CERAMIC MEMBRANES FOR

HYDROGEN PRODUCTION FROM COAL

Annual Technical Report

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DISCLAIMER

Abstract

The present project is devoted to developing hydrogen permselective silica membranes supported on composite supports to achieve high flux and selectivity. The supports consist of a thin zeolite silicalite layer coated on α-Al$_2$O$_3$ tubes of mean pore size 1 μm. The zeolite layer is grown by reaction in a suitable silicate solution at 95°C. After two or three reaction periods a layer of silicalite crystals about 20 μm thick grows inside the pores of alumina. In addition to the zeolitic pores, this layer contains voids of a few nanometer diameter that remain between the crystals or between the crystals and the pore walls. The quality of the silicalite/alumina composites was evaluated by gas permeation measurements and by nitrogen adsorption and it was found that the residual voids were below 5 nm in diameter.

Three techniques were investigated for chemical vapor deposition (CVD) of the silica layer on the silicalite/alumina composite support. The first was TEOS pyrolysis at approximately one millibar partial pressure and 650°C. After 8 h reaction the fluxes of hydrogen and nitrogen at ambient temperature had declined by a factor of approximately100 indicating sealing of defects and zeolitic pores alike. The second CVD technique investigated was SiCl$_4$ hydrolysis at 90°C. Deposition in this case was conducted in a series of cycles, each cycle comprising two half reactions, i.e. exposure to SiCl$_4$ followed by exposure to water vapor. The deposition was interrupted every five cycles to measure the permeation properties of the nascent membrane at 120°C. After a few cycles the membrane pores were sealed, but the silica layer was not thermally stable when the temperature was raised to 400°C. In the third technique investigated, silica deposition was carried out by SiCl$_4$ hydrolysis at 400 ^{o}C, again in a sequence of half reaction cycles. After 15 cycles the membrane pores were well sealed by a layer stable to at least 400°C.

# TABLE OF CONTENTS

List of Figures

1. INTRODUCTION

1.1 Membrane Separation in Hydrogen Production

Hydrogen production is a major option in the utilization of fossil fuels for power generation and chemicals production. A major potential use of hydrogen is fuel cell power generation. 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. Utility power generation by highly efficient solid oxide (SO) fuel cells can use reformate gas directly, but prior removal of CO_2 would help sequestration of this greenhouse gas. Hydrogen-rich fuel gas can also be used in combined cycle power generation to reduce CO_2 emissions. Chemical use in hydrotreating of heavy oil or coal liquids, or in ammonia and other chemical synthesis is another yet 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 included to further increase CO conversion. The final step depends on the application. 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 CO_2 from reformate or synthesis gas 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

$$CO + H_2O = CO_2 + H_2$$
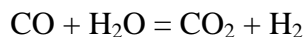
is driven to the right, and the CO at fixed feed H_2O:CO ratio is increased. Alternatively, the feed H_2O:CO can be reduced at fixed CO conversion. The product hydrogen will not require further purification if the membrane has adequate hydrogen selectivity. For example if the gas in the feed

side of WGS membrane reactor has 50 ppm H_2S and 50% H_2, the permeate gas obtained using a membrane with a $H_2:H_2S$ selectivity of 100 will have about 1 ppm H_2S. Higher purification is obviously possible with a more selective membrane. Hydrogen of that purity will be suitable for power generation in a combined cycle or high temperature fuel cell, or for refinery hydrotreating uses. The retantate gas containing primarily CO_2 with smaller quantities of hydrogen would be treated for CO_2 sequestration or burned directly for additional power.
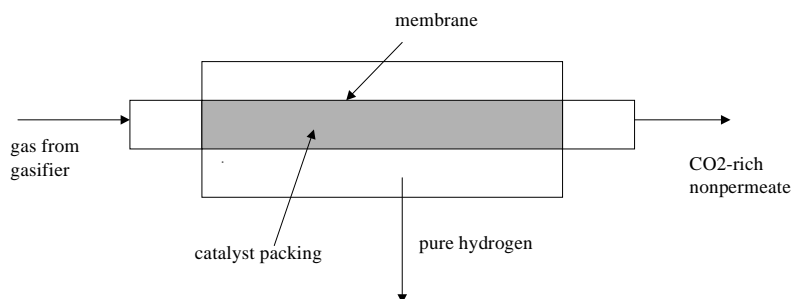
Figure 1. Schematic of a membrane reactor for hydrogen production

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

   i)   It reduces the excess steam used in the conventional WGS reactor to attain high CO conversion

   ii)   It eliminates the second, low temperature shift reactor also used to reduce the product CO content

   iii)   eliminates the CO_2 and N_2 diluents in the gas fed to the fuel cell stack, thus increasing the cell's EMF.

Two types of high temperature membranes are known to have high selectivity for H_2 separation: metallic membranes (e.g. palladium alloy-based), and dense silica membranes. In Pd-alloy membranes, H_2 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, H_2

molecules permeate in molecular form through the silica matrix and have much higher permeability than larger molecules like CO, CO_2 , H_2S and N_2.

1.2 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 are formed by chemical vapor deposition (CVD) of a thin, dense, silica layer within the pores of Vycor glass support by the overall reaction
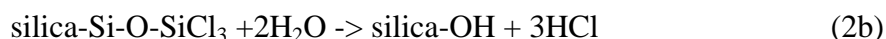
$$SiCl_4 + 2 H_2O \rightarrow SiO_2 + 4 HCl \qquad (2)$$

This CVD reaction was carried at about 600°C by simultaneous or alternating flows of $SiCl_4$ and steam and involves the two half-reactions

$$silica\text{-}OH + SiCl4 \rightarrow silica\text{-}Si\text{-}O\text{-}SiCl_3 + HCl \qquad (2a)$$
$$silica\text{-}Si\text{-}O\text{-}SiCl_3 + 2H_2O \rightarrow silica\text{-}OH + 3HCl \qquad (2b)$$

where the silica in Eq. 2b has appropriated one SiO_2 from the gaseous precursor.

The silica membranes prepared previously in the PI's laboratory yielded H_2:N_2 selectivity of 300-1000 and H_2 permeance (flux divided by the transmembrane partial pressure difference) 2-3 MPU (1 MPU= 10^{-8} mol/m^2-s-Pa) at 600°C. This membrane selectivity exceeds the requirements of the application. The hydrogen permeance, however, needs to be increased to improve the process economics given that the membrane cost is roughly inversely proportional to the permeance. The H_2 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 porous Vycor glass tubes of 1 mm wall thickness and hydrogen permeance about 3.7 MPU (MPU=10^{-8} mol/m^2-s-Pa). By increasing the permeance of the support by a factor of 5, it is estimated that the H_2 permeance can be increased to 5-10 MPU with a corresponding reduction of the membrane cost.

1.3 Basic Concept

To increase the membrane permeance it is necessary to replace the Vycor glass support by a more permeable material. Porous α-alumina with pore size in the range 0.1-1μm is highly permeable but cannot be directly used for CVD because to seal the large pores CVD would take a very long time

and the resulting silica layer would be very thick. The solution to this difficulty is to modify the 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 (intertwined) as shown in Figure 2. The intermediate layer could be made out of a phase-separated glass (Vycor) or a zeolite such as ZSM-5 (or silicalite).
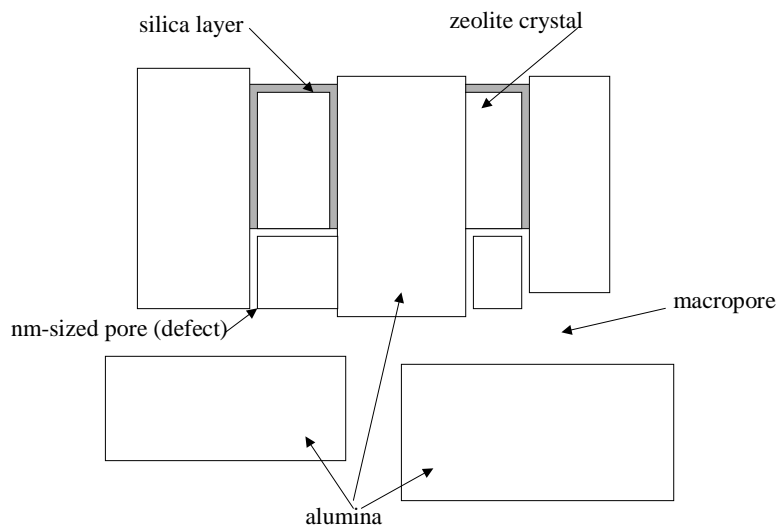

Figure 2. Schematic of the composite silica/zeolite/alumina membrane

This project, therefore, has two tasks, the development of techniques for depositing the intermediate layer, and the development of techniques for depositing the final silica layer. The original plan was to make the intermediate layer out of phase-separated glass. However, in early experiments it was found that the glass melt used as a coating material penetrated the pores of the support and dissolved large amounts of alumina. The resulting composite had low permeance. Subsequent work focused on zeolite as the material of choice for the intermediate layer. Zeolite ZSM-5 or silicalite was chosen for that purpose because of previous experience in this laboratory. ZSM-5 zeolite layers free of defects have uniform pores of 0.55 nm diameter and would be very easy to seal by a thin silica layer. In practice, zeolite layers as commonly prepared have a certain number density of residual gaps 1-4 nm wide between the crystallites. Voids of that size can be sealed by silica and are not of great concern. Voids much larger than 4 nm would require longer time to seal by silica CVD resulting in a thicker and less permeable intermediate layer, or if left unsealed, they would reduce the membrane selectivity. It is important, therefore that the intermediate zeolite layer

is of high quality, i.e., it does not contain defects (gaps between the crystals) above a few nm diameter.

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. The same reaction can be carried out at near ambient temperatures by using a base like pyridine or ammonia to remove the HCl product and thus suppress the reverse reaction that limits conversion at ordinary temperatures [4,5]. Another CVD technique is by TEOS thermal decomposition. This technique reportedly gave very good results for coating porous Vycor glass [6]. In the present project all three techniques were tested in the deposition of dense silica layers on silicalite/alumina supports.

2. EXECUTIVE SUMMARY

The objective of this project is to develop ceramic membranes for hydrogen separation from coal gas or synthesis gas at elevated temperatures, as high as $500^{o}C$. This separation is relevant to the production of pure hydrogen from coal, petroleum liquids or natural gas for fuel cell use or production of chemicals. The membrane of choice in this project is dense silica coated on a porous support by chemical vapor deposition (CVD). At elevated temperatures dense silica is highly selective to hydrogen but its permeability is low. To obtain useful fluxes it is therefore necessary that the membrane has a composite structure consisting of a very thin layer that accomplishes the separation supported on a thicker but highly permeable support. Dense silica stable at elevated temperatures can be produced by chemical vapor deposition (CVD). To obtain a thin layer by CVD, the support must have pores below about 5 nm in diameter. In past work Vycor glass of 4.5 nm mean pore diameter and 1 mm thickness was used for that purpose, but that support offered significant resistance to permeation and thus limited the overall membrane permeance (flux normalized by the partial pressure difference of the permeating gas). To improve the permeance, the support must also have composite structure consisting of a thin skin with pores below 5 nm diameter coated on a much thicker body of large pores.

In this project composite support were made consisting of a zeolite silicalite layer (skin) coated on highly permeable α-Al_2O_3 tubes of mean pore size 1 μm and wall thickness 0.6 mm. The zeolite layer is grown by immersing the support in a suitable

silicate solution at 95°C for 12-20 hours. This treatment is repeated 1-3 times to obtain a polycrystalline silicalite layer extending from the surface down to about 20µm inside the pores of alumina. In addition to containing zeolitic pores of about 0.55 nm diameter, the silicalite layer contains residual voids of 1-4 µm diameter between the crystals or between the crystals and the pore walls. A large number of zeolite-coated support tubes were prepared using this technique. The quality of these tubes was evaluated by gas permeation measurements and by nitrogen adsorption and it was found that the residual voids were below 5 nm in diameter.

Three techniques were investigated for chemical vapor deposition (CVD) of the silica layer on the silicalite/alumina support. The first was TEOS (tetraethoxysilane: $Si(OC_2H_5)_4$) pyrolysis at TEOS partial pressure approximately 0.001 bar and 650°C temperature. After 8 h of CVD the fluxes of hydrogen and nitrogen at room temperature had declined by a factor of 100 indicating sealing of defects and zeolitic pores alike. At such high CVD temperatures the zeolite layer was found to undergo undesirable structural changes such as growth of the residual intercrystalline voids necessitating lengthy CVD. Although permeation properties at high temperatures were not evaluated, it was anticipated that the lengthy CVD would result in low fluxes. Therefore, in the second and third techniques CVD was carried out by silicon tetrachloride hydrolysis at 90°C and 400°C respectively. Hydrolysis at 90°C was conducted in a series of cycles, each cycle comprising two half reactions, i.e. exposure to $SiCl_4$ followed by exposure to water vapor. After a few cycles the membrane pores were sealed but the silica layer formed at this temperature was not thermally stable. After heating to 400°C the tube became permeable to nitrogen and hydrogen at a ratio closed to the Knudsen value ($H_2:N_2=3.74$). In the third technique investigated, silica deposition was carried out by $SiCl_4$ hydrolysis at 400 $^{\circ}$C, again in a sequence of half reaction cycles. After 15 cycles the membrane pores were well sealed by a layer stable to 400°C. After only 4 cycles the membrane had become impermeable to isobutane indicating that the membrane defects had narrowed down to no more than 0.6 nm. After 15 cycles the membrane had become impermeable to all gases but hydrogen. Permeation measurements at higher temperatures will be conducted during the second year of the project.

3. EXPERIMENTAL

3.1 Coating of Porous Alumina Tubes with the Zeolite Layer

Figure 3 shows the protocol for growing the zeolite layer on the alumina support. To attain better thermal and mechanical stability, the zeolite layer was grown inside the pores just below the ID or the OD of the porous support tubes. The various steps are shown in Fig. 3 and are described below.
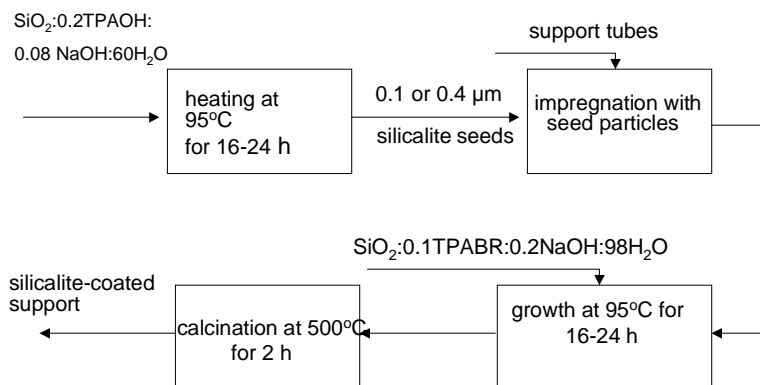

Figure 3. Protocol for growing a silicalite layer in the ores of the alumina support

Alumina Supports

α-Al_2O_3 support tubes were purchased from Dongsuh Company in Korea. The bulk of the experiments were conducted using tubes of 6 mm ID, 7.2 mm OD, 1μm mean pore diameter and 0.4 pore volume fraction.

Seed Preparation

Seeding was used to achieve internal growth of the zeolite. Seeds of suitable size were prepared by heating a solution of composition

$$SiO_2: 0.2TPAOH: 0.08NaOH: 60H_2O$$
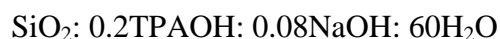
at 95°C for 16-23 hours. The particles were then filtered, washed, dried and later resuspended in water with the aid of ultrasonication. The particles were of about 0.1 μm diameter as measured by SEM Suspensions of 1 wt% seed particles were used to seed the

11

internal pore surface area of the support tubes of 1μm pore size. For this purpose the dry support tube was immersed in the seed suspension for 10 minutes. Capillary flow filled the pores with suspension including particles. After drying and heating at 200°C the seeding was repeated once to increase the seed loading to about 0.2 wt% of the support.

Growth of Zeolite Layers on Seeded Supports

The growth of the seeds to a zeolite layer was carried out by holding the seeded tube in a solution of composition

$$SiO_2: 0.1TPABr: 0.2NaOH: 98H_2O$$
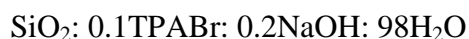
at 95°C temperature for 20 hours. To grow the layer at the tube ID, the OD surface was protected from solution by wrapping with Teflon tape. To grow the layer at the OD surface a Teflon rod was snugly fitted in the tube bore to prevent liquid entrance. Subsequently the tubes were withdrawn, washed, and dried at 180°C. Measurement of nitrogen flux through the tubes was used to test whether the zeolite layer had fully sealed the support pores. In most cases the zeolite growth treatment was repeated once or twice more to reduce the size of the gaps between the crystallites. The coated tube was finally washed, dried, and calcined at 500 or 650°C to remove the organic template and open up the zeolitic channels. The former temperature is sufficient for template removal, and the higher temperature was used to stabilize the zeolite layer for the subsequent high temperature CVD. Typically the temperature was raised at 10°C per minute to the final temperature at which the membrane was held for one hour.

Testing of the Silicalite-Alumina Tubes

Permeation measurements were carried out using an apparatus that can accommodate up to four tubes (Fig. 4). The Viton seals in this permeation cell allow operation at temperatures up to 200°C. After mounting and drying, the silicalite/alumina composites are ready for permeation testing with single gases or gas mixtures. To conduct the testing, the feed gas is passed continuously through the shell while the permeate gas is collected through the tube bores and conducted to a bubble flowmeter or a gas chromatograph. In the pressure difference mode (PD) of measurement, feed gas passes through the shell around the tubes at 1.5-2.5 bar pressure, while the permeate gas is collected from the bore of the selected tube and conducted to a bubble flowmeter (at 1 bar) for measurement of the flux. In the Wicke-Kallenbach mode (WK), both the feed and permeate sides are at 1

bar and the permeate gas is carried from the tube bore by a sweep gas and analyzed by gas chromatography. The flowrate of the sweep gas and the composition measured using the chromatograph are used to calculate the flux of each component through the wall of each tube. Measurements of nitrogen flux using the PD mode are used to monitor the progress of zeolite growth. The growth is considered complete when the permeance of nitrogen (flux divided by transmembrane difference) before calcination (before opening up the zeolitic channels) falls below 0.01 MPU (1 MPU=10^{-8}mol/m^2-s-Pa). Calcination at 500°C causes the zeolitic channels to open up and creates defects between the crystallites. A technique is currently being developed to estimate the maximum defect size of the silicalite/alumina composites.

3.2 Silica CVD on the Zeolite/Alumina Tubes

CVD by TEOS Pyrolysis.

Pyrolysis of TEOS (tetraethoxy silane) was carried out at 600-700°C. This reaction deposits amorphous silica that seals the gaps between the crystals and forms an ultrathin layer over the external silicalite surface. The CVD must be stopped once the nitrogen flux is sufficiently reduced (e.g. by a factor of 50) because continuation of CVD beyond this point would result in an unnecessarily thick membrane. For this purpose it is necessary to conduct in-situ permeation measurements during the CVD reaction. To carry out the in-situ measurements the alumina tube was connected to two longer nonpermeable tube segments. Joining the porous α-Al$_2$O$_3$ tube with nonpermeable extensions is carried out using a sealing glass in the form of a paste. This paste is applied around the joint and after drying it is fired at 1000°C. In view of the high firing temperature, the tube extension was carried out before seeding and growth of the zeolite layer. During zeolite growth the glass seal was wrapped with Teflon tape to protect it from the alkaline solution.

After silicalite growth, the extended tube was mounted and sealed within a larger concentric tube and placed in an electrical furnace to conduct the CVD reaction. This arrangement permits permeation measurements during and after the completion of CVD. Silica CVD was carried out by passing a 0.1% TEOS in N2 mixture generated by bubbling N2 through liquid TEOS and further diluting it with nitrogen. The mixture was passed through the annulus between the alumina support and the surrounding quartz tube

at flowrate 20 ml/min while the bore of the support tube was evacuated using a rotary vacuum pump. For constant pumping speed the pressure level in the bore declined as CVD gradually narrowed down and eliminated the zeolitic channels and the gaps between the crystals. This pressure decline provided a rough measure of the progress of CVD.

CVD was interrupted periodically to measure the hydrogen and nitrogen fluxes through the nascent membrane. The fluxes were measured by the pressure rise technique or the pressure difference technique. When using the pressure rise technique, the tube bore and annulus are fully evacuated and isolated from the flow lines by shutting suitably located valves. The valves to the annular space are then opened and flow of nitrogen at fixed pressure 1-1.5 bar is quickly established. The tube bore remains isolated but its pressure slowly rises due to the transmembrane flux. Measurement of the pressure rise by a Baratron capacitance gauge allows calculation of the transmembrane flux using a suitable calibration. In the pressure difference technique a steady flow of nitrogen at 1.5-2.5 bar pressure passes trough the shell. At steady state the transmembrane nitrogen flux is measured using a bubble flowmeter.

CVD by SiCl$_4$ Hydrolysis at near Ambient Temperatures

This type of CVD was first applied by a University of Colorado group (George and associates [4]) to deposit a dense silica film on a smooth silicon wafer. This technique has the advantage of the near-ambient temperature. In the present project silica deposition was carried out by a modified procedure containing the following steps:

A: immersion in 0.5 vol% solution of SiCl$_4$ in acetone at room temperature for 1 min

B: drying at 90°C for 10 min

C: immersion in 1 vol% H$_2$O, 1 vol% pyridine in acetone at room temperature for 1 min

These steps were applied in the sequence: C;ABCB;ABCB;ABCB…Each ABCB sequence constitutes a single reaction cycle consisting of the two half reactions A (silylation) and B (hydrolysis) with the drying step between the two half reactions.

CVD by SiCl$_4$ Hydrolysis at Elevated Temperatures

This type of CVD follows a protocol similar to that used in our earlier project [3]. The reactions are carried out at temperatures 400-600°C in the sequence:

EFGFEFGFEFG…where

E: exposure of the tube to SiCl$_4$ vapor at 0.1 bar pressure for 1 minute

F: evacuation

G: exposure of the tube to H_2O vapor at 0.2 bar pressure for 5 minutes

One reaction cycle comprises the four steps EFGF

4. RESULTS AND DISCUSSION

4.1 Growth of the Zeolite Layer on the Alumina Supports

Results of Seeding

The seed size after growth at 95°C for a certain length of time was measured by SEM. After 16 hours it was approximately 0.1 μm and after 23 hours it was approximately 0.2 μm. Additional reaction time did not increase the particle size much beyond 0.2 μm. Table 1 shows the results of impregnation of support tubes of different pore size in seed 1% seed suspensions of different seed size. It appears that the formation of an external layer of 0.2 μm seed particles on 1 μm pore support is due to gelation of the suspension as it becomes more concentrated near the pore mouths of the support. Figure 5 shows a layer of 0.1μm seed particles coated on an alumina tube of 0.15 μm mean pore diameter.

Based on the results shown in Table 1 all zeolite-coated supports were prepared using 1 μm pore supports and 0.1 μm seeds. The mass of seeds deposited in the pores of the support following a 10-minute impregnation was too low to weigh accurately but was on the order of 0.5% by weight of the support.

Growth of the Zeolite Layer on Seeded Support Tubes

Table 2 shows the weight gain of silicalite grown on a support tube in several successive growth periods. The results of this table show that the weight gain levels off after the second cycle. Furthermore there is a big difference between growth on seeded and unseeded supports. On unseeded supports, growth is much slower, initially, but it increases with successive growth periods. The first growth period is essentially equivalent to seeding the membrane tube after which growth is comparable to that on a seeded tube.

The zeolite/alumina composites were characterized by measuring the permeation rates of several gases. The permeation results listed in Table 3 below show that after the first growth cycle the zeolite crystals are not large enough to close the pores. During the first growth period crystallization stops when the concentration of silicate precursors in Table 1. Location of seed layer after impregnation of support tubes in a 1wt% seed

suspension.

support pore size (μm)	seed pore size (μm)	
	0.1	0.2
0.15	external layer	internal layer
1	internal layer	external layer

the solution falls below supersaturation. The depletion of soluble precursors is due to zeolite formation in the bulk of the solution as well as inside the support pores. To continue growth it is necessary to use a fresh solution in a second reaction cycle. To obtain a good quality zeolite layer it was usually necessary to carry out a total of two or three growth cycles. The growth cycles were deemed sufficient when the tube became impermeable to nitrogen (the zeolitic channels at this stage are blocked by the template TPA ions).

SEM micrographs of support tubes before and after zeolite growth show that silicalite particles grow outside as well as inside the pores. It is believed, however, that the outside layer has numerous gaps between the crystals. The lack of nitrogen flux prior to calcinations can therefore be attributed to the internal zeolite layer. The permeation results of Table 3 show that under the conditions of these experiments at 2 or 3 cycles are needed to obtain sufficient n-butane:isobutane selectivity. A high selectivity indicates that the zeolite layer is virtually free of pores above a few nm diameter. The second and third reaction cycles can be collapsed into one by adding silica and TPA source (eg TEOS and TPABr) into the solution during reaction in order to maintain supersaturation.

Table 2. Zeolite deposition on a seeded (1,2,3) and unseeded (4) support tubes in
        successive growth cycles

growth cycle	cumulative weight gain (%)			
	tube 1	tube 2	tube 3	tube 4
1st	2.59	2.06	2.16	0.21
2nd	5.38	4.74	4.61	1.60
3rd	5.41	5.02	4.69	3.31

Table 3. Permeance of three tubes at room temperature after successive growth cycles

permeance (MPU)[b]									
growth cycle	tube 1			tube 2			tube 3		
	N_2	nC4	nC4:iC4	N_2	nC4	nC4:iC4	N_2	nC4	nC4:iC4
1st	>100			>100			>100		
2nd a	10	10.2	1.7	10	10.1	1.7	10	9.6	2.2
3rd a	<0.1	6.1	20	<0.1	6.9	35	<0.1	6.7	24

a: nitrogen flux measured before calcinations, butanes fluxes measured after calcinations

b: 1 MPU = 10^{-8}mol/m^2-s-Pa

4.2 CVD of Dense Silica on the Zeolite/Alumina Supports

CVD by TEOS Pyrolysis

 It was found that the silicalite layer (previously calcined at 500°C) undergoes pore enlargement at 600-700°C that is the temperature required for TEOS pyrolysis. To avoid this change during CVD the tubes were pretreated at 700°C. TEOS pyrolysis at 600-700°C required about 8 h to eliminate the permeance of hydrogen and nitrogen measured at room temperature. Permeation measurements at 400°C were not carried out but it was anticipated that the thick silica layer resulting from the lengthy CVD treatment would

have relatively low permeance. Subsequent work focused on silica deposition by silicon tetrachloride hydrolysis.

Silica CVD by SiCl₄ Hydrolysis at Near Ambient Temperatures

Figure 6 shows the permeance of several gases (single gas measurements) at 120°C versus the number of reaction cycles. After only 4 cycles the flux of n-C_4H_{10}, N_2, CO_2, H_2 had decreased by a factor of 67, 20, 10, and 6 respectively. Additional cycles further decreased these fluxes and increased the membrane selectivity. Unfortunately, upon heating the membrane to 400°C, all fluxes returned to their original values. Additional CVD-coated membranes were prepared but all showed the same instability at 400°C. Evidently, the silica deposit was not sufficiently dense and collapsed at 400°C. Although it may be possible to refine this technique to achieve thermally stable films, our effort turned to the next technique that gave better results.

High Temperature Silica CVD by SiCl₄ Hydrolysis

Following the protocol described in the experimental section, CVD was carried out at 400°C. Figure 7 shows the evolution of the permeance (at 120°C) of several gases with successive reaction cycles. After only 4 cycles the membrane has become impermeable to isobutane indicating that the membrane defects have narrowed down to no more than 0.6 nm. After 15 cycles the membrane has become impermeable to all gases but hydrogen. These results are very encouraging because and higher temperature measurements will be conducted in the near future.

CONCLUSIONS

To achieve high permeance and selectivity at 400-500°C, CVD of dense silica membranes needs to be carried out on highly permeable and stable supports of pore size below about 5 nm. Macroporous α-Al_2O_3 coated by a thin zeolite silicalite layer appears to be a suitable support for that purpose. In this project such supports were developed by growing a layer of silicalite crystals, about 20µm thick, inside the pores of alumina. The silicalite crystals grow to occupy the pore space leaving only gaps of 1-4 nm size between the crystals and the pore wall.

CVD of dense silica on the silicalite/alumina composite was pursued by threee techniques. The first technique tested was pyrolysis of tetraethoxy silane (TEOS) at

650°C. After eight hours treatment the permeances of all gases (at 120°C) had drastically declined but the resulting silica layer was probably too thick. The second technique involved silicon tetrachloride hydrolysis at 90°C. After a few reaction cycles the membrane became virtually impermeable to all gases but hydrogen. However, after heating at 400°C, the gas permeances returned to their pre-CVD values indicating that the film was thermally unstable. The third technique tested was silicon tetrachloride hydrolysis at 400°C. After fifteen reaction cycles the film was impermeable to all gases but hydrogen. The film was thermally stable up to 400°C. Silicon tetrachloride hydrolysis at either temperature involves alternating exposures to the tetrachloride and water vapor. Because of the self-limiting character of these two reactions, the silica product grows in a layer-by-layer fashion allowing good control of the deposit thickness.

The high-temperature hydrolysis appears the most suitable for depositing thin silica films that are stable at high temperatures.
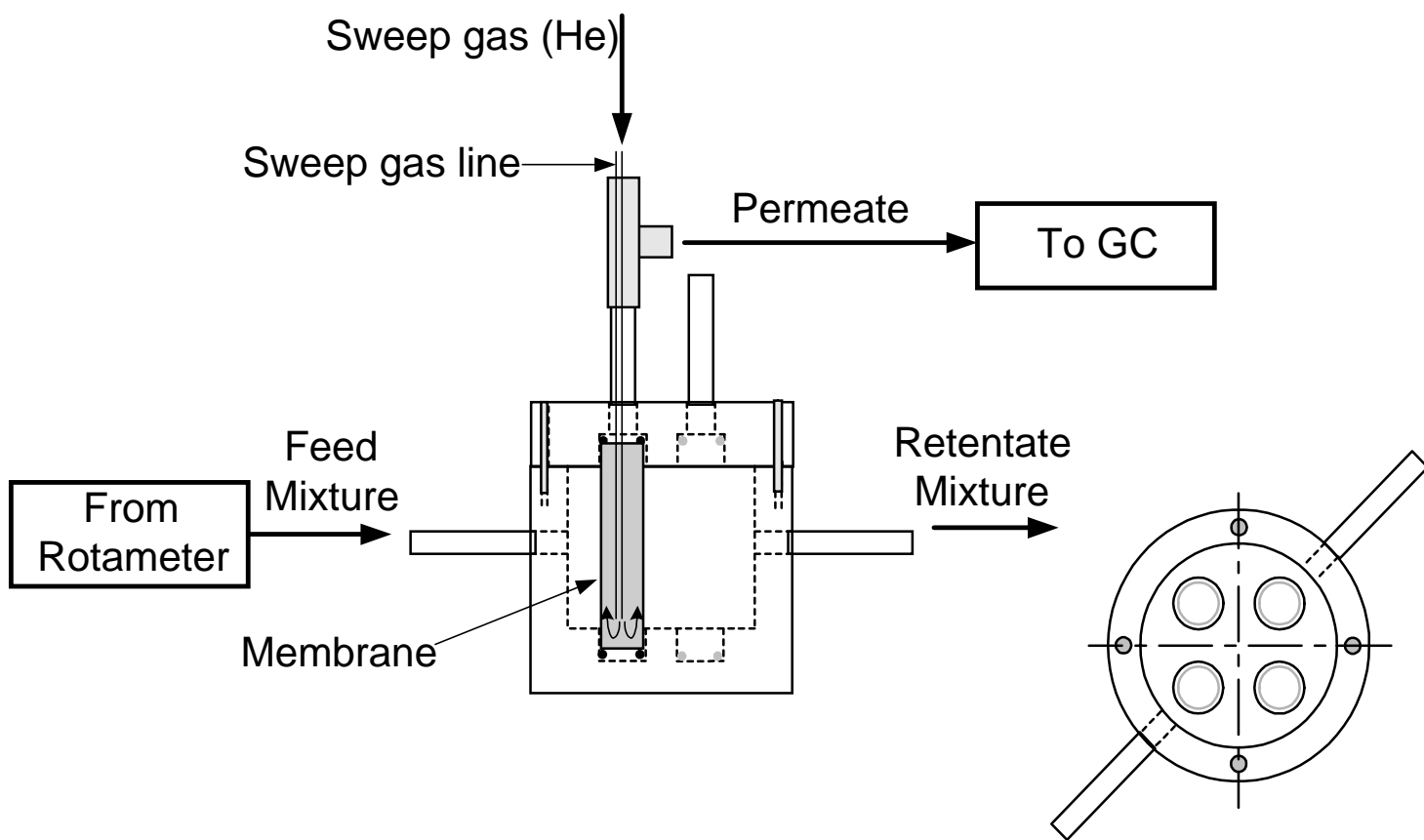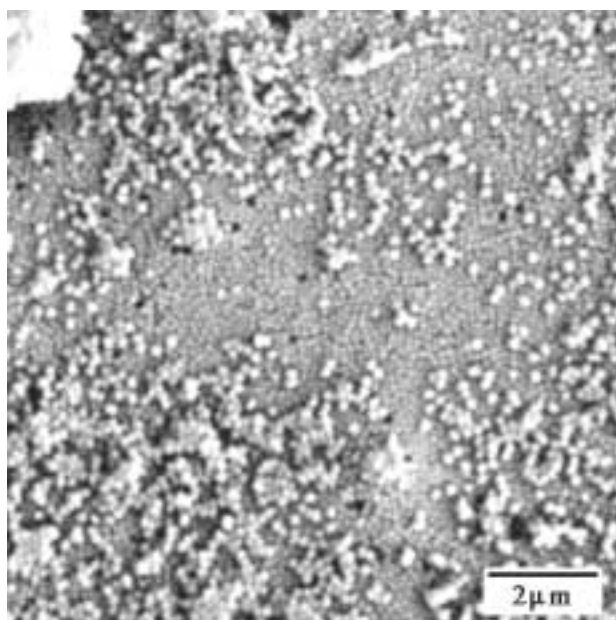
Figure 4. Permeation cell
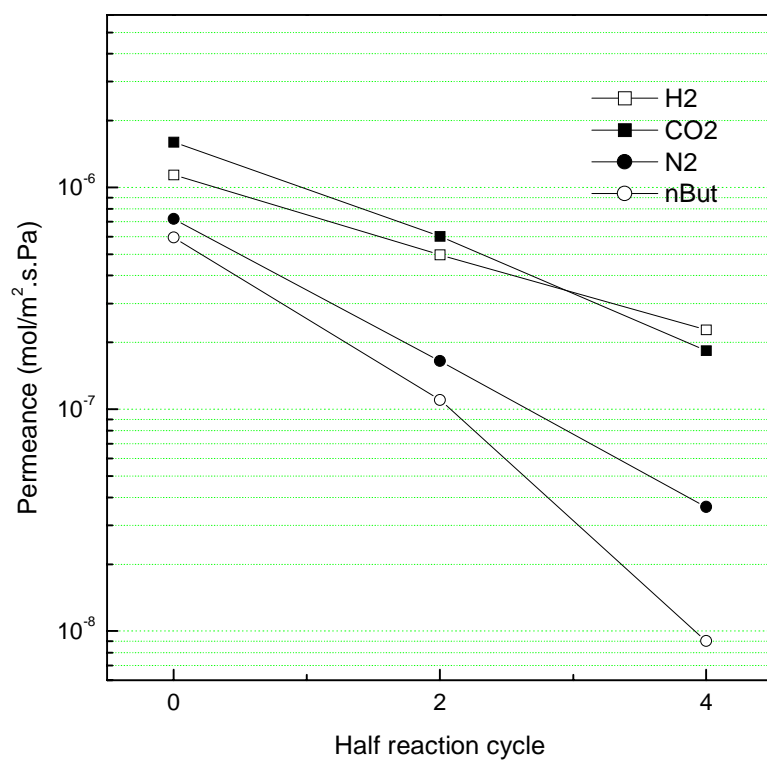
Figure 5. Scanning electron micrograph of seed particles.

Figure 6. Evolution of gas permeation after consecutive cycles of SiCl$_4$ hydrolysis at 95°C. Reaction was carried out by alternating exposure to SiCl$_4$ and water-pyridine at 95°C. Permeance was measured by the PD technique at 120°C.
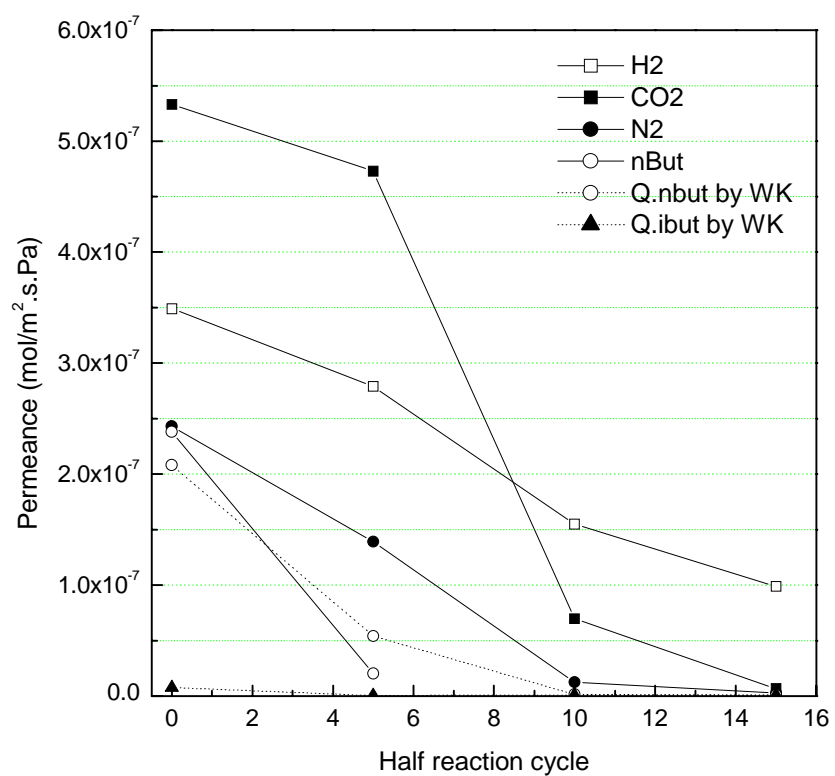
Figure 7. Evolution of gas permeation after consecutive cycles of $SiCl_4$ hydrolysis at 400^oC. Reaction was carried out by alternating exposure to $SiCl_4$ and H_2O vapor. Permeance was measured by the PD (solid line) or WK (dotted line) for a 50-50 mixture.