Given the large thickness of the internal layer and the gradually declining zeolite occupancy of the pores below the surface, it is possible that only the first few tens of microns from the surface provide useful separation properties. The material deposited deeper into the pores reduces the selectivity as well as the permeance because it adds a less selective resistance in-series to the composite membrane. In this chapter the preparation, characterization, and permeation properties of internally grown zeolite layers will be described. Intrapore growth of zeolite membranes has some practical advantages, the major of which is the ability to use less expensive supports of relatively large pore size without concern about surface smoothness. Additional details on silicalite growth on alumina supports are contained in a journal publication from our laboratory [8].

Experimental

Supports

The supports used in this study were α -Al₂O₃ tubes (99.5%, Dongsuh company, Korea) of 1.0 μ m mean pore diameter, 7.2mm OD, 6.0mm ID, and ca. 40% porosity. Tubes were cut into 2.8 cm long segments, ultrasonicated in deionized (DI) water for 30 min and dried at 200°C before use.

Seeding

Seeding the alumina prior to hydrothermal reaction is known to greatly facilitate zeolite growth and was employed in all silicalite/alumina preparations reported in this chapter. The seed particles employed were of colloidal size grown using the protocol of Persson et al. [9] by heating a mixture of tetraethyl orthosilicalite (TEOS), (98%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 1M aqueous solution, Aldrich), NaOH (1M aqueous solution, Aldrich), and deionized (DI) water at 95°C for 16-23 hours. The molar composition of the

mixture was TEOS : 0.2 TPAOH : 0.08 NaOH : 60 H₂O. The resulting silicalite particles were separated by filtration, washed with DI water and dried. Before use, the particles were redispersed in water with the help of ultrasonication, forming a suspension at pH about 8. Seeding was carried out by immersing the alumina tubes for about 10 minutes in a suspension of 1 wt% particle content. After withdrawal, the tubes were briefly washed with DI water, dried in air and heated for 1 h at 200°C to bond the particles to the alumina pore surface. Seeding was repeated once to increase the particle loading

Silicalite Growth

The silicalite growth solution was prepared by stirring at room temperature for one day deionized water, NaOH, tetrapropylammonium bromide (TPABr, 98%, Aldrich), and TEOS in the molar ratio of TEOS : 0.1 TPABr : 0.1 – 0.7 NaOH : 98 H₂O. The seeded tubes were secured vertically in 14 mL Teflon vials (with screw cap) with the aid of Teflon holders. The vials were filled with 10 mL of growth solution, sealed, and attached to a rotating shaft inside a forced convection oven preheated to 95°C. The shaft carrying the vials was tumbled at 40~50 rpm to enhance mass transfer. After 20 h the vials were removed from the oven, cooled, opened, and the membranes were thoroughly washed with water and dried at room temperature and then at 200°C. The growth procedure was repeated two to three times to obtain a membrane that was gas-tight before leaching.

After completion of growth, calcination was carried out to remove the TPA molecules occluding the zeolitic channels. For this purpose the membranes were heated in a stream of air first to 350°C at 10°C/min, and after maintaining the temperature at that level for 1 h the tubes were heated to 500°C at 5°C/min. After soaking at the final temperature for 3 h, the tubes were cooled to ambient temperature by turning off the furnace power. In a few preparations calcination

was carried out after the second growth period and repeated after the final growth period.

Membrane Characterization

After each period of growth and drying the membranes were weighed to determine the amount of product deposited. The external OD surfaces and cross-sections of selected membranes were examined using a scanning electron microscope (SEM, Camscan) and a few cross-sections were subjected to energy dispersive analysis (EDS) for tracing the elemental composition profile. Nitrogen adsorption (ASAP 2010, Micromeritics) was carried out at 77K on selected membranes to obtain information about mesopore and micropore size distribution.

Permeation Measurements

After calcination, the permeation fluxes of several gases and gas mixtures were measured as a means of detailed characterization of the silicalite/ α -Al₂O₃ tubes. The measurements were carried out using a permeation cell that can accommodate up to four tubes (Fig. 2) and operates at temperatures up to 200°C. After mounting to the permeation cell, the tubes were tested with single gases or gas mixtures. In each set of measurements, the feed gas was passed continuously through the shell (space surrounding the tubes) while the permeate gas was collected through the tube bores. Single gas measurements were carried out using the pressure rise technique where the feed gas passed continuously through the shell. The permeate side was first evacuated, and then shut off from vacuum and the pressure rise was measured by a sensitive capacitance gauge. The rate of pressure rise gave the membrane permeance by means of a suitable calibration. Mixture permeation properties were obtained using the Wicke-Kallenbach (WK) type of measurements where both feed and permeate sides were kept at 1 bar while the permeate side was continuously swept by a stream of He. The mixture of sweep

gas and permeate gas was analyzed downstream using a gas chromatograph HP 5890 with a packed column (0.19% picric acid on Graphpac GC, Alltech) and a thermal conductivity detector. The known sweep gas flowrate and the outlet gas composition measured with the chromatograph were used to calculate the transmembrane flux of each component.

Results and Discussion

Seeding

The seed particles were produced by 16 h reaction at 95°C and had about 0.1µm diameter, as estimated from SEM. Figure 3 shows particles of that size coated onto an alumina tube of 0.15µm pore size. After 23 hours the particles had grown to about 0.2µm but longer reaction did not result in substantial additional growth, perhaps due to depletion of silica in the solution. Each support tube was seeded twice by impregnation resulting in an average weight gain of 0.084% ± 0.045%. The large variation was due to the small weight gain and to water adsorption during handling and weighing. A suspension volume equal to the pore volume carries particles 0.168% by weight of the support. Hence, about one half of the particles were not retained during impregnation. Figure 4 shows an EDS trace of silicon on the cross-section of a tube that had been seeded twice. The concentration of silicon decreases with distance from the surface, and after 50 µm it falls below the measurement error. Hence, the seed particles are preferentially retained within the first 50 µm from the external surface.

Membrane Characterization

Figure 5 shows the cumulative reaction product of an unseeded tube and a tube seeded by impregnation versus the number of growth cycles at 95°C. Product formation in the tube seeded by impregnation was rapid in the first and second

periods and leveled off thereafter. For the unseeded tube, product formation was low in the first period but accelerated thereafter so that, in effect, the first growth period provided seeding for subsequent growth. A 5% weight gain is equivalent to a 97 μm region of pores fully occupied by silicalite. A 8% weight gain corresponds to 157 μm of pores fully occupied with product. Figure 6 shows SEM of surface and cross sections of an untreated tube and a tube seeded by impregnation and subjected to four growth periods. Reaction product is evident in the support 20-30 μm from the external surface. There is also an external film 2-3 μm thick but this film does not appear to be fully continuous. A more quantitative view of product distribution is provided in Figure 4 that shows EDS traces of silicon over the cross-sections of a tube seeded by impregnation and of an unseeded tube, both after three growth periods. The product concentration in the seeded tube is high near the surface and after about 20 μm drops to a lower level that is maintained until at least 80 μm . Based on the mass gain shown in Figure 4, the lower level of silicon must extend for several hundred μm from the surface. The product concentration in the unseeded tube remains at a low level throughout the 80 μm region including the first 5 or 10 μm from the surface.

Figure 7 shows the nitrogen adsorption-desorption isotherm of a membrane after three growth periods followed by calcination. The isotherm has two hysteresis loops the first at P/P_0 below 0.3 and the second at P/P_0 above 0.5. The first loop belongs to the microporous region and is very similar to that of zeolite powder collected under the same synthesis conditions. The loop at higher P/P_0 derives from pores above 1.5 nm. The distribution of these pores calculated using the BJH procedure (based on the desorption branch) and shown on Figure 7 has a peak centered at less than 2 nm, the descending part of which is beyond the applicability of Kelvin's equation used in the BJH procedure. Figure 7 also shows a smaller

peak at about 4 nm. The pores of about 2 nm seem to be nonzeolitic pathways of the type discussed by previous authors [10].

Permeation Properties

After the second or third growth periods the uncalcined membranes were impermeable to nitrogen but after calcination they became permeable to nitrogen and other gases. Permeation measurements for single gases conducted by the pressure rise technique are shown in Figure 8. The membrane has high n-butane permeance and high n-butane:isobutane ideal selectivity but very low ideal selectivity among hydrogen, nitrogen, and n-butane. The hydrogen to nitrogen permeance ratio is well below its Knudsen value and rises with temperature, suggesting that the bulk of transport takes place through zeolitic pores, or fine nonzeolitic pores, below 2 nm diameter. A small component of transport could take place by Knudsen or viscous flow through larger defects.

Measurements were also carried out by the WK technique for a 50-50 mixture of n-butane and isobutane. Table 1 lists room temperature results for several membranes. The n-butane:isobutane separation factor increases with each additional growth period and after three or four periods it reaches 30-40 but remains well below the ideal selectivity (ratio of single gas permeances) in Figure 8. As shown in Figure 9 the butane separation factor declines with temperature, opposite to the trend observed for the ideal selectivity in Figure 8.

The permeation results suggest that the silicalite/ α -Al₂O₃ prepared in this project contained a small number of gaps between crystals or between crystals and the pore surface. These gaps were in the tens of nanometers range. Since membranes dried at 200°C were impermeable before calcination, the gaps were generated during calcination. Their relatively large size but small number suggests that they are associated with the larger pores of the alumina support, at the tail end of the pore size distribution.

Table 1. Permeation properties of several silicalite/ α -Al₂O₃ tubes.

separation factor	n-butane permeance MPU (1 MPU = 10 ⁻⁸ mol/m ² .s.Pa)	measurement temperature °C
37	9.9	25
39	15	25
32	17	25
17	29	150

One possible source of these gaps is dimensional changes and stresses accompanying calcination as discussed in references [11, 12]. Another possible source of gaps is intrinsic to the chemistry of zeolite growth, especially at relatively low alkalinity and temperature as in the present experiments. Under most conditions crystallization takes place within a gel layer formed on the alumina surface (externally and internally) soon after immersion in the synthesis solution [6]. In subsequent crystal growth the gel is consumed until its changed composition cannot support growth any further. Enrichment of the gel with aluminum leached from the support may inactivate the gel after some length of time. Although additional growth components can be supplied from the bulk of the synthesis mixture, the transport of these components to the gaps may be hindered by the residual inactive gel trapped there. Shrinkage of the residual gel by loss of water and TPA during calcination at ca. 500°C would tend to generate gaps of low permselectivity. Both possibilities are consistent with our observation that a second or third growth period is more effective in increasing membrane selectivity if preceded by calcination rather than by mere drying.

Conclusions to Chapter 1

Internal seeding of alumina tubes of 1 μm mean pore diameter allows the growth of silicalite layers inside the pores at a depth 100 μm or more below the external surface. Zeolite penetration is even deeper in membranes grown under the same conditions on unseeded supports. Despite the large thickness of the internal zeolite layers, the silicalite/ $\alpha\text{-Al}_2\text{O}_3$ tubes had relatively high permeance. After three growth periods the tubes were gas-tight but after calcination a small number of defects of tens of nanometer size were generated. The tubes had n-butane to isobutane separation factor in the 30 – 40 range but showed no hydrogen selectivity because the 0.55 nm size of the zeolitic channels is considerably larger than the kinetic diameter of N_2 , CO_2 and other molecules of interest.

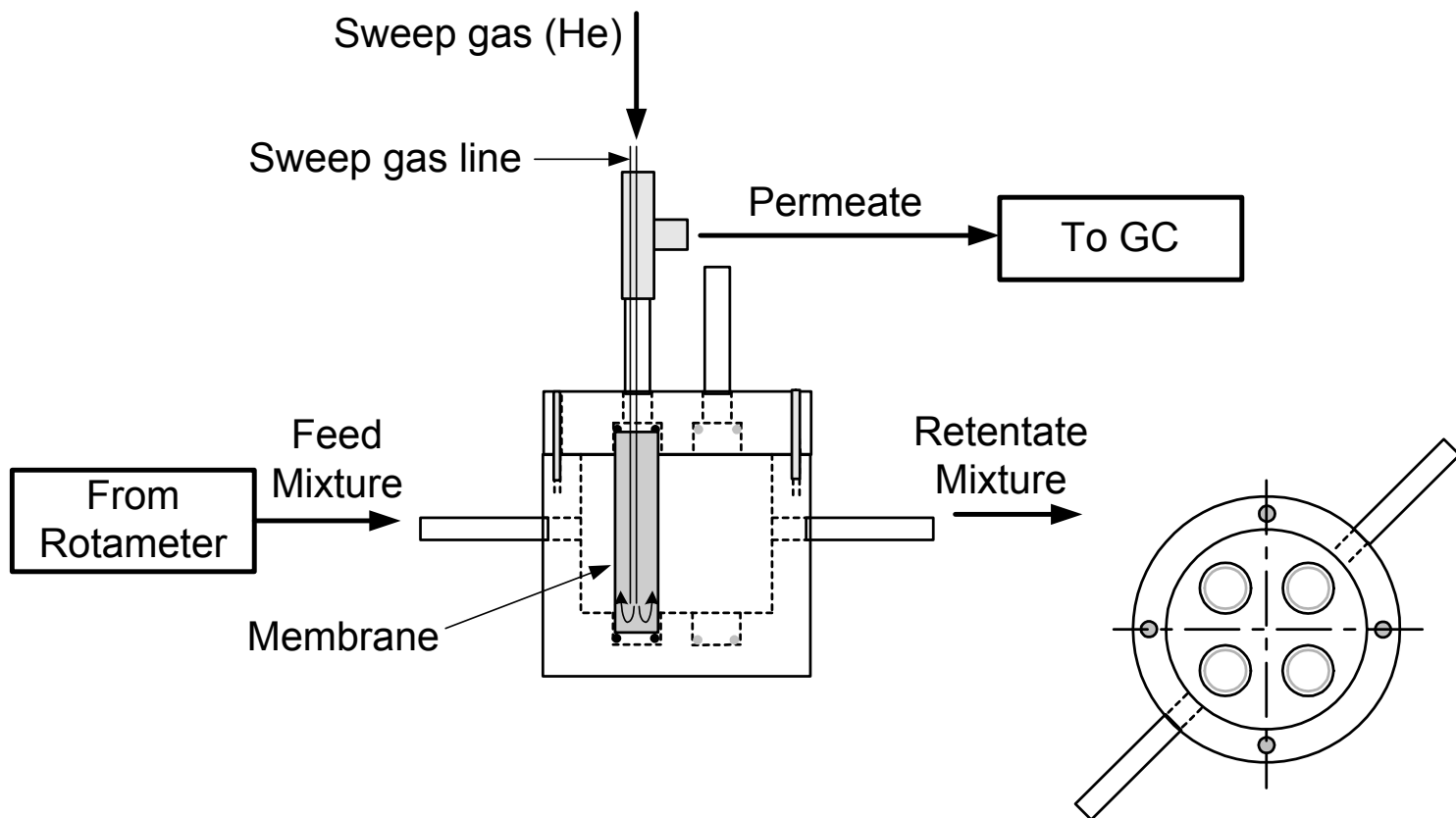


Figure 2. Four-port permeation cell.

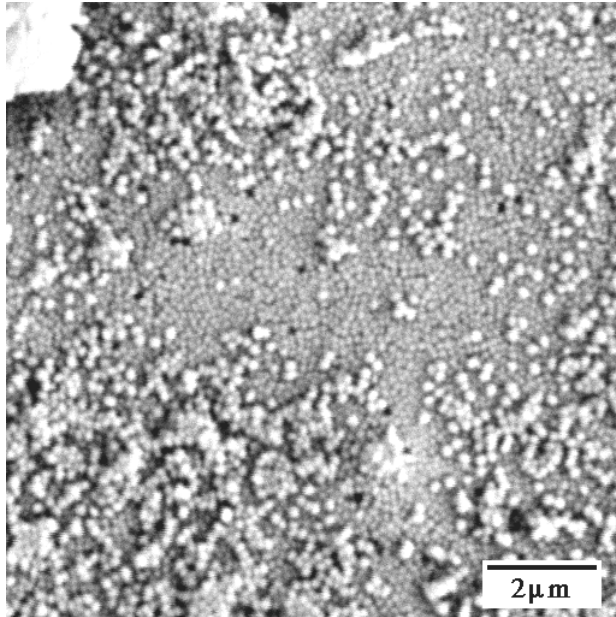


Figure 3. Scanning electron micrograph of seed particles.

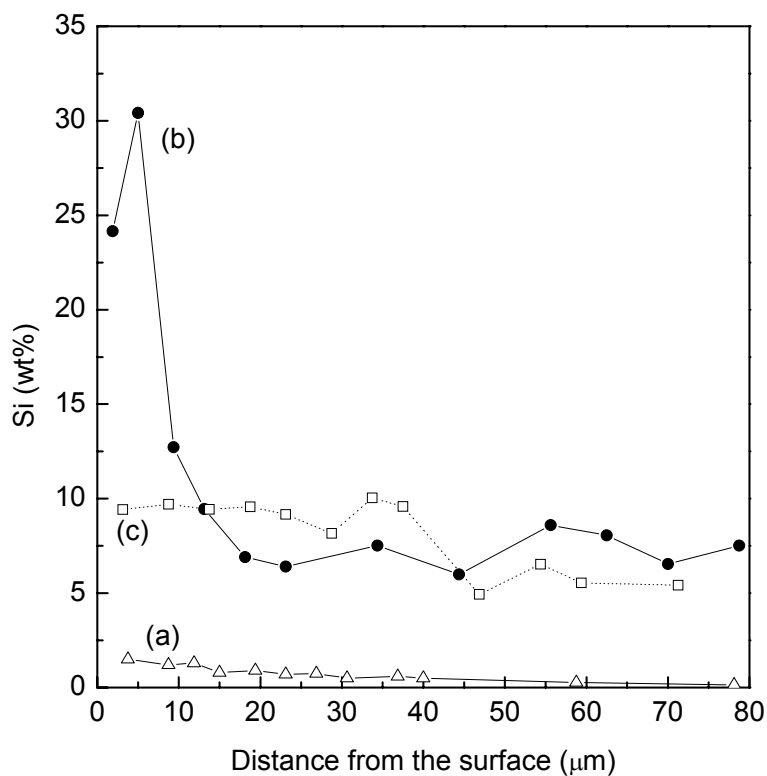


Figure 4. EDS profiles of silicon over the cross-section of membranes at different stages of preparation : (a) seeded before growth, (b) after seeding and three growth cycles, and (c) unseeded after three growth cycles.

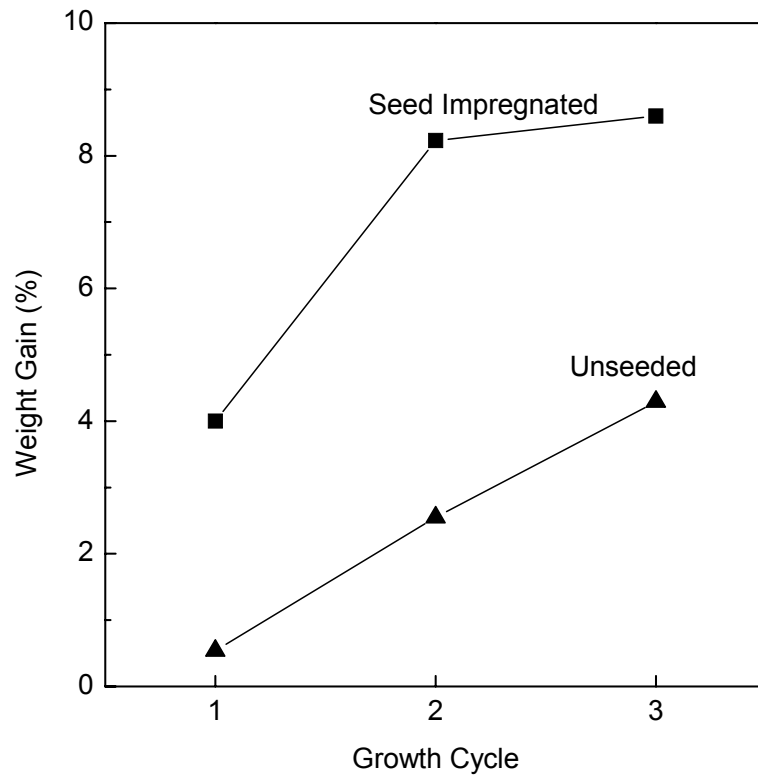


Figure 5. Weight gain vs. growth cycle.

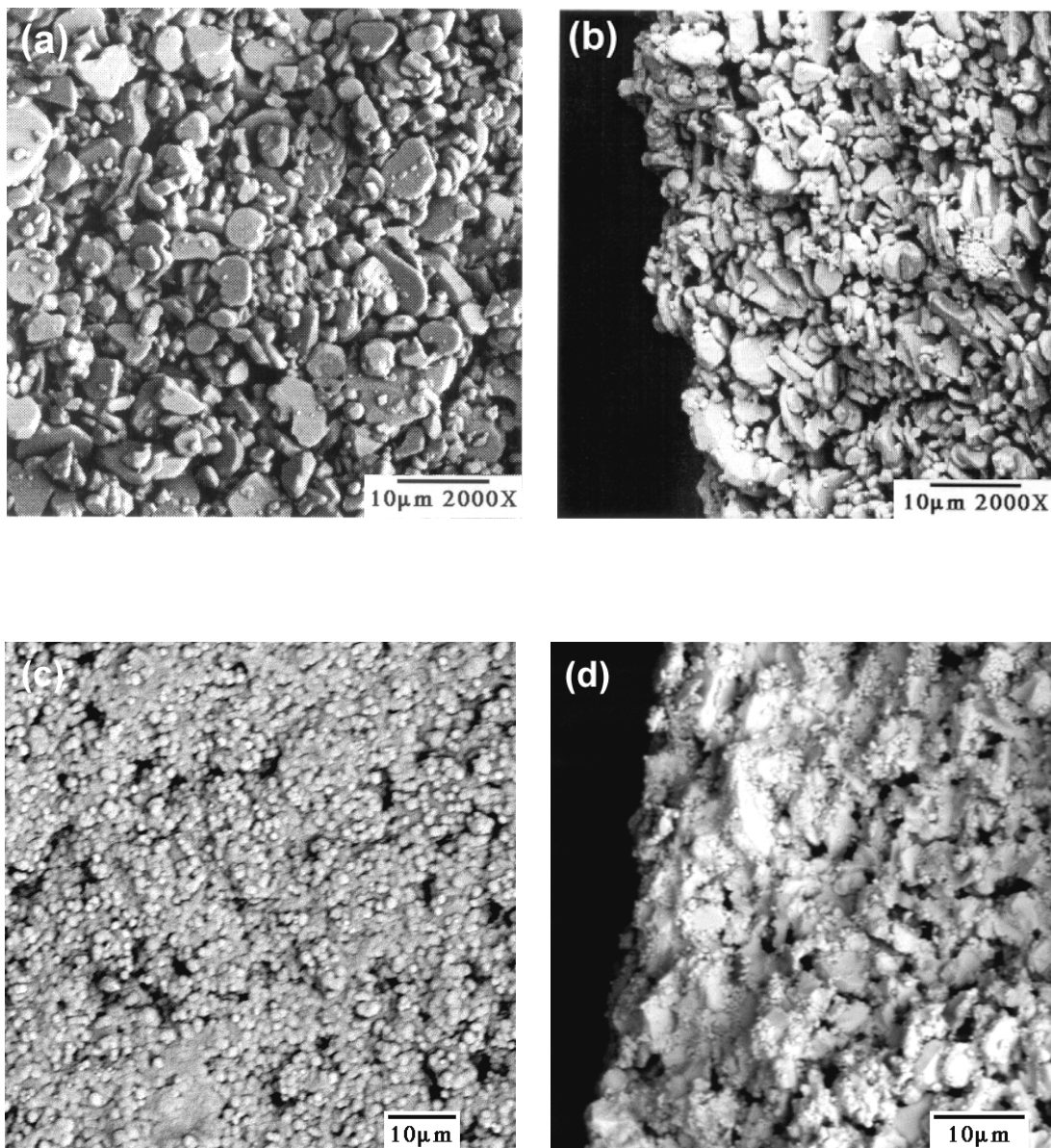


Figure 6. Scanning electron micrographs of a bare support and a silicalite membrane : (a) support surface, (b) support cross-section, (c) membrane surface, and (d) membrane cross-section.

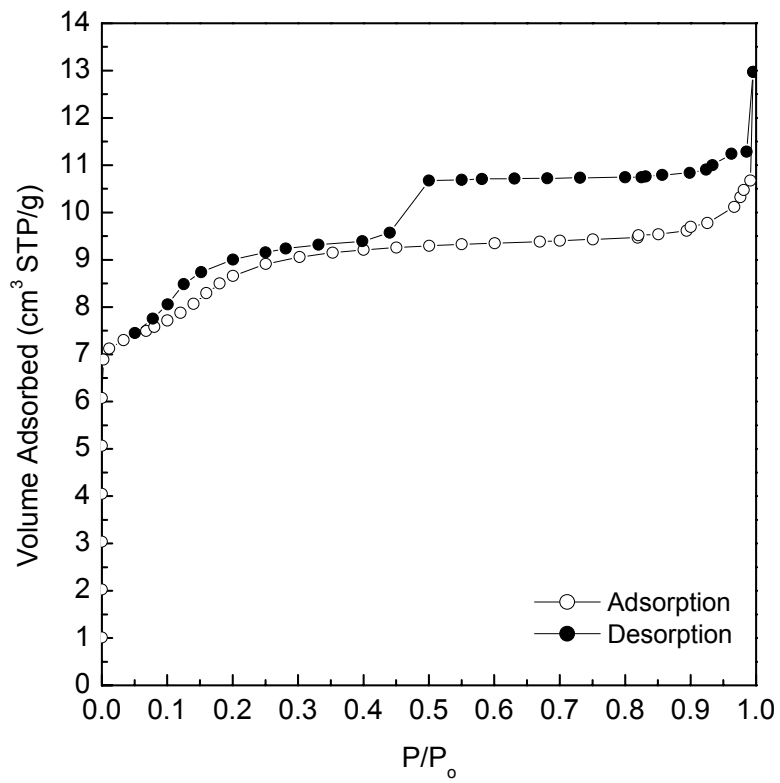


Figure 7. Nitrogen adsorption – desorption isotherm at 77K of a membrane after three growth cycles and calcination.

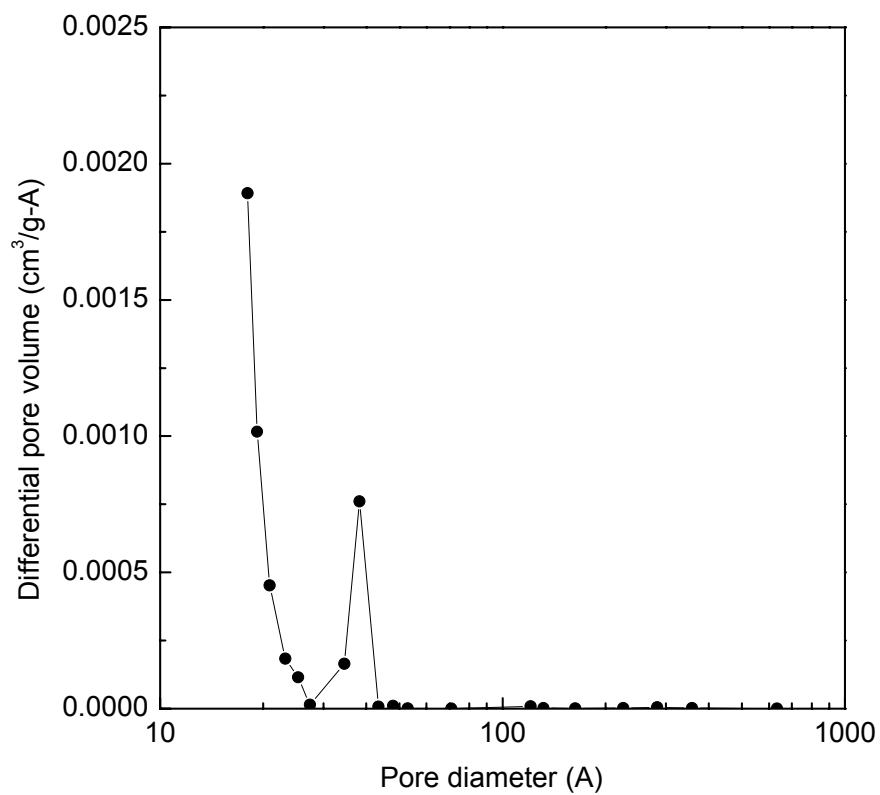


Figure 8. Differential pore size distribution of the membrane of Figure 7, calculated from the desorption isotherm by the BJH procedure.

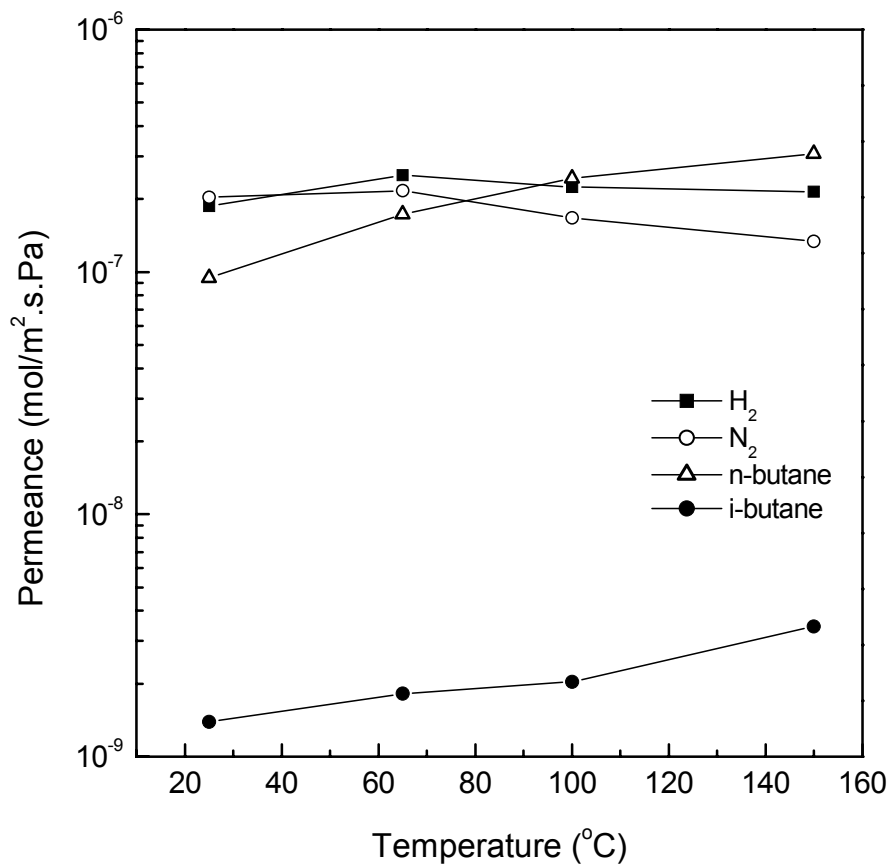


Figure 9. Temperature dependence of gas permeances of a silicalite membrane measured by the pressure rising method.

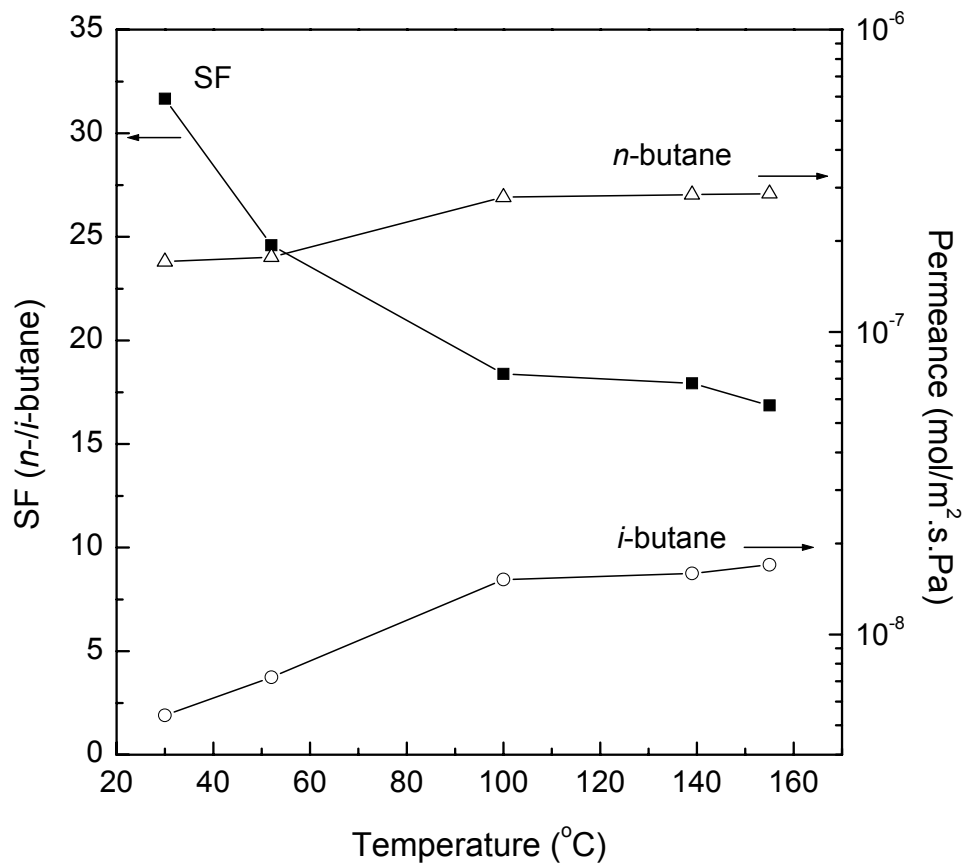


Figure 10. Temperature dependence of permeance and separation factor (SF) of a silicalite membrane after three growth cycles.

CHAPTER 2. Deposition of Silica Hydrogen-Permselective Layers on Silicalite/ α -Al₂O₃ Supports

This chapter describes the chemical vapor deposition (CVD) of silica layers on composite silicalite/ α -Al₂O₃ supports, the preparation of which was the subject of the previous chapter. Silicalite is known to have high selectivity for certain hydrocarbon separations but has little selectivity for separation of hydrogen from mixtures with N₂, CO₂, CO, H₂O because all these molecules have diameter below 0.36 nm and readily pass through the 0.55 nm channels of the zeolite. The function of the final dense silica layer deposited by CVD is precisely to provide the desired hydrogen separation selectivity.

As mentioned in chapter 1, the silicalite layers deposited on α -Al₂O₃ contain defects such as cracks or voids between the crystals. These voids are due to incomplete growth of the crystals or, more commonly, are generated during the calcination employed to remove organic templates employed in the growth solution [11, 12]. In the present chapter we describe results on silica/silicalite/ α -Al₂O₃ membranes prepared by deposition of silica using silicon tetrachloride hydrolysis at temperatures 400-600°C.

It has been known from earlier research that chemical vapor deposition (CVD) of silica from alcoxide precursors can modify the transport properties of ZSM-5 and silicalite single crystals (not membranes). The alcoxide precursors were too large to enter the zeolitic channels, hence, the property change was attributed to narrowing of pore mouths and elimination of acidic centers on the external surface of the crystals. In later studies, silica CVD was also examined as a means of eliminating zeolite membrane defects. Silica CVD was applied to silicalite or ZSM-5 membranes by ambient-temperature oxidation of tetraethyl orthosilicate (TEOS) with ozone supplied at opposite sides of the membranes. This

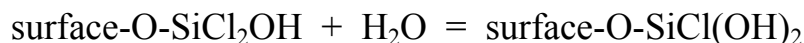
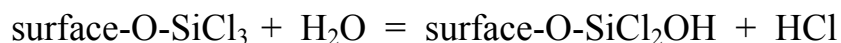
treatment increased the membrane ideal selectivity between n-butane and isobutane from 9 to 88 after 8 hours of reaction at the cost of some decrease of membrane permeance [13]. In another study [14] larger defects in silicalite membranes were sealed by dip-coating in a colloidal silica suspension by means of which the membranes were rendered selective for separation of xylene mixtures.

In previous research in our laboratory silica deposited at high temperatures from silicon tetrachloride precursors on porous glass tubes (Vycor glass) was highly hydrogen permeable in a wide temperature range. Deposition was carried out by a series of alternating (non-overlapping) exposures to silicon tetrachloride and water vapor selected to control the membrane thickness to the minimum required for sealing the pores of the glass support. Deposition of silica by alternating reactions with silicon tetrachloride and water vapor has also been studied for γ -Al₂O₃ substrates. The generally accepted reaction mechanism is as follows:

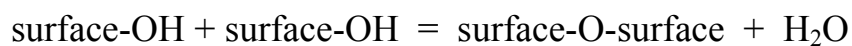
Reaction of surface with SiCl₄ (silylation)



reaction with H₂O (hydrolysis)



Condensation (occurring throughout the cycle)



where in the last two reactions the OH and Cl moieties are attached on surface silicon atoms. It is clear that once the reaction gets started the nature of the original substrate becomes immaterial. However, the number of silanol (Si-OH) groups on the original surface is bound to influence the early phase of silica growth.

In the present study the main objective was to use the alternating CVD reaction to deposit a hydrogen permselective silica layer. Infiltration in the zeolitic channels was not expected to be extensive given that the molecular diameter of silicon tetrachloride (0.55 nm based on covalent atomic radii) is very close to that of the MFI channels (0.51-0.55 nm).

Experimental

Silica CVD

The preparation of silicalite/ α -Al₂O₃ supports was described in the previous chapter. CVD on these supports was carried out using the apparatus shown in Figure 11. The support was held horizontally in a quartz tube connected to vacuum and to two reactant reservoirs through on-off valves. One of the reservoirs contained water, the other contained the silylating agent (silica precursor). In most experiments, the silylating agent was silicon tetrachloride, SiCl₄ (ST), in a few experiments the trimer hexachlorodisiloxane, Cl₃SiOSiCl₂OSiCl₃ (HCDS) was used instead. The quartz tube was held inside a furnace at a specified temperature between 400 and 700°C. Deposition was carried out in a sequence of cycles, each of which consisted of the following 1-minute steps:

- (i) with the reservoir valves closed the quartz tube was evacuated for 1 minute,
- (ii) the valve to vacuum was shut and the valve to silicon tetrachloride reservoir was opened for 5 seconds and then shut; all valves were maintained shut for 1 minute,
- (iii) the valve to vacuum was opened for 1 minute and then shut,
- (iv) the valve to the water reservoir was opened for 5 seconds and then shut; all valves were kept closed for 1 minute

The temperature of each of the two reactant reservoirs was controlled independently so that when the respective valve was shut the vapor pressure soon came to equilibrium with the liquid. When the valve was subsequently opened up

the vapor filled a larger volume with a corresponding drop in the vapor pressure. After a few seconds the valve to the reservoir was shut and the reaction proceeded in a batch fashion so that its extent in each cycle was controlled by the reservoir temperature and by the length of the period before evacuation.

Characterization

Zeolite crystal powder grown in the bulk of the solution was examined by solid state NMR and gas adsorption before and after CVD.

Permeation Measurements

The permeance of several gases was measured every 5 reaction cycles by removing the tube from the reaction apparatus and placing it in a temperature controlled permeation cell. Most measurements were conducted with single gases (H₂, N₂, CO₂, CH₄, n-C₄H₁₀, i-C₄H₁₀). Permeance above 0.1 MPU (1 MPU= 10⁻⁸ mol/m²-s-Pa) was measured using continuous flow with the feed passing outside of the tube at 1.5-2 bar pressure, and the permeate gas collected from the tube bore at atmospheric pressure. The flowrate was measured using an electronic flowmeter. When the permeance was below 0.1 MPU, the measurements were conducted using the pressure rise method. For that purpose the feed was passed at the outside of the tube at 1 bar pressure while the tube bore was kept under vacuum. After allowing sufficient time to reach steady permeation through the membrane, the valve to vacuum was shut and the rising pressure was measured by a sensitive capacitance gauge. The permeance was then calculated from the rate of pressure rise and the calibrated volume of the tube bore plus the volume of the tube connecting to the pressure gauge.

Results and Discussion

Characterization

Solid state NMR of zeolite powder was taken before and after CVD to probe the silica species deposited on the zeolite. The spectrum before silica deposition

had considerable peak overlap, but after deposition the spectrum had sharply defined peaks, all of which correspond to the known spectrum of silicalite (MFI structure). There was no peak characteristic of a new species.

Nitrogen adsorption and desorption isotherms were performed before and after deposition. Figure 12 shows the micropore volume distribution calculated from the low relative pressure region of the isotherm using the MP method. Although the absolute pore sizes using the MP and other methods are model dependent and subject to considerable uncertainty, the comparison between the results before and after silica deposition is meaningful. The larger peaks at about 0.1-0.3 nm pore radius can be attributed to the zeolitic channels. Deposition clearly shifts the peak center from around 0.23 to 0.2 nm and increases the total volume in this region. Before deposition, the membrane also possessed micropores of radius 0.5-0.75 nm. Deposition appears to have shifted these nonzeolitic micropores to lower radii. The size of SiCl_4 sets a lower bound of about 0.25 nm below which no further pore reduction is possible.

Permeation Results

Permeation rates of single gases during silica deposition on one membrane are shown in Figures 13 and 14. The decline of the hydrogen flux is much slower than that of other gases as deposition proceeds. Among the other gases n-butane has the most rapid flux decline until about cycle 15. Isobutane declines more slowly and both butanes stop declining after about 20 cycles. These results are consistent with a distribution of transport pathways. The bulk of the transport for all gases takes place through the zeolitic channels as evidenced by the high initial ideal selectivity between the two butanes. The faster decline of flux of n-butane vs. isobutane suggests that a significant fraction of the isobutane flux proceeds through nonzeolitic pathways, i.e., through defects.

Some information about the membrane defects can be obtained by comparing the flux decline of the two butanes. If we assume that zeolitic channels narrowed by silica CVD are inaccessible to both butanes, then the fractional decline of both fluxes through the *zeolitic channels* must be the same. The overall decline factor in 15 cycles is about 600 for n-butane but only 25 for isobutane, implying that the bulk of the isobutane flux is through nonzeolitic pathways that are only very slowly obstructed by the silica CVD. In fact, there is little flux change of either butane after 20 reaction cycles. This residual flux must be due to a few relatively large defects, tens of nanometer in diameter, that are only very slowly narrowed by silica deposition. As shown in previous work each reaction cycle adds only about 0.03 nm of silica on a flat silicon chip.

Figure 15 shows the temperature dependence of the permeances of three gases vs. temperature in the range 100-250°C. The hydrogen and nitrogen permeances increase slightly with temperature while the permeance ratio declines from 140 at 100°C to 110 at 250°C. The carbon dioxide permeance declines slightly with increasing temperature, consistent with the role of adsorption for this particular gas. Although measurements were not conducted above 250°C, it is expected that the membrane separation selectivity will decline further with increasing temperature. Measurements on several other membranes prepared under similar conditions yielded similar results.

In an effort to verify that the change of permeation properties was due to narrowing of the zeolitic channels, experiments were carried out using the “dimer” HCDS instead of SiCl₄. Although of similar cross section, the longer dimer was expected to diffuse more slowly through the zeolitic channels. Figure 16 plots again the fluxes of several gases vs. number of CVD cycles using HCDS up to cycle 30 followed by SiCl₄. The hydrogen and nitrogen fluxes were unaffected even after 30 cycles, while the flux of butanes remained constant for the first 10

cycles but declined afterwards. These results imply negligible penetration of HCDS in the zeolitic channels. Moreover, the decline of the flux of butanes after the 10th cycle could be due to deposition of a thin silica layer around the crystals gradually restricting the flux of butanes but not that of hydrogen and nitrogen.

Conclusion to Chapter 2

Chemical vapor deposition on the silicalite/ α -Al₂O₃ tubes was carried out by alternating reactions of the support with silicon tetrachloride and water vapor. Permeation measurements with several gases (H₂, N₂, CO₂, CH₄, n-C₄H₁₀, i-C₄H₁₀) at different extents of CVD showed that (i) silicon tetrachloride penetrates and restricts the silicalite channels (ii) CVD is insufficient to seal the 100 nm defects in the silicalite layer. The final membranes have hydrogen permeance about 0.6×10^{-7} mol/m²-s-Pa (0.8 mL(STD)/cm²-min-atm) at 150°C, and H₂:N₂ ideal selectivity of about 200.

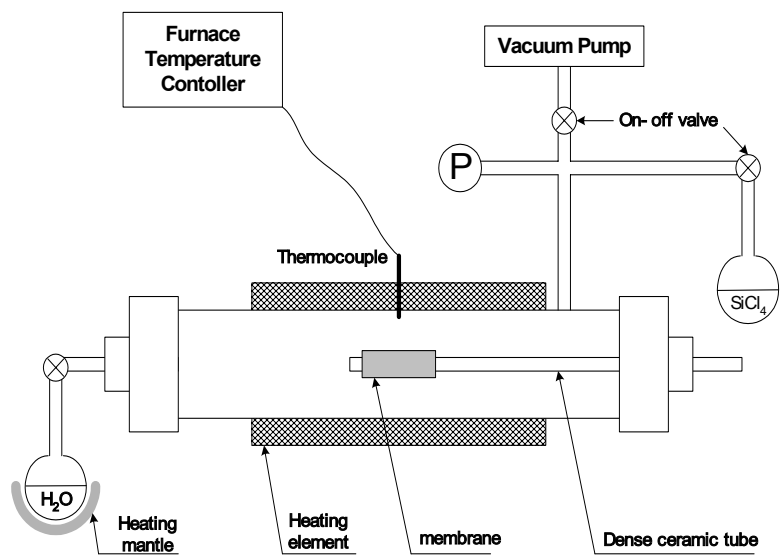


Figure 11. Apparatus for silica CVD by half reactions of $SiCl_4$ and H_2O

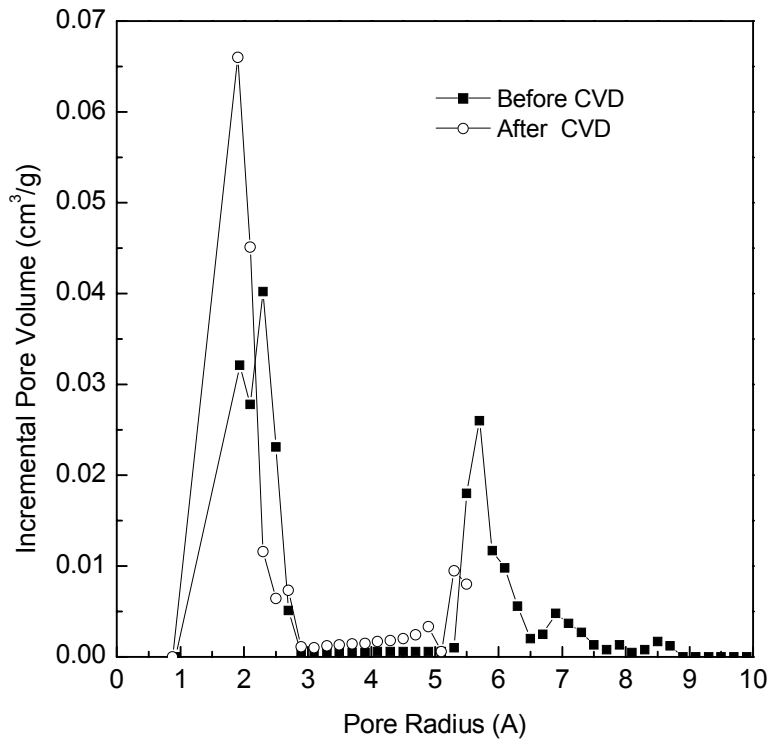


Figure 12. Pore size distribution of silicalite powder before and after CVD

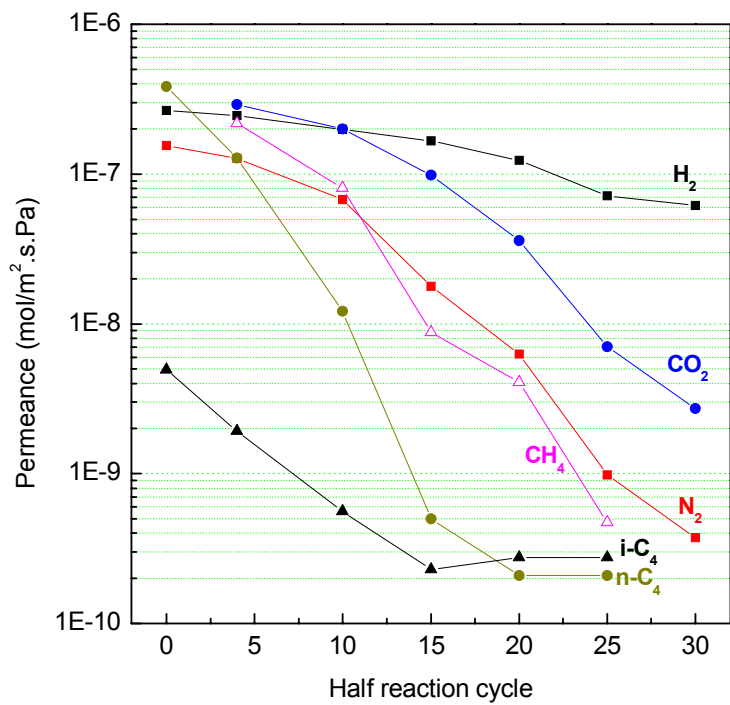


Figure 13. Permeance of single gases at 150°C vs. CVD cycle at 450°C.

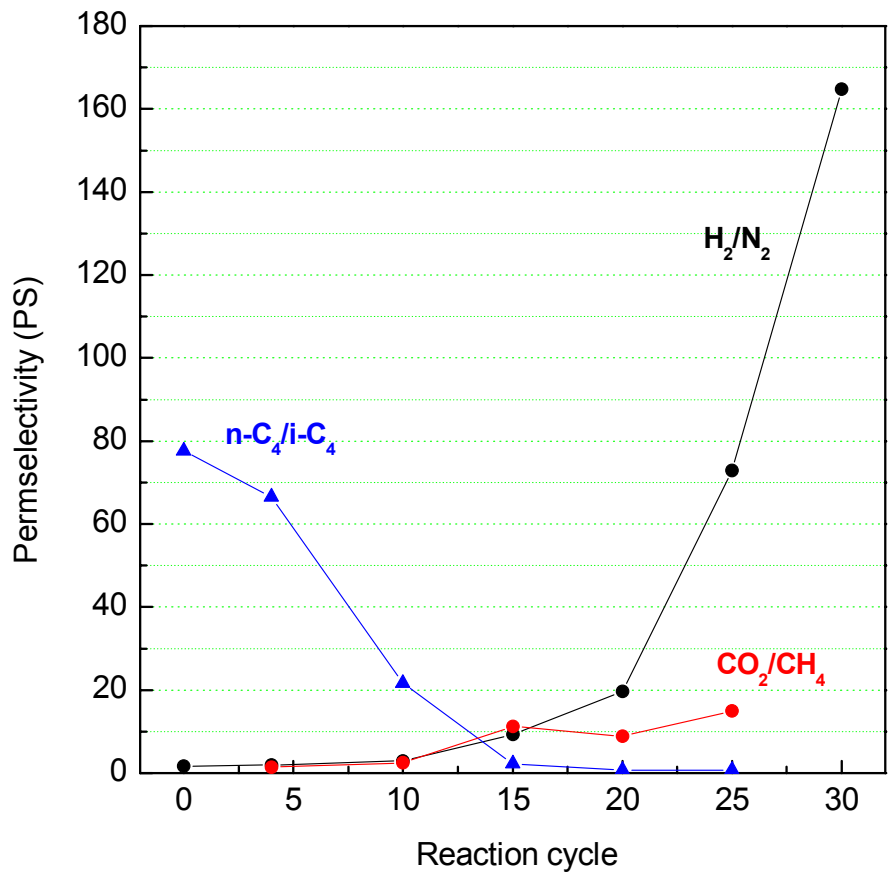


Figure 14. Ideal selectivity of a membrane at 150°C vs. number of CVD cycles at 450°C.

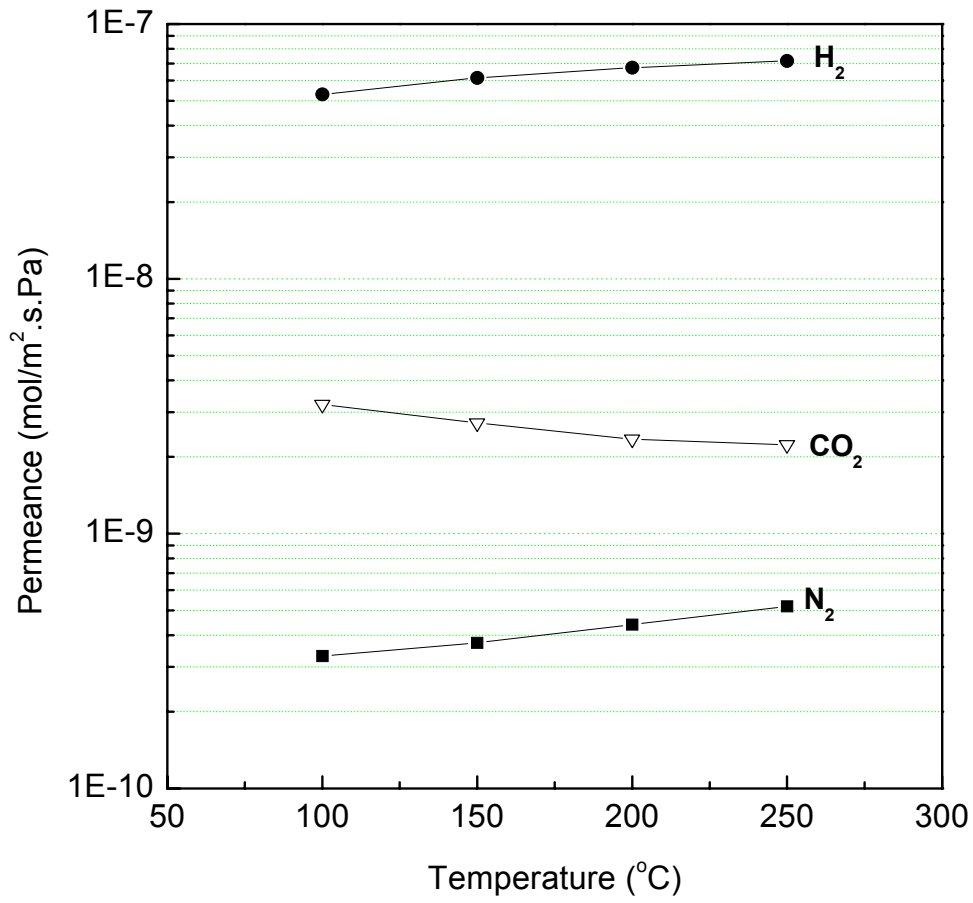


Figure 15. Temperature dependence of single gas permeances

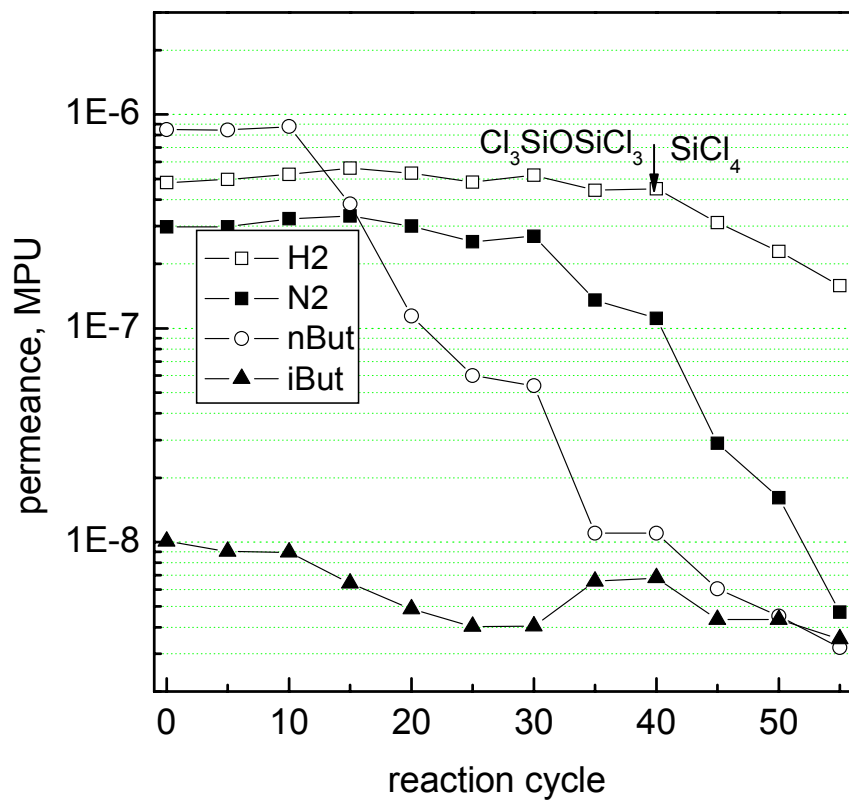


Figure 16. Permeance of several gases at 150oC vs. CVD cycle number at 450oC. Cycles 1-40 carried out with the dimer HDS, cycles above 40 with the monomer ST.

CHAPTER 3. Development of Porous Glass Tubes

As detailed in chapter 2, CVD treatment of silicalite/ α -Al₂O₃ supports yielded membranes with hydrogen to nitrogen single gas selectivity up to 200 which, however, declined with temperature. In an effort to develop membranes with higher temperature capability work was carried out on the development of porous glass supports of high permeance, as mentioned in the general introduction. The results of this work are described in this chapter.

Thin ceramic tubes (alumina, zirconia etc) had been previously made by extrusion of a ceramic powder mixed with a polymer or some other binder [15,16], or by extrusion of a particle-polymer-solvent mixture followed by gelation (phase-inversion) in a nonsolvent [17-21]. In both techniques the gelled precursors containing the ceramic powder and the polymer are heat-treated in air to decompose the polymer and burn out the residual carbon. The ceramic particles are then sintered to a dense or porous structure.

In contrast to ceramic tubes, very thin glass tubes (hollow fibers) have been made by extrusion from the *melt* [22, 23] which, however, requires special high temperature extrusion equipment. In the present project it was decided to employ room temperature extrusion from a suspension of glass particles rather than extrusion from the melt. Extrusion was carried out using a home-made apparatus. After extrusion and heat treatment the nonporous glass tubes were leached in water to generate connected porosity by removing the soluble phase generated during cooling. Additional details on the preparation of porous glass tubes by extrusion are given in a recent report from our laboratory [24].

Experimental

Materials

A glass of composition 9.1% Na₂O–29.7% B₂O₃–61.2% SiO₂ (by weight) was supplied by Corning Inc. in the form of chips approximately 0.5 mm thick. The chips were crushed and ball-milled to a glass powder that was used as the starting membrane material. Polyethersulfone (PESf) [Radel A-300, Ameco Performance, USA], and N-methyl-2-pyrrolidone (NMP) [Synthesis Grade, Merck] were used for preparing the starting suspension. Polyvinylpyrrolidone (PVP, K90) [GAF[®] ISP Technologies, Inc. M_w = 630,000] was used as an additive. Tap water was used as both the internal and external gelation medium (nonsolvent).

Tube Preparation

PESf was slowly added under stirring in NMP to form the polymer solution. After the polymer solution was formed, a given amount of glass powder was added and the mixture was stirred for 24 hours to ensure that the glass particles were dispersed uniformly. PVP was also introduced into the solution as an additive to adjust the viscosity. Finally the suspension was degassed at room temperature, transferred to a stainless steel reservoir, and pressurized with nitrogen to 40 psig. The degassed suspension was extruded through a *tube-in-orifice* spinneret with orifice diameter and inner diameter 2.5 and 0.72 mm respectively. The extruded tubes emerging from the spinneret at 10 cm/min were passed through an air gap of 4 cm and immersed in a water bath to complete gelation.

After thorough washing in water, the gelled tubes were heated in an electrical furnace at 800-950°C for several hours to decompose the polymer, burn out any residual carbon, and sinter the glass particles. For that purpose a glass-polymer tube of approximately 8 cm length was placed in an alumina tube of 3.5 mm ID, 5 mm OD and 20 cm length, plugged at one end, serving as a sample holder. The sample holder was inserted in a furnace so that the glass-polymer tube was located

in the central, relatively uniform temperature section. The open end of the alumina sample holder protruded 8 cm outside of the furnace and was open to the atmosphere. The details of the heat treatment are crucial to the properties of the final tube. When the glass-polymer precursor is inserted in a *preheated furnace*, heating is relatively rapid so that the polymer is converted to relatively unreactive carbon before oxidation can be completed [24]. By inserting the sample in the furnace at room temperature and heating it to the final temperature at a specified heating rate it is possible to oxidize the polymer residue before sintering of the glass particles takes place.

After heat treatment, the glass tubes were leached in aqueous acid or in hot water at a specified temperature and for a specified time to generate connected porosity. The conditions of leaching are also important to the final tube properties [24].

Tube Characterization

The glass-polymer tubes were examined with a scanning electron microscope (JEOL JSM-5600 and LEO 1550 VP field emission SEM). After immersion in liquid nitrogen for about 5 minutes these precursor tubes were slowly flexed until a clear cross-sectional fracture occurred. The tubes were subsequently gold-coated using sputter coating under vacuum. In the case of the sintered glass tubes, the clear cross-sectional fracture was obtained by direct breaking. SEM micrographs of tube surfaces and cross-sections were taken at various magnifications.

The original glass powder and the crushed heat-treated glass samples were examined using an X-ray diffractometer for the possible presence of crystalline phases. The permeance of several gases was measured at several stages of tube preparation, i.e. for the glass-polymer precursor, the heat-treated tube, and the leached tube. To measure gas permeation, one end of the tube was sealed by a

quick-setting epoxy resin and the tube was placed within a larger concentric steel tube. Nitrogen or other gases were passed at about 2 bars through the annulus while the permeate collected at the ID side was conducted to a bubble flowmeter. The permeance was calculated from the tube dimensions, permeate flow rate, and feed pressure by the equation:

$$J = \frac{Q}{\pi L D \Delta p}$$

where J, Q, D, L and Δp are the gas permeance ($\text{mol/m}^2 \cdot \text{Pa} \cdot \text{s}$), permeate flowrate (mol/s), fiber OD (m), length (m), and partial pressure difference across the fiber wall (Pa), respectively.

Results and Discussion

When subjected to relatively mild heat treatment the glass particles do not undergo densification and the resulting tubes are not gas-tight, even before leaching. By using more severe heat treatment the pores can be partially or completely eliminated resulting in a gas-tight structure. Our results indicate that dense tubes can be prepared using the following conditions:

- (i) The glass to polymer weight ratio in the starting suspension is about 8.
- (ii) The glass-polymer tubes are heated to a final temperature in the range 800 to 930°C for 5 to 15 hrs.

At lower temperatures there is little particle consolidation, at higher temperatures the glass melts to a shapeless mass.

Following heat treatment the densified glass tubes were leached in aqueous acid solution to generate connected porosity. It was found that glass tubes leached in aqueous acid solution (i.e., HCl, HNO₃) had low mechanical strength and were usually broken during leaching. When, instead, leaching was carried out in hot

water, the mechanical strength of the leached tubes improved greatly. Figures 17 and 18 show SEM micrographs of a glass tube cross section and OD surface before leaching. The cross section micrograph indicates complete fusion of the glass particles. Figure 19 shows SEM of the glass surface after leaching. The cross section is covered with pits of about 100 nm diameter, suggesting that the actual pore size is also about 100 nm.

In the traditional Vycor process in which the tubes are made using melt extrusion, the pores that result from leaching have usually about 4.5 nm mean diameter. The major cause for the larger pore size obtained in this project may be the facile phase separation resulting in domains of about 100 nm size. Phase separation takes place during cooling at about 700°C. Evidently, the BSG composition used has relatively low viscosity at the temperature that phase separation takes place enhancing diffusion and growth of the phase domains. Future work should consider the addition of small amounts of ZrO₂ or some other additive additives to retard phase separation and lower the resulting pore size.

Figure 20 is a lower magnification SEM of a tube cross section before leaching. The micrograph shows voids as large as 20 μm in the interior of the cross section but very few of these voids reach the tube surface. SEM observations show that the large voids are generated during gelation by complex diffusion and phase separation mechanisms similar to those encountered in the preparation of polymeric membranes. The presence of large particles in the initial glass powder may also contribute to these inhomogeneities. The glass powder had been prepared by the traditional ball-milling method resulting in a wide size distribution, including particles on the order of 10 μm. Presence of such large particles may hinder complete densification during heat treatment leaving a distribution of large

voids. Incomplete densification may also be responsible for the loss of mechanical strength upon leaching. .

Table 1 shows the gas permeation and ideal selectivity factors of glass tubes prepared under different heat treatment conditions. In all cases the tubes were leached in boiling water for 24 hours. The lack of separation selectivity shown in Table 1 indicates transport in the Transition (viscous-Knudsen) or viscous flow regimes consistent with the pore size observed in Figs. 19 and 20.

Table 1 Gas permeation and ideal selectivities for SBS glass membranes

Samples Sintering Temp. °C	Permeance (10^{-6} mol/m ² sPa) (1atm)												Selectivity					
	Room Temperature						105°C						Room Temperature			105°C		
	H ₂	He	N ₂	CO ₂	nC ₄	iC ₄	H ₂	He	N ₂	CO ₂	nC ₄	iC ₄	He/N ₂	N ₂ /CO ₂	iC ₄ /nC ₄	He/N ₂	N ₂ /CO ₂	iC ₄ /nC ₄
800	30.2	19.0	11.2	11.1	15.7	15.4	21.62	13.9	8.00	7.40	8.43	9.01	1.70	1.01	1.02	1.7	1.1	0.93
800	25.0	14.0	9.8	9.81	14.0	13.4	14.2	8.96	5.55	5.35	8.13	8.26	1.42	1.00	1.04	1.6	1.0	0.98
850	2.9	2.0	0.97	0.89	1.37	1.13	-	1.67	0.78	0.65	0.67	0.72	2.09	1.09	1.21	2.1	1.2	0.92
900	18.8	11.5	6.53	7.1	12.0	11.16	-	0.93	5.24	5.02	7.0	7.18	1.76	0.91	1.08	1.7	1.0	0.97
900	13.7	5.6	4.86	4.61	-	-	-	-	-	-	-	-	1.76	1.05	-	-	-	-
930	31.9	21.0	11.4	10.6	20.3	18.9	14.0	98.4	30.1	28.6	25.3	23.9	1.84	1.08	1.07	3.3	1.0	1.07
930	8.3	6.1	2.98	2.80	4.23	3.96	15.4	8.32	5.42	4.36	5.60	4.94	2.04	1.06	1.07	1.5	1.2	1.13
930	29.9	19.4	10.5	10.1	-	-	-	-	-	-	-	-	1.84	1.04	-	-	-	-

Conclusion to Chapter 3

An extrusion technique was developed for making glass tubes about 2 mm OD and 0.25-0.5 mm wall thickness. After heat treatment and leaching these tubes developed pores of approximately 100 nm size, possibly due to rapid phase separation of the glass during cooling and solidification. Some glass tubes contained voids of 10-20 μm formed during gelation of the extruded glass-polymer tubes. The presence of large particles in the mixture is a contributing factor to the persistence of these large voids, but it is not certain that the large voids penetrate through the tube surface to provide alternate transport pathways. Permeation

measurements indicate transport in the transition or viscous flow regimes resulting in very low separation selectivity.

Because of the presence of pores above 10 nm diameter, the porous glass tubes reported in the present chapter were not suitable as supports for the deposition of hydrogen permselective membranes. Achieving smaller pore size, below 5 nm, requires changes in the glass composition to retard phase separation, and use of finer glass particles to eliminate inhomogeneities in the glass-polymer suspension.

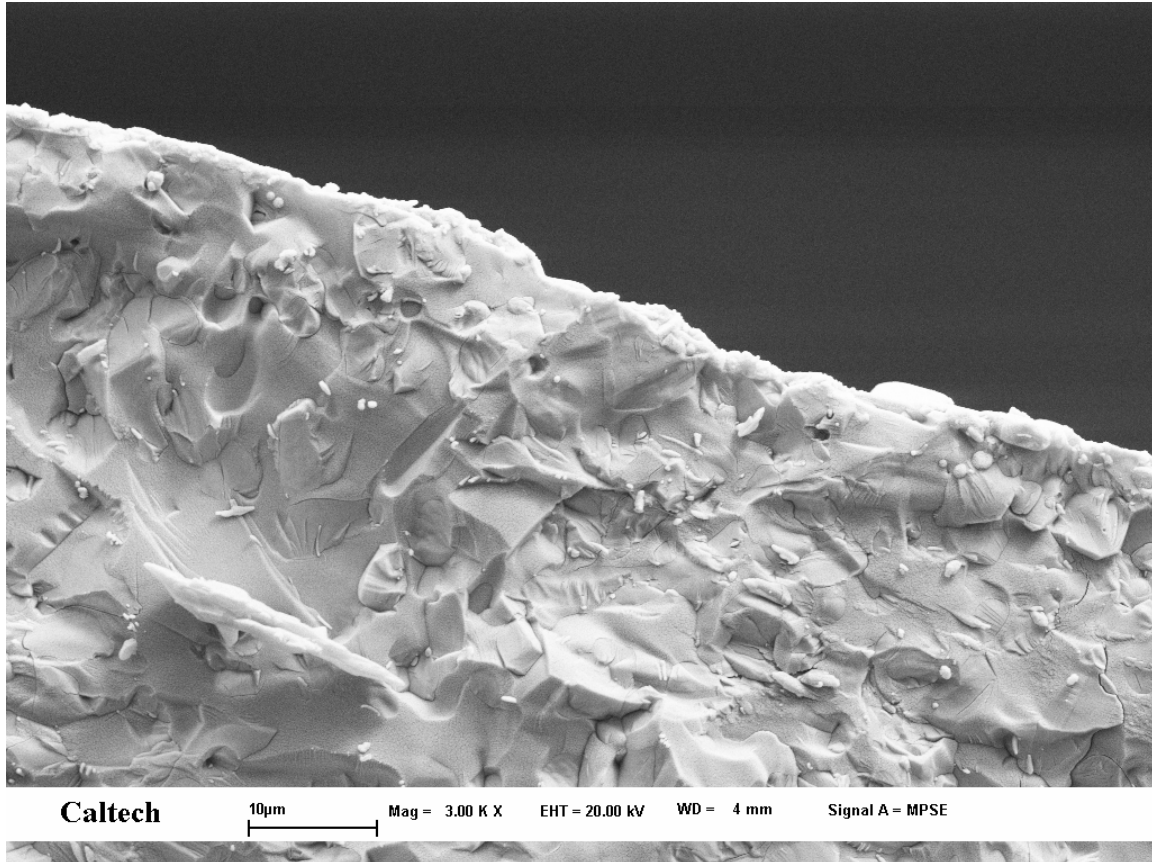


Figure 17. SEM of cross section of a glass tube after heat treatment but before leaching.

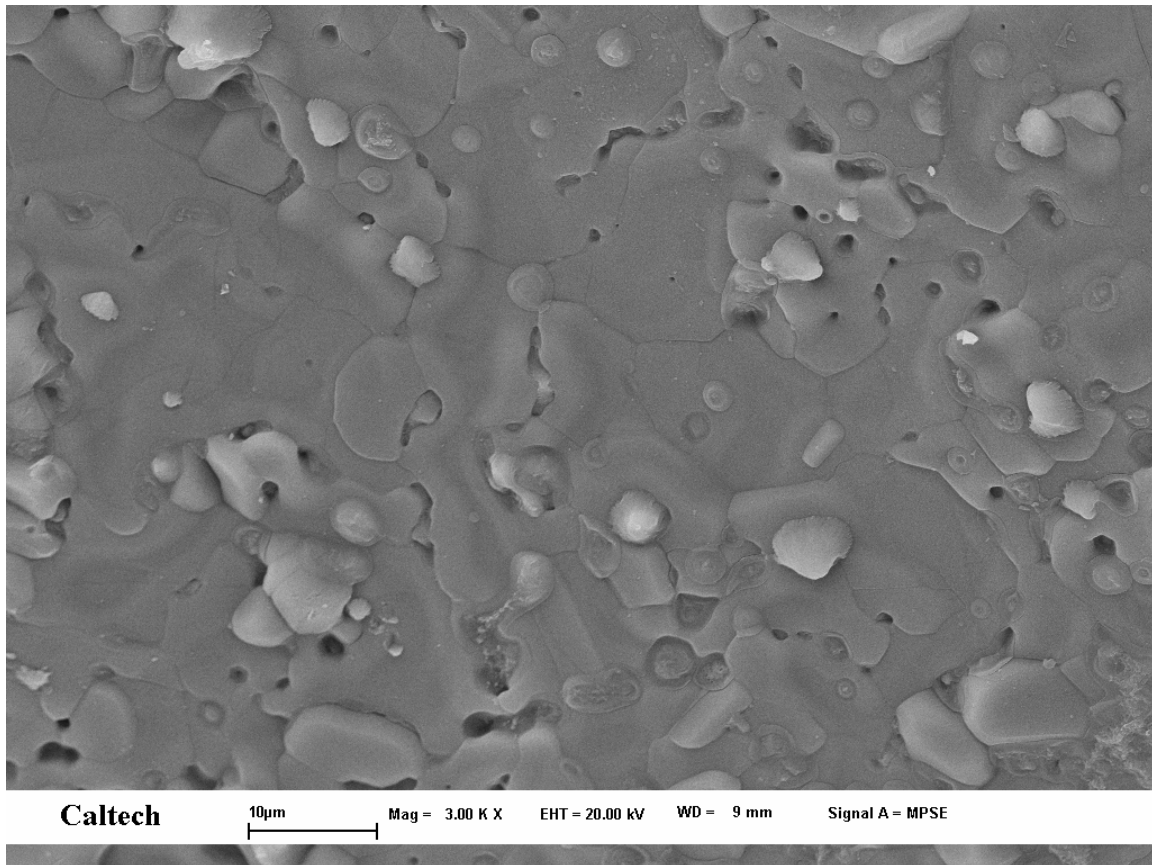


Figure 18. SEM of the surface of a glass tube after heat treatment but before leaching.

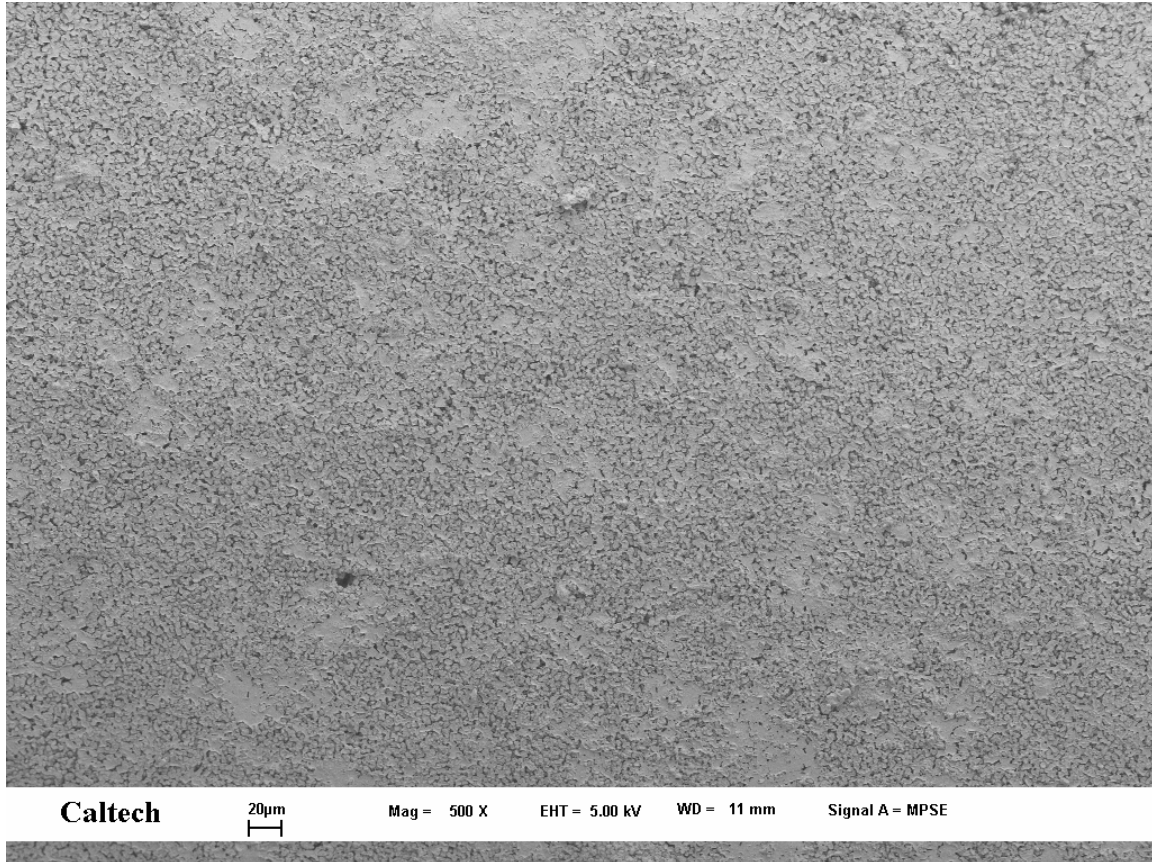


Figure 19. SEM of the surface of a glass tube after heat treatment and leaching.

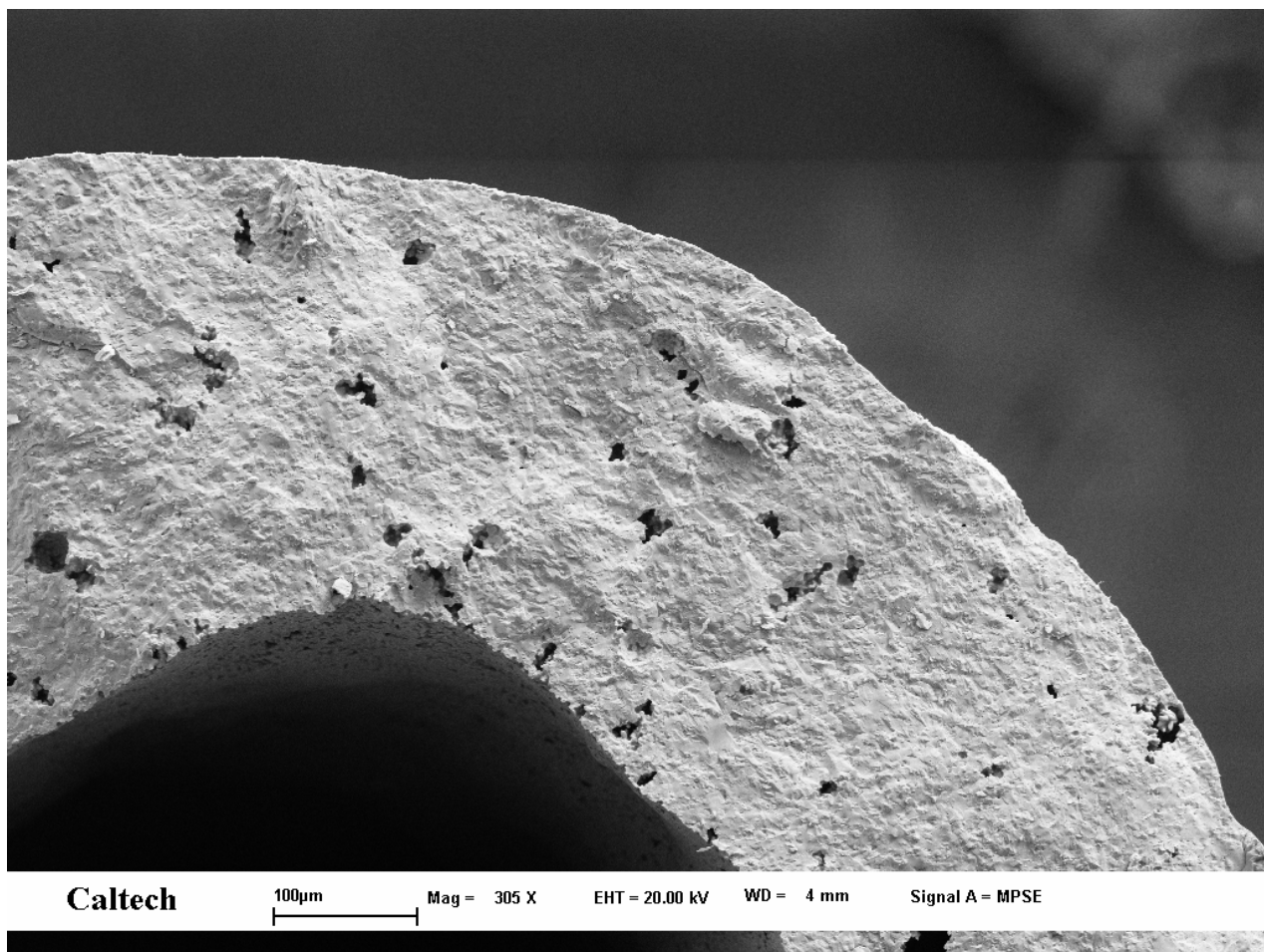


Figure 20. SEM of another glass tube cross section after heat treatment but before leaching.

CONCLUSION

Silicalite/ α -Al₂O₃ tubes were employed as supports for hydrogen permselective silica membranes. The tubes were prepared by hydrothermal growth of zeolite silicalite on α -Al₂O₃ tubes. Permeation and porosimetry experiments showed the presence of a limited number of defects with size on the order of 100 nm in the silicalite layer.

Chemical vapor deposition on the silicalite/ α -Al₂O₃ tubes was carried out by alternating reactions of the support with silicon tetrachloride and water vapor. Permeation measurements with several gases (H₂, N₂, CO₂, CH₄, n-C₄H₁₀, i-C₄H₁₀) at different extents of CVD showed that (i) silicon tetrachloride penetrates and restricts the silicalite channels (ii) CVD is insufficient to seal the 100 nm defects in the silicalite layer. The final membranes have hydrogen permeance, about 0.6×10^{-7} mol/m²-s-Pa (0.8 mL(STD)/cm²-min-atm) at 150°C, and H₂:N₂ ideal selectivity of about 200.

Membranes previously made in this laboratory using Vycor tubes as supports had H₂ permeance 0.1- 0.3 mL/cm²-min-atm and H₂:N₂ ideal selectivity about 1000 at 450°C, but had very low permeance at 200°C. In contrast, the membranes made in the present project had substantial permeance at moderate temperatures (about 200°C) but their H₂:N₂ selectivity declined rapidly with the temperature. Their H₂:CO₂ selectivity was only about 20, therefore, membrane separation of the water gas shift product would yield hydrogen containing up to 10% CO₂. Thus the membranes would be useful for hydrogen separation after the low temperature water gas shift when a 10% concentration of CO₂ is not a problem.

Work was also carried out on thin Vycor-type tubes as an alternative support for the CVD membranes. Tubes were made by extrusion of a glass suspension in a polymer solution followed by gelation and heat treatment. Upon leaching, the extruded glass tubes acquired pores of about 50 nm diameter which is too high for

further CVD processing to a useful membrane. Certain modifications in the glass composition and particle size are recommended to reduce the pore size down to the useful range of 3-5 nm.

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LIST OF ACRONYMS

BSG	borosilicate glass
CVD	chemical vapor deposition
DI	deionized water
EDS	energy dispersive spectroscopy
HCDS	hexachlorodisiloxane
ID	inside diameter
MPU	molar permeance unit
OD	outside diameter
PESf	polyethersulfone
SEM	scanning electron microscopy
ST	silicon tetrachloride
TEOS	tetraorthosilicate
TPA	tetrapropyl ammonium ion
WGS	water gas shift