DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SILICA MEMBRANES FOR HYDROGEN SEPARATION FROM COAL GAS

FINAL REPORT, JANUARY 1996

G. R. GAVALAS

Work Performed Under Grant No. DE-FG22-92PC92525
of the University of Coal Research Program

For

U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

By

California Institute of Technology
Pasadena, CA 91125

HH
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

SUMMARY	1
INTRODUCTION	6
Chapter 1: MEMBRANE PREPARATION	10
Introduction.....	12
Experimental Section	16
Experimental Results and Discussion	19
Model Description	24
Numerical Results	27
Concluding Remarks	31
Nomenclature	33
Acknowledgment	34
Literature Cited	35
Tables 1 - 6	38-43
Figures 1 - 9	44-52
Chapter 2: MEMBRANE CHARACTERIZATION	53
Introduction.....	54
Experimental	56
Results and Discussion	57
Conclusions	67
Acknowledgments.....	67
References	67
Appendix.....	68
Chapter 3: TGA STUDY OF KINETICS OF SiO₂ CVD	70
Introduction.....	72
Experimental	73
Results	74
Conclusions	83
References	85
Nomenclature	86
Tables 1 - 2	87-88
Figures 1 - 15	89-103

Chapter 4: MEASUREMENTS OF MEMBRANE PERMEABILITY	104
Introduction.....	105
Experimental	105
Results and Discussion	107
Figures 1 - 5	109-113
 Chapter 5: MATHEMATICAL MODEL OF CVD	 114
Introduction.....	116
Model Formulation	119
Numerical Results and Discussion	125
Conclusions	129
Acknowledgments.....	129
Notation	130
Literature Cited	133
Appendix	136
Figures 1 - 7	139-145
 Chapter 6: CONCLUSIONS	 146

SUMMARY

This project is a continuation of a previous DOE-UCR project (DE-FG22-89PC89765) dealing with the preparation of silica membranes highly permselective to hydrogen at elevated temperatures, suitable for hydrogen separation from coal gas. The membranes prepared in the previous project had very high selectivity but relatively low permeance. Therefore, the general objectives of this project were to improve the permeance of these membranes and to obtain fundamental information about membrane structure and properties. The specific objectives were: (1) to explore new silylation reagents and reaction conditions with the purpose of reducing the thickness and increasing the permeance of silica membranes prepared by chemical vapor deposition (CVD), (2) to characterize the membrane structure, (3) to delineate mechanism and kinetics of deposition, (4) to measure the permeability of silica layers at different extents of deposition, and (5) to mathematically model the relationship between structure and deposition kinetics. The work performed in each of these areas is summarized in the following subsections:

1. Improved Membrane Preparation Techniques

Hydrogen-permselective nonporous silica membranes have been prepared previously in our laboratory by CVD of SiO_2 on porous glass tubes (Vycor, 5 mm ID, 7 mm OD, 40 Å mean pore diameter) using a mixture of SiCl_4 and H_2O vapors at 600-800°C. Formation of SiO_2 proceeds by reaction SiCl_4 with silanol (Si-OH) sites on the pore surface of the Vycor to form Si-Cl sites, simultaneous hydrolysis of Si-Cl back to Si-OH , and condensation of Si-OH sites to siloxane bonds (Si-O-Si). Being depleted by the reaction, SiCl_4 penetrates only a limited depth below the external surface of the support. Within this penetration depth the pores are gradually narrowed by the accumulating SiO_2 product and finally close down completely forming the permselective membrane. Since the thickness of the membrane is roughly proportional to the depth of

SiCl₄ penetration, in order to increase membrane permeance it is necessary to decrease the depth of penetration. Two techniques were investigated for this purpose. One was to use a nominally more reactive silylating agent which would be depleted faster in the porous support (larger Thiele modulus). The other was to change the mode of reaction from steady state to unsteady, alternating, CVD.

The initial preparation studies were focused on increasing the rate of CVD by using reactants more active than the previously used SiCl₄. For this purpose a class of trichlorosilyl triflates were synthesized in our laboratory by the reaction of triflic acid with tetrachlorosilane or phenyltrichlorosilane. The rate of (silylation) reaction of these triflates with Vycor glass was tested using a thermogravimetric analyzer (TGA) and found to be ten times lower than the rate of silylation with SiCl₄. This lower reactivity may be due to steric hindrance caused by the large triflate groups. In view of these negative results no membrane synthesis was attempted with these new reagents.

The second approach to preparing membranes of improved permeance was to carry out CVD by alternating rather than simultaneous flow of tetrachlorosilane and water vapor. This "alternating deposition" reduces the penetration depth by limiting the dosage of SiCl₄ used in each cycle. It also has another major advantage, that of preventing the formation of SiO₂ particles in the gas outside of the porous support. In practice the alternating CVD consists of introducing to the evacuated reactor a certain quantity of SiCl₄, allowing reaction for approximately one minute, evacuating again, introducing water vapor for three to five minutes and evacuating again to begin a new cycle. At 600°C the membranes prepared by alternating deposition had H₂ permeance about 0.3 cm³/cm²-min-atm and H₂:N₂ permeance ratio 2000. By comparison the H₂ permeance of membranes prepared earlier by one-sided CVD (simultaneous contact with SiCl₄ and H₂O) was 0.15 cm³/cm²-min-atm and the H₂:N₂ selectivity 1000-2000. Thus, using alternating CVD produced a two-fold increase in the hydrogen permeance. Furthermore, the net permeance of the deposition layer after subtracting the resistance of the Vycor

support was about $0.65 \text{ cm}^3/\text{cm}^2\text{-min-atm}$. The preparation work is described in Chapter 1 and has been published in I&EC Research.

2. Membrane Characterization

The deposit layers of membranes prepared by one-sided CVD (not alternating) were examined by TEM, SEM, and EPMA. When the deposit was confined inside the pores of the Vycor substrate, the membranes were mechanically stable, but when it extended substantially outside of the porous matrix the stresses induced by thermal cycling led to crack formation and propagation. Electron microscopy revealed that the SiO_2 deposit density is maximum in a region $\sim 0.5 \text{ }\mu\text{m}$ thick adjacent to the surface of CVD and gradually declines to zero within a depth of $\sim 10 \text{ }\mu\text{m}$ from the surface. The thin region of maximum deposit density is responsible for permselectivity, for it essentially blocks the permeation of nitrogen and larger molecules while allowing substantial permeation of hydrogen. This region contains $\sim 10\%$ by volume trapped voids and as a result has relatively high permeability as suggested by percolation theory. Annealing at high temperatures causes densification of the deposited material as evidenced by increased activation energy for H_2 permeation and correspondingly reduced permeance. The presence of H_2O vapor accelerates the densification process. The characterization work is described in Chapter 2 and has been published in Journal of Membrane Science.

3. Mechanism and Kinetics of SiO_2 Deposition

Work begun under the previous project on the mechanism and kinetics of SiO_2 growth by CVD with $\text{SiCl}_4\text{-H}_2\text{O}$ reactants was continued and completed. The reaction of SiCl_4 with surface silanols

and of water vapor with surface silicon chloride groups

were studied using a thermogravimetric analysis system at 400-600°C. The mechanism and kinetics of silylation by SiCl_4 and subsequent hydrolysis of the chloride groups were investigated at 400-600°C by thermogravimetric analysis. In addition to the silylation of surface hydroxyl groups and the subsequent hydrolysis of chloride groups, condensation reactions between a surface chloride with a silanol and between two silanols contribute to the overall reaction.

The silanols can be approximately classified as isolated and vicinal or paired, with the latter being the more abundant. After reaction of the first silanol of a pair with gaseous SiCl_4 , the second $-\text{OH}$ can either combine with a second gaseous SiCl_4 or condense with the already attached $-\text{SiCl}_3$ group. The competition between these two sterically hindered and slow reactions controls the overall extent of silylation. Steric effects were found to be very important for the silylation of paired SiOH groups of SiCl_4 with an isolated silanol or with an unreacted silanol pair is very fast and pore-diffusion limited. But once the first group of a silanol pair has reacted with SiCl_4 , reaction of the second group either with SiCl_4 from the gas phase or with the neighboring $-\text{SiCl}_3$ group is very slow.

A kinetic model postulating two types of silanols and including the silylation, hydrolysis, and condensation steps gave good agreement with the TGA data after appropriate adjustment of its parameters. The results of these kinetic studies are included in Chapter 3 and have been published in the journal of Colloid and Interface Science.

4. Fundamental Permeability Measurements

To understand better the membrane properties considerable effort was devoted to measuring the permeability of the deposit layer as a function of the volume fraction of the pores occupied by deposited SiO_2 . In view of the spatially nonuniform structure of the deposit layer, there is a permeability profile that cannot be determined from the measured

overall permeance. True permeabilities can only be determined by measurements on spatially uniform membranes.

In this project we attempted to prepare spatially uniform membranes by a series of alternating reactions with SiCl_4 and H_2O , with each reaction allowed to reach completion in each cycle. The self-limiting nature of this alternating deposition would ensure the formation of a spatially uniform deposit layer. This program was only partially successful. The Vycor support tube could withstand only up to 6 deposition cycles beyond which it failed mechanically--cracked or shattered--for some unknown reason. The limited data gathered indicate that the permeability decrease accompanying deposition is much faster than would be calculated on the basis of SiO_2 product buildup in a layer-like fashion. Product buildup seems to occur in individual lumps or domains and this mode of deposition has important implications on membrane properties.

5. Mathematical Modeling

An important consideration in membrane formation by CVD is the structure of the deposit layer. As shown by the thermogravimetric experiments summarized in subsection 3 and by the aforementioned TEM work the deposit layer contains considerable residual porosity due to the interruption of pore network connectivity at a nonzero void fraction. The generation of this residual porosity and the whole course of the deposition process was described by a mathematical model taking into account transient heterogeneous kinetics and incorporating results of percolation theory. It is shown that for typical deposition conditions the pseudosteady state approximation for surface species could lead to erroneous predictions. Pore connectivity interruption at a nonzero void fraction leads to thinner deposits and shorter deposition times for pore plugging compared to the corresponding ones for an infinitely connected medium. The results of this modeling work have been submitted for publication to AIChE Journal.

INTRODUCTION

This project was a continuation of a previous DOE-UCR project dealing with the preparation and testing of silica membranes suitable for hydrogen separation from coal gas at temperatures 400-600°C (1). Hydrogen from coal can be used for the production of chemicals like ammonia or methanol or for hydrotreatment of coal liquids. Separation of hydrogen from coal gas can be conducted at ambient temperatures using pressure swing adsorption (PSA) or by the use of polymeric membranes. Carrying out this separation at higher temperatures in close integration with the water gas shift reaction substantially improves the conversion of the equilibrium-limited reaction and the overall process efficiency. Hydrogen separation at high temperatures would also be beneficial in the recovery and recycle of hydrogen in molten carbonate fuel cells.

Such high temperature separations can only be carried out with inorganic membranes. Two types of inorganic materials are known to be highly permselective to hydrogen. One is palladium--or its alloys--and certain other metals forming hydrides conducting hydrogen in atomic form. Palladium alloy (with Ag usually) membranes are currently under development by several groups in the United States and Japan. They have the advantage of very high hydrogen permselectivity. They also have high permeance when prepared as thin films supported on porous ceramic tubes or plates. Their disadvantages are poisoning by coke or sulfur when contacted by hydrocarbons or hydrogen sulfide, respectively. There is also concern about the mechanical stability of palladium-ceramic composite membranes. Nevertheless, palladium membranes continue to be promising for high temperature hydrogen separation.

The second material suitable for high temperature hydrogen separation is dense silica glass (1). Hydrogen diffuses through the silica network in molecular form and its permeability is much larger than that of other gases, except He. At 500°C, for example, the permeability of oxygen through Vycor glass (Corning code 7900, 97% SiO₂ - 3%

Bi_2O_3) is four orders of magnitude below that of hydrogen, and N_2 has even lower permeability. Although the hydrogen permselectivity of glass is very high, its hydrogen permeability is low, hence, a practical membrane must comprise a very thin glass layer supported on some porous substrate providing mechanical strength. Several years ago under a DOE-UCR project (1), we started preparing membranes by chemical vapor deposition (CVD) on porous Vycor tubes (5 mm ID, 7 mm OD, 40 Å mean pore diameter). Initially we used two-sided CVD with SiCl_4 and H_2O reactants, passing SiCl_4 through the bore of the tube and water vapor from the outside (or the other way around). The membranes obtained had rather low hydrogen permeance about $0.05 \text{ cm}^3/\text{cm}^2\text{-min-atm}$ $\text{H}_2:\text{N}_2$ ratio above 2000 at 600°C . Heating these membranes in the presence of water vapor over a prolonged period causes densification of the deposit layer accompanied by a decline of the hydrogen permeance by a factor of two or more. Failure of these membranes was also frequently observed upon prolonged heating.

In the course of the previous DOE-UCR project we switched from two-sided CVD to one-sided CVD whereby both reactants, SiCl_4 and H_2O , are passed from the same side of the tube, inside or outside. This new deposition geometry produced a more favorable reactant concentration profile resulting in generally thinner membranes (1). Now the H_2 permeance immediately after deposition was about 0.3 but upon prolonged (three weeks) heating under 3 atm of water vapor it declined to $0.1 \text{ cm}^3/\text{cm}^2\text{-min-atm}$ (1). In one-sided CVD the reaction time has to be carefully controlled. Sufficient time should be allowed to reach pore plugging, but excessive time should be avoided to avoid the thickening of the deposit layer by adhesion of homogeneously formed silica particles. Increasing the thickness of the deposit layer by particle deposition reduces the membrane permeance and causes thermomechanical stresses that sometimes result in cracking of the membrane tube.

In a project funded by DOE-METC (2) an economic evaluation was carried out for the application of the silica membranes to hydrogen production from coal gas for

ammonia synthesis. It was found that the membrane application was not economical at hydrogen permeance of $0.1 \text{ cm}^3/\text{cm}^2\text{-min-atm}$ but would become competitive if the permeance was tripled to $0.3 \text{ cm}^3/\text{cm}^2\text{-min-atm}$ at 500°C . Although these particular numbers were based on very rough and uncertain estimates of membrane fabrication costs, they are nevertheless indicative of the great sensitivity of the process economics to the hydrogen permeance of the silica membranes. The present project had, therefore, as its major objective the improvement of the membrane permeance by suitable changes in the CVD protocol. Developing a better fundamental understanding of CVD mechanism and membrane structure was also an expressed objective of this project.

Increasing the membrane permeance can be framed as a problem in chemical reaction engineering. Ignoring for the moment the spatially nonuniform structure of the membrane, the permeance is inversely proportional to the thickness which, in turn, is proportional to the depth of penetration of the CVD precursors into the porous matrix of the support. The penetration depth can be decreased by increasing the reaction rate constant or by decreasing the diffusion coefficient. The diffusion coefficient can be decreased only by using supports of smaller pore size. Since decreasing the pore size also increases the resistance of the support, it would be desirable to use layered supports comprising a thin top layer containing very fine pores and a thicker layer containing larger pores. Such composite structures can be prepared by sol-gel techniques and are promising as supports for dense silica membranes.

A second approach for decreasing the penetration depth of the deposit layer is to increase the rate constant of the CVD reaction. This can be accomplished by raising the temperature or replacing SiCl_4 by some other more reactive silica precursor. The temperature can only be raised up to 700°C or at most 800°C beyond which the precursor surface becomes unreactive due to loss of silanol groups. Replacing SiCl_4 by more reactive silica precursors was pursued in this project but without much success.

The above two approaches for decreasing the penetration depth are associated with CVD at steady state operation. During the course of this project it occurred to us that unsteady CVD consisting of alternating periods of exposure to SiCl_4 and H_2O offers another way of decreasing the penetration depth. Most of the membrane preparations employed in this project were, in fact, carried out by alternating reactants CVD. In addition to substantially increasing the membrane permeance, this technique eliminated completely the undesirable homogeneous formation of SiO_2 particles.

Much of the remaining effort in the project was devoted to characterizing and mathematically modeling the structure of the SiO_2 deposit layer. The outstanding feature of this structure is the presence of trapped porosity which enhances the membrane permeance. To explain this and other features of membrane structure we modified our previous deposition model by using more realistic heterogeneous kinetics and by taking into account the connectivity of the porous structure using concepts from percolation theory.

Literature Cited

1. Gavalas, G. R., "Silica Membranes for Hydrogen Separation in Coal Gas Processing," Final Report for DOE Grant DE-FG22-89PC89765 by California Institute of Technology.
2. Gavalas, G. R., "Hydrogen Separation by Ceramic Membranes in Coal Gasification," Final Report for DOE Contract DE-AC21-90MC26365 by California Institute of Technology.

Chapter 1

MEMBRANE PREPARATION

*The material in this chapter has been published in
Industrial and Engineering Chemistry Research 34, 168 (1995).*

Preparation of H₂-Permselective Silica Membranes by Alternating Reactant Vapor Deposition

Soojin Kim and George R. Gavalas

*Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, CA 91125*

Abstract

Thin SiO₂ layers were deposited on the surface of porous Vycor glass by alternating vapor phase reaction with SiCl₄ and H₂O. The membranes prepared by this technique had H₂ permeance of 0.3-0.4 cm³(STP)/(min-cm²-atm) and H₂:N₂ selectivity of 500-1000 at 600°C. The SiCl₄ dosage at each silylation cycle, the concentration of initial surface-OH groups, and the reaction temperature influence significantly the deposit layer thickness. After two weeks of heating at 550°C under 3 atmospheres of water vapor, the membrane H₂ permeance decreased by about 20%, and the selectivity increased to more than 2000. The membrane properties after this hydrothermal treatment are superior to those of membranes prepared earlier by one-sided (steady flow) deposition. A simple model incorporating diffusion and surface reaction was used to study the effect of various parameters on the formation of the deposit layer.

Introduction

Inorganic membranes have potential for improving the efficiency of high temperature chemical processes; in membrane-reactor configuration, combining reaction and product separation can greatly increase conversion (Sun and Khang, 1988; Armor, 1989). Hydrogen permselective membranes, in particular, have potential applications in several large volume catalytic processes such as water gas shift reaction, dehydrogenation of hydrocarbons, and hydrogen sulfide decomposition (Kameyama et al., 1981; Mohan and Govind, 1988; Raymont, 1975).

Various amorphous oxides are known to be highly selective to H_2 permeation due to small molecular size of H_2 (Shelby, 1979; Altemose, 1962). Amorphous silica (dense), for example, has hydrogen permeability $1.6 \times 10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$ and $H_2:N_2$ permeability ratio above 10^5 at 500°C . Because of the very low permeability membranes made of silica or other dense oxides need to have a composite structure comprising a thin layer of the selective oxide material supported on a much thicker porous substrate that provides mechanical strength.

Thin oxide layers can be prepared by chemical vapor deposition (CVD) on porous substrates. Using CVD, the desired films can be prepared at high temperatures obviating the drying and calcination required in film formation by liquid-phase techniques. As is well known, the removal of solvent or condensation products accompanying drying and calcination often causes shrinking and crack formation (Brinker, 1990; Yoldas, 1975). Thus, films produced by CVD are generally denser and more uniform than those produced by liquid-phase techniques.

CVD of amorphous silica membranes has been pursued by several investigators. Our group has employed hydrolysis of chlorosilane compounds at $600\text{--}800^\circ\text{C}$ to prepare SiO_2 membranes supported on porous Vycor tubes (Tsapatsis et al.,

1991). The two reactants (e.g., SiCl_4 and H_2O) were passed at steady flow either at opposite sides of the tube wall (opposing-reactants geometry) or at the same side of the tube wall (one-sided geometry). One sided deposition gave thinner and, therefore, more permeable layers on account of a more favorable balance between reaction and diffusion. Silica membranes have also been prepared by low pressure oxidation of triisopropylsilane (Megiris and Glezer, 1992) and by pyrolysis of tetraethylorthosilicate (Ha et al., 1993). During CVD the mesopores within a certain depth from the inside or outside cylindrical surfaces of the support tube become filled with the silica product. Hydrogen permeates through this deposit layer in molecular form via a solution-diffusion mechanism. Other molecules like nitrogen diffuse much more slowly on account of their larger size.

The formation of silica from chlorosilanes and water vapor involves reaction of the chlorosilane with surface hydroxyls (silylation reaction), hydrolysis of the surface chloride groups, and hydroxyl-hydroxyl and hydroxyl-chloride condensation, all proceeding simultaneously according to the following mechanism (Tsapatsis et al., 1991; Tsapatsis and Gavalas, 1992; Kim and Gavalas, 1993):

Kinetic studies (Kim and Gavalas, 1993) have shown that the reaction of chlorosilanes with surface hydroxyls is very rapid at temperatures above 600°C . As desirable as the high rate is for producing a thin deposit layer, the fast depletion of the chlorosilane reactant causes significant concentration gradients along the axial

direction when the support is a long tube or capillary. The longer the tube, the more severe this mass transfer limitation, resulting in nonuniform thickness along the length of the tube with the upstream part overdeposited to ensure adequate deposition in the downstream part. Overdeposition causes problems of reduced overall H_2 permeance and stability. When deposition is prolonged beyond the time required for pore plugging, the deposit layer continues to grow outside of the pores. This external growth occurs by deposition of particles formed in the gas phase as well as by the heterogeneous mechanism (1)–(4). Regardless of the mechanism, a thick external layer lowers the permeance and can also cause thermomechanical stresses leading to crack formation (Tsapatsis and Gavallas, 1993). Using low concentrations of $SiCl_4$ to minimize the homogeneous particle formation would accentuate concentration gradients especially if this technique were to be applied to the fabrication of multi-tube membrane modules. A more practical means of minimizing homogeneous particle formation and deposition gradients is, therefore, desirable.

Particle formation in the gas phase can be eliminated by flowing the chlorosilane and water vapor past the support surface alternately rather than simultaneously. This alternating deployment of reactants is well known in electronic device fabrication and sometimes referred to as atomic layer epitaxy (ALE) (Ritala et al., 1993; Suntola and Simpson, 1990). Compared to simultaneous flow of the reactants, ALE provides strict control of the stoichiometry but is much slower. ALE is particularly attractive for self-limiting reactions when after exhaustion of the surface active sites, the surface becomes “saturated” and the reaction stops. Extending the flow of the reactants beyond saturation will not have any further effect. After surface saturation by the first reactant, flow is switched to the second reactant until once more saturation occurs, completing one reaction cycle. Sev-

eral consecutive reaction cycles are necessary to build up a layer of the desired thickness. ALE by means of self-limiting reactions has been used to deposit GaAs films (Usui, 1993).

In electronic device fabrication, deposition takes place over a nonporous substrate. By contrast, in membrane preparation deposition is carried out over a porous substrate. In the latter case it is undesirable to continue reactant flow in any given cycle until the whole pore surface becomes saturated, for then the deposit layer would be formed throughout the thickness of the substrate and the resulting structure would be useless as a membrane. To limit the thickness of the deposition layer it is necessary to change one half of the reaction cycle from continuous flow until saturation to a limited dosage of the reactant. For this purpose, the reactor volume above the substrate surface is evacuated, a metered dosage of the first reactant (e.g., SiCl_4) is admitted, and the volume is isolated. Reaction then proceeds not until surface saturation but until exhaustion of the reactant. Under these conditions the depth of penetration within the porous matrix is limited both by the reactant dosage and by the balance between the reaction and diffusion coefficients. The other half cycle involving reaction with H_2O need not be limited in dosage or time; it can be conducted by continuous flow, for the reactant can only react with the surface chloride groups resulting from the first part of the cycle.

It may be argued that admitting a limited dosage of the first reactant is equivalent to passing a steady flow of the reactant for a limited time. This would indeed be the case in the absence of longitudinal concentration gradients. However, admitting a dosage of the reactant to an evacuated space takes place very rapidly so that reaction subsequently proceeds uniformly over the external surface of the substrate.

In this paper we report experimental results on the preparation of silica membranes using the atomic layer epitaxy method modified to control the reactant dosage as described above, which we shall simply call "alternating reactant deposition." We also present a simple model used to explore the effect of reactant dosage, number of cycles, and other deposition parameters.

Experimental Section

A schematic of the apparatus for membrane deposition and permeation measurements is shown in Figure 1. The reactor consisted of a quartz tube of 11 mm ID containing a concentric Vycor tube (7 mm OD, 4.8 mm ID, and 4 nm mean pore diameter, 0.28 void fraction) secured by vacuum tight fittings. The porous Vycor tubes were supplied by Corning, Inc. A new Vycor tube was used in each experiment. The tube consisted of a porous section welded on the one side or from both sides to nonporous sections. The reactor was placed inside a tubular furnace with a temperature controller. The reactants SiCl_4 and H_2O were carried by N_2 gas from bubblers maintained at appropriate temperatures. In the arrangement shown in Figure 1, the Vycor tube was welded on one side to a nonporous section and sealed at the other side. The length of the porous section was about 10 cm. In this geometry the reactants could only be admitted in the annular space between the Vycor tube and the larger quartz tube, and the deposit layer was formed in the pores below the external surface of the Vycor tube. In other experiments, the Vycor tube was welded on both sides to nonporous segments, and the reactants were admitted in the bore of the tube to form a layer on the inside surface.

Before each deposition experiment the porous Vycor tube in place in the reactor was heated slowly to 600°C and kept for a few hours under flow of a N_2 -

O₂ mixture for a few hours to remove adsorbed water and organic impurities. The reactor was then heated up to the reaction temperature of 700°C or 800°C.

Each membrane preparation experiment consisted of a number of cycles, each cycle comprising silylation, purge with N₂, hydrolysis, and another purge. For each cycle, the reactor was first evacuated while the storage bulb (1000 ml) was filled with 7% of SiCl₄ in N₂ at atmospheric pressure by steady flow from the bubbler. The composition of the input to the storage tank was controlled by passing a 25 cm³/min nitrogen stream through the bubbler and subsequently diluting it with more N₂ to bring the final composition to the desired level. Because of the slow flow the outlet stream from the bubbler was assumed to be saturated at the ambient temperature. After the storage bulb was filled it was isolated from the flow and connected to the evacuated reaction chamber for a few seconds. The SiCl₄/N₂ mixture instantly filled the reactor, and after one or two seconds the valve was closed to isolate the reactor. At this point the reactor total pressure was slightly below 1 atm. The amount of SiCl₄ divided by the geometric area (not pore area) of the porous support tube contacted with SiCl₄ will be referred to below as "dosage" and will be listed in μmol/cm². The reaction was allowed to progress for 1 minute after which the reactor was purged for 1 minute with dry N₂. Subsequently a stream of 100 cm³/min of 10% H₂O-N₂ was passed through the reactor at atmospheric pressure for 5 minutes. The reactor was then purged once more for 5 minutes with dry N₂ to remove H₂O from the flow lines and the reactor surfaces.

After every 1 or 2 cycles, the permeation rate of N₂ was measured by a pressure rise technique. First, the inside of the Vycor tube and the annular space between the Vycor tube and the surrounding quartz tube were connected to vacuum. A flow of N₂ (or H₂) was then initiated through the inside at 2 atm pressure

while the annulus continued being evacuated. Finally, the annulus was isolated from vacuum and the pressure buildup was measured with a sensitive pressure transducer and recorded by a computer. The permeance was then computed from

$$Q[\text{cm}^3(\text{STP})/\text{cm}^2 - \text{min} - \text{atm}] = \frac{K}{A\Delta p} \frac{dp}{dt}$$

where Δp is the transmembrane pressure difference, A the membrane area and K a calibration factor established in a separate run with a bubble flowmeter. For N_2 and H_2 at the beginning of deposition and for H_2 at the end, the permeance was also measured with the bubble flowmeter as an additional check. The membrane area A was taken as the inside geometric area of the support tube $A = \pi d_i L$ where $d_i = 0.48$ cm and the length L varied from experiment to experiment in the range 8-16 cm.

The cycles of deposition and hydrolysis were repeated until the permeance of N_2 decreased by a factor of 30-100 below its original value. At this point the permeation rates of H_2 and N_2 were measured at several temperatures. The tube was subsequently heated under flow of 10% H_2O - N_2 resulting in further decrease of the N_2 permeance.

For some experiments, the tubes were subjected to intermittent hydrothermal treatments during deposition. The tubes were exposed to flow of 10% H_2O in N_2 at the deposition temperature for 5-10 hours between some cycles. The purpose of the intermittent treatment was to allow the deposit layers densify sufficiently before the final deposition and thus avoid uncontrollable densification in subsequent hydrothermal annealing.

Experimental Results and Discussion

Figure 2 shows the evolution of permeance with successive reaction cycles for two preparations (Membrane 1 and Membrane 2) using support tubes of different length. SiO_2 layers were deposited on the outside surface of the support tubes at 700°C . The permeance of N_2 decreased slowly during the first several cycles, rapidly during the next few cycles, and again slowly during the final cycles. This trend is not obvious on the semilog plot of Figure 2 but would be obvious on a linear plot. While the permeance of N_2 decreased by approximately a factor of 30, the permeance of H_2 decreased by about 10% during deposition. Table 1 lists the permeances of membranes 1 and 2 before deposition and after the final cycle of deposition. To be consistent with our previous work, the listed permeances were calculated on the basis of the inside cylindrical surface area of the membrane tubes.

After deposition the two tubes were exposed to flow of 10% H_2O in N_2 at 700°C and atmospheric pressure for one day. This treatment caused approximately 8% decline in the permeance of H_2 and 50% decline in the permeance of N_2 . The permeances of H_2 and N_2 after the treatment are shown by dotted lines in Figure 2 and are also listed in Table 1. This decrease of permeance during hydrothermal treatment can be attributed to densification of the deposit structure catalyzed by H_2O as discussed in our previous reports (Nam and Gavalas, 1989; Tsapatsis and Gavalas, 1993).

As mentioned earlier, the dosage of SiCl_4 in each silylation cycle is an important operating variable. Throughout this paper the dosage is given in μmol of SiCl_4 per cm^2 of the geometric (not pore) area of the tube, outside or inside,

exposed to the reactant. It is noted that the Membranes 1 and 2 described by Figure 2 and Table 1 were prepared with different SiCl_4 dosages, $0.62\mu\text{mol}/\text{cm}^2$ and $0.33\mu\text{mol}/\text{cm}^2$, respectively. Membrane 2 prepared with the smaller dosage required a greater number of cycles to attain equivalent reduction of the nitrogen permeance. Clearly, with the smaller amount of SiCl_4 per unit surface area per cycle, the reactant was depleted faster requiring more cycles to attain the desired reduction of N_2 permeance. Duplicate preparations have shown about 10% variation of final hydrogen permeance. The main components of this variation are probably the surface condition of the tube—surface density of hydroxyl groups—and small variations in the porous structure. The permeance measurement error is no more than 2%. In view of these variations the higher hydrogen permeance of Membrane 2 cannot be reliably attributed to the different dosage, although such an interpretation would be consistent with the expectation that lower dosage results in a thinner deposit layer.

The two membrane preparations described by Figure 3 and Table 2 were carried out using the same dosage per cycle and varied only by the deposition temperature. The permeance decreased more rapidly with cycle number and fewer cycles were needed to complete the deposition at 800°C . In these two experiments, intermittent hydrothermal treatment was interposed every few cycles as described in the experimental procedure section. Figure 3 shows the N_2 permeance decreasing after each of the hydrothermal treatments conducted after the 10th, 17th, and 23rd cycle for Membrane 3, and after the 9th and 15th cycle for Membrane 4. These decreases were relatively small in the earlier cycles but increased in the later cycles. The small change in early cycles was expected, since early during deposition the deposit layer makes a small contribution to the overall resistance. However, the direction of change at the early cycles was unexpected. With a small

volume of deposit and with N_2 permeance at 90% of its original value, the pore cross sections should have been largely open. Shrinkage of the deposit should have increased rather than decreased the open pore cross section. One possible explanation for the decrease of permeance following the hydrothermal treatment is that the deposit grows in a cluster-like or "tree-like" fashion rather than as a smooth layer. Hydrothermal treatment could lead to cross-linking, between clusters reducing diffusion through the narrower pore cross-sections. Yet, more complete understanding of the structural effect of hydrothermal treatment is necessary to understand the changes of the N_2 permeance.

After deposition, Membranes 3 and 4 were annealed at 550°C under 3 atm of H_2O (and 7 atm of N_2) for several days. The changes in the gas permeances during this treatment are listed in Table 2. The H_2 permeance at 700°C and 800°C decreased by at most 13% after 15 days of the treatment. At the lower temperature of measurement (450°C) the decrease was somewhat larger because the activation energy of the permeance increased after the treatment. The permeances listed in Table 2 are the result of in-series combination of the resistances of the support tube and the deposit layer. To examine the properties of the deposit layer by itself we subtracted the resistance of the support tube was subtracted and the permeances recalculated as follows:

The tube cross section is considered as two resistances in series, the resistance of the deposit layer and the resistance of the remaining unobstructed part of the tube. In view of the small thickness of the deposit layer, less than 1% of the wall thickness, the resistance of the unobstructed layer is set equal to the resistance of the untreated Vycor tube. If P , P_{DL} , P_S are the permeances of the whole membrane, the deposit layer, and the support tube we have

$$\frac{1}{P} = \frac{1}{P_{DL}} + \frac{1}{P_S}$$

which is used to calculate P_{DL} from the measured P , P_S .

The permeance of the deposit layers is listed in Table 3. The activation energies for the H_2 permeances of the deposit layers in Membranes 3 and 4, excluding the resistances of the support tube, are listed in Table 4. The activation energies of the two membranes for H_2 permeance were different initially but reached similar values, about 26 kJ/mol, after 15 days of the hydrothermal treatment. It is noted that Membrane 3 with lower initial activation energy underwent a sharper permeance decline by the hydrothermal treatment. The final activation energy of 26 kJ/mol reached after the hydrothermal treatment is somewhat lower than the activation energy, 30–32 kJ/mol, of nonporous Vycor (Altemose, 1962). This difference is easily accounted by the nonuniform structure of the deposit layer consisting of in-series resistances of a thin region with no open pore paths followed by a thicker region of gradually increasing pore size. The thin region itself has some residual closed porosity which tends to lower the activation energy (Kim and Gavalas, 1993; Tsapatsis and Gavalas, 1993). The initially higher activation energy of deposit layer 4 can be easily explained by the higher deposition temperature leading to a denser deposit.

Activation energies for N_2 permeance are not presented in Table 4 because the measurements of the very small N_2 permeances were inaccurate especially at the lower temperature (450°C). Any small leaks in the system could cause significant error in the permeance measurements.

To compare the membranes prepared in this study with membranes prepared by one-sided deposition and subjected to the same hydrothermal treatment, selected data from a previous study (Tsapatsis and Gavalas, 1993) are reproduced

in Table 5. After 21 days of hydrothermal treatment, the membrane prepared by one-sided deposition showed a 70% decrease of its H_2 permeance which reached $0.11 \text{ cm}^3(\text{STP})/(\text{min} \cdot \text{cm}^2 \cdot \text{atm})$ at 600°C . On the other hand, the membranes prepared by alternating reactants deposition had final H_2 permeances of $0.28\text{--}0.30 \text{ cm}^3(\text{STP})/(\text{min} \cdot \text{cm}^2 \cdot \text{atm})$ at 600°C after 15 days of hydrothermal treatment. The membrane produced by one-sided deposition had lower initial activation energy before the treatment ($10\text{--}15 \text{ kJ/mol}$ (Tsapatsis and Gavalas, 1993)). The final activation energies for H_2 permeance were the same for the two types of membranes, suggesting that the difference in the final H_2 permeances is due to a difference in thickness rather than in the state of densification. The same trend was previously observed in the comparison of Membranes 3 and 4 where the membrane with the higher initial activation energy underwent a smaller decrease of H_2 permeance after the treatment.

In view of the diffusion-limited nature of the deposition reaction, the deposit layer is expected to be spatially nonuniform with its density monotonically decreasing from the boundary towards the interior. To measure the profile density one could, in principle, use electron microprobe analysis (EMA). Unfortunately, for SiO_2 deposition on porous Vycor ($96+\% \text{ SiO}_2$), small variations in the substrate porosity near the boundary superimposed on measurement error made the deposit density measurement very unreliable. To obtain some idea of the deposit density profile, we carried out TiO_2 deposition using alternating reaction with TiCl_4 and H_2O . In this instance, measurement of the $\text{TiO}_2/\text{SiO}_2$ ratio is much more reliable. Figure 4 shows the mass ratio of TiO_2 to the SiO_2 substrate as calculated from an EMA linescan over the tube cross section. The Ti density decreases sharply with depth and declines to zero within $6\mu\text{m}$. In previous TGA studies we had found the TiCl_4 reaction with $-\text{OH}$ groups on Vycor to

be slower (about 5 times at 600°C) than the corresponding reaction with SiCl_4 . Consequently, the density profile of the SiO_2 deposit should be sharper with total thickness perhaps about $3\mu\text{m}$, on account of the inverse square root dependence of the depth of reactant penetration on the reaction rate constant.

An attempt can be made to estimate the deposit layer thickness from a mass balance. Assuming full utilization of SiCl_4 in a total of 23 cycles (membrane 3), each with $0.28\ \mu\text{mol}/\text{cm}^2$ dosage, and taking the molar volume of SiO_2 as $28\ \text{cm}^3/\text{mol}$ (full density) and the void fraction of the porous tube 0.28, we estimate a thickness of $6.4\ \mu\text{m}$ for a deposit layer of uniform density. However, the degree of SiCl_4 utilization can be considerably lower, especially in the later cycles, and the density of the layer decreases with distance from the surface. Hence a more realistic estimate for the thickness of the deposit layer is between 3 and $10\ \mu\text{m}$. Of that, only a thin surface layer is actually nonporous and controls the permeation selectivity of the membrane.

Model Description

The purpose of the calculations described below was to obtain a semiquantitative understanding of the effect of reactant dosage and other parameters on the deposit layer thickness and to identify the most important parameters for membrane optimization. To describe the growth of the deposit layer it was sufficient to treat only the silylation part of each cycle when new material was added on the deposit. The role of the hydrolysis part of the cycle is to regenerate the -OH groups after each silylation. For each silylation period diffusion and reaction can be described by the equations:

$$\frac{\partial}{\partial z} \left(D_{eff}(\epsilon) \frac{\partial C_{si}}{\partial z} \right) = k C_{si} C_{oh} \quad (5)$$

$$\frac{\partial C_{oh}}{\partial t} = -k C_{si} C_{oh} \quad (6)$$

$$V \left(\frac{dC_g}{dt} \right) = A \left(D_{eff}(\epsilon) \frac{\partial C_{si}}{\partial z} \right)_{z=0} \quad (7)$$

with the initial and boundary conditions:

$$z = 0 : C_{si} = C_g(t) \quad (8)$$

$$z \rightarrow \infty : C_{si} \rightarrow 0 \quad (9)$$

$$t = 0 : C_{oh} = m_o S(\epsilon), \quad C_g = C_{bo} \quad (10)$$

where C_{si} is the concentration of SiCl_4 in the voids and C_{oh} is the concentration of surface -OH groups per unit total volume of the material, respectively, C_g is the bulk concentration of gaseous SiCl_4 in the reaction chamber, $D_{eff}(\epsilon)$ is the effective diffusivity of SiCl_4 in the porous medium, V is the volume of the tube bore or the annulus containing the SiCl_4 reactant, A is the surface area of the reaction boundary (inside or outside cylindrical surface), m_o is the initial concentration of -OH groups per unit pore surface area, and $S(\epsilon)$ is the pore surface area per unit total volume of the porous material. The deposit layer is treated as nonporous, hence, $S(\epsilon)$ and the pore radius are calculated from the amount of deposit at each position. Clearly both $S(\epsilon)$ and $D_{eff}(\epsilon)$ are functions of position.

The plane geometry used in Equation (5) and the boundary condition at $z \rightarrow \infty$ are justified by the very small deposit layer thickness compared to the wall thickness ($3\mu\text{m}$ versus $1100\mu\text{m}$). In the formulation of Equation (5) the gas phase accumulation term was omitted because of the small ratio, $\frac{C_{bo}}{m_o S(\epsilon)}$ (less than 0.01). The reaction was assumed to be first order in the concentration of gaseous

SiCl_4 and in the concentration of -OH groups in the solid. The resistance due to external mass transfer of SiCl_4 in the radial direction was neglected because of the short diffusion path. Whether the reactant was introduced in the bore of the tube or in the annulus, the diffusion path in the radial direction was 2–2.5mm. With the binary diffusivity of SiCl_4 in N_2 at the reaction temperature of 700°C being estimated at about $0.6 \text{ cm}^2/\text{sec}$, the characteristic time for diffusion was only 0.07 sec compared to the reaction time of several seconds.

During each hydrolysis and the succeeding purge all -Cl groups are replaced by -OH groups. At the same time condensation reactions between two -OH groups and between -OH and -Cl reduce the concentration of the -OH groups available to the following silylation period. Since the time allowed to the hydrolysis and purge periods was held constant from cycle to cycle, it was assumed that the surface concentration of -OH groups was the same at the beginning of each cycle. However, since the deposit layer thickness and the pore surface area changed from cycle to cycle, the volumetric concentration of -OH groups also changed. Moreover, since the deposit layer thickness after the first cycle became a function of position, the volumetric concentration of -OH was also a function of position.

At the beginning of the first cycle the diffusivity was spatially uniform, but as the deposit layer developed with repeated cycles, D_{eff} developed a spatial dependence. During each cycle the deposit growth was limited to a fraction of a monolayer, therefore, the change of $D_{eff}(z)$ was very small for the duration of any single cycle. Thus to simplify the calculations, during any given cycle D_{eff} was treated as a function of z , independent of time. Likewise, the void fraction, ϵ , the local average pore radius, r , and the surface area, S , were treated as functions of x , independent of time, during any single cycle. The equations were solved repeatedly for successive cycles, and at the end of each cycle new profiles of

D_{eff} , ϵ , r and S were calculated according to the amount of deposit accumulated during the cycle. More specifically, the local void fraction was calculated using the relation,

$$\epsilon(z) = \epsilon_{no}(z) - v_s k \int_0^{t_p} C_{si} C_{oh} dt \quad (11)$$

where ϵ_{no} is the void fraction at the beginning of the cycle, v_s is the molar volume of the deposit, and t_p is the silylation time of each cycle.

The local pore radius and the surface area per unit volume were related to the void fraction using on the random capillary model (Gavalas, 1980). The material deposited in each cycle (in moles per unit total volume of the support) were expressed as

$$C_d(z) = C_{do}(z) + k \int_0^{t_p} C_{si} C_{oh} dt \quad (12)$$

where C_{do} is the value of C_d at the beginning of the cycle. The diffusion of SiCl_4 was assumed to be in the Knudsen regime so that

$$D_{eff} = \frac{2}{3\tau} \sqrt{\frac{8RT}{M}} \epsilon r \quad (13)$$

where τ is an empirical tortuosity factor taken as 3. In the calculation of $D_{eff}(z)$, the pore radius, $r(z)$, was corrected by subtracting the kinetic radius of SiCl_4 (Lennard-Jones diameter, 5.78Å (Prausnitz et al., 1986)). For the calculation of the N_2 flux performed at the end of each cycle, the diffusivity was calculated correcting the pore radius by the kinetic diameter of N_2 (Lennard-Jones diameter, 3.68Å).

Numerical Results

Equations (5)-(10) were solved by a semianalytical technique akin to that introduced by Del Borghi et al. (1976). The details of the solution procedure can

be found in Kim (1993). The parameters used in the calculations are listed in Table 5. The average initial pore radius was calculated from BET surface area and porosity data supplied by Corning using Equations (12) and (13).

The molar volume of the deposit, v_s , (in Table 5) was estimated from previous thermogravimetric measurements of weight gain in repeated silylation and hydrolysis cycles until pore plugging (Kim and Gavalas, 1993). The estimated value was larger than that of amorphous silica because of the highly defective nature of the deposit and the inclusion of a certain amount of trapped voids in the layer. The rate constant of silylation was estimated by extrapolation from the previous thermogravimetric measurements at 400–500°C (Kim and Gavalas, 1993). The initial surface density of -OH groups was also estimated from the previous thermogravimetric measurements.

Figure 5 shows the calculated deposit density profiles after each cycle versus the normalized distance from the boundary, for SiCl_4 dosage $0.33\mu\text{mol}/\text{cm}^2$ and for the other parameters corresponding to the preparation of Membrane 2 (Table 1). The deposit density declines to 10% of its boundary value within $15\mu\text{m}$. This thickness is larger than the $3\mu\text{m}$ penetration depth estimated earlier. The difference may be due to underestimating the reaction rate constant in extrapolating from lower temperature data, or overestimating the effective diffusion coefficient as discussed below.

The effect of reactant dosage on the deposit layer thickness is shown in Figure 6. Smaller dosage necessitates a larger number of cycles to reach pore plugging. For the smallest dosage shown in Figure 6, the total number of cycles required for pore plugging was 83. As the dosage is further reduced, the extent of silylation at each cycle becomes smaller because of fast exhaustion of the reactant, and the consumption of surface -OH groups is accordingly smaller. In the limit of zero

dosage and infinite number of cycles, the concentration of -OH groups is constant, thus the reaction occurs with the initial surface concentration of -OH maintained at all values of x . As that limit is approached, the deposit density profile also reaches a limit as shown in Figure 6. This limit represents the thinnest membrane that can be theoretically prepared within the assumptions of the model. Figure 7 shows the calculated evolution of N_2 permeance versus the product of dosage and cycle number, i.e., versus the total amount of $SiCl_4$ introduced. As the dosage decreases, the permeance curve tends to a limiting curve corresponding to the limiting density profile.

Figure 7 shows the calculated flux for different dosages, and the experimental flux for $0.33\mu\text{mol}/\text{cm}^2$ dosage (Membrane 2). The poor agreement between calculated and experimental curves for the $0.33\mu\text{mol}/\text{cm}^2$ dosage can be attributed to the drastic assumptions made in the calculation of D_{eff} . These assumptions were:

(i) Uniform pore size distribution

Vycor has a unimodal pore size distribution with mean pore diameter $40\text{\AA}$ and upper and lower cutoff points at about $100\text{\AA}$ and $20\text{\AA}$, respectively. The pores have the shape of capillaries with varying cross sections. Replacing the pore size distribution by a single pore size would tend to underpredict the diffusivity. It also explains the calculated steep decrease to zero during the last few cycles, which is at variance with the measured gradual decline. On the other hand, replacing a varying cross section with a uniform cross section would overpredict the diffusion coefficients throughout deposition. A related factor in overpredicting the diffusion coefficient is the decrease of connectivity (generation of open non-conducting pores), not taken into account in the calculations.

(ii) Layer-like growth

If as discussed earlier the deposit growth is cluster-like or tree-like, the decrease of diffusivity at the beginning of deposition would be steeper than if growth was layer-like. The differences between calculated and experimental permeances during the early cycles are probably largely due to the different modes of deposit growth.

(iii) Knudsen diffusion

The calculations were carried out assuming Knudsen diffusivities (corrected for the size of the diffusing molecule) until the pore diameter reached the kinetic diameter of SiCl_4 at which point the pores were regarded "plugged," i.e., completely blocked to flow. However, as the pore diameter declines below $20\text{\AA}$, the Knudsen formula becomes increasingly inaccurate and becomes totally inadequate for pores below $10\text{\AA}$. Using the Knudsen formula throughout deposition would again overpredict the effective diffusivity.

In view of the above uncertainties the calculation of diffusivities and permeances is increasingly in error as the deposition progresses. Figure 7, therefore, was included only to illustrate the inadequacy of standard diffusion models for calculations of membrane permeance.

To investigate the effect of the aforementioned assumption (i), we introduced a pore size distribution to the model using three initial pore radii ($25\text{\AA}$, $20\text{\AA}$, and $10\text{\AA}$). For simplicity of calculation the parallel pore model was used instead of random capillary model. Figure 8 compares the flux calculated using a single pore size ($20\text{\AA}$ radius) and those calculated using different pore size distributions. The curves calculated for the pore size distributions show more gradual decline during the last few cycles, as observed experimentally. On the other hand, the slow decline during the early cycles is still at variance with the experimental

steeper decline. The steeper experimental decline during the early cycles could be attributed to the varying cross section of individual pores and to the cluster-like growth of the deposit. To explore the first effect calculations were performed treating each pore as two in-series sections of different initial diameters. The flux calculated with this modified pore geometry featured a steeper decline in the early cycles, but was in poor agreement with the later part of the experimental curves.

Figure 9 shows the effect of the initial -OH concentration on the deposit profile. Higher initial concentrations of -OH increase the reaction rate and thus decrease the penetration depth and the number of cycles to complete pore plugging. To maintain the initial -OH groups at as high a level as possible, it is important to limit the length and temperature of pretreatment preceding membrane deposition.

Concluding Remarks

Hydrogen permselective silica membranes were deposited on porous Vycor tubes by a series of alternating reactions with SiCl_4 and H_2O . Upon prolonged hydrothermal treatment the membrane permeance decreased about 20–30%. Comparison of the membranes prepared by alternating deposition with those prepared in our earlier work by one-sided deposition revealed the following differences. Immediately after deposition both types of membranes have approximately the same permeance. Upon prolonged hydrothermal treatment, however, the membranes prepared by alternating deposition suffer much smaller decline in permeance (20–30% vs. 70–80%) and have better $\text{H}_2:\text{N}_2$ selectivity. These results strongly suggest that the membranes prepared by alternating deposition are thinner and initially denser. Both types of membranes reach approximately equal densities after prolonged hydrothermal treatment. The smaller thickness of the membranes prepared

by alternating deposition is mainly due to the elimination of axial reactant concentration gradients and gas-phase particle formation both of which result in thicker deposit layers.

Nomenclature

- A External surface area of support tube, cm^2
- C_{bo} Initial concentration of bulk SiCl_4 concentration in gas phase, mol/cm^3
- C_d Concentration of SiO_2 deposit, mol/cm^3
- C_g Concentration of bulk SiCl_4 concentration in gas phase, mol/cm^3
- C_{oh} Concentration of $-\text{OH}$ groups in porous medium, mol/cm^3
- C_{si} Concentration of SiCl_4 in porous medium, mol/cm^3
- D_{eff} Diffusion coefficient of SiCl_4 in porous medium, cm^2/min
- k Reaction rate constant for silylation reaction, $\text{cm}^3/(\text{min}\cdot\text{mol})$
- L Thickness of the support tube wall, cm
- M Molecular weight of SiCl_4 , g/mol
- m_o Concentration of initial $-\text{OH}$ per unit surface area, mol/cm^2
- R Gas constant, $\text{erg}/(\text{mol}\cdot\text{K})$
- r Average local pore radius, cm
- S Surface area of porous Vycor per unit total volume, cm^2/cm^3
- t Time, min
- t_p Time period for one reaction cycle, min
- V Volume of the reactor, cm^3
- v_s Molar volume of SiO_2 deposit, cm^3/mol
- z Distance in Vycor wall cross section, cm
- ϵ Void fraction
- λ Probability density function characterizing the porous medium (in random capillary model)
- τ Empirical tortuosity factor

Acknowledgement

The authors appreciate the funding of this work by the Department of Energy under the University Coal Research Program, Grant DE-FG22-92PC92525. Corning Inc. graciously donated the porous Vycor tubes.

Literature Cited

- Altemose, V. O. Permeation of Gases in Glass. *Seventh Symposium on the Art of Glassblowing* 1962 The American Scientific Glassblowers Society, Wilmington, Del.
- Armor, J. N. Catalysis with Permselective Inorganic Membranes. *Applied Catalysis* 1989, 49, 1.
- Brinker, C. J. Structure of Sol-Gel-Derived Glasses. In *Glass Science and Technology*; Academic Press: New York, 1990; Vol. 4A, p. 169.
- Del Borghi, M.; Dunn, J. C.; Bischoff, K. B. A Technique for Solution of the Equations for Fluid Solid Reactions with Diffusion. *Chem. Eng. Sci.* 1976, 31, 1065.
- Gavalas, G. R. A Random Capillary Model with Application to Char Gasification at Chemically Controlled Rates. *AIChE J.* 1980, 26, 577.
- Ha, H. Y.; Nam, S. W.; Hong, S. A.; Lee, W. K. Chemical Vapor Deposition of Hydrogen Permselective Silica Films on Porous Glass Supports from Tetraethylorthosilicate. *J. Membr. Sci.* 1993, 85, 279.
- Kameyama, T.; Dokiya, M.; Fujishige, M.; Yokokawa, H.; Fukuda, K. Possibility for Effective Production of Hydrogen from Hydrogen Sulfide by Means of a Porous Vycor Glass Membrane. *Ind. Eng. Chem. Fundam.* 1981, 20, 97.
- Kern, W. Densification of Vapor-Deposited Phosphosilicate Glass Films. *RCA Review* 1976, 37 (3), 55.
- Kim, S.; Gavalas, G. R. Kinetic Study of the Reactions of Chlorosilanes with Porous Vycor Glass. *J. Colloid and interface Sci.* 1993, 161, 6.

- Mohan, K.; Govind, R. Analysis of Equilibrium Shift in Isothermal Reactors with a Permselective Wall. *AIChE J.* 1988, 34, 1493.
- Megiris, C. E.; Glezer, J. H. E. Preparation of Silicon Dioxide Films by Low-Pressure Chemical Vapor Deposition on Dense and Porous Alumina Substrates. *Chem. Eng. Sci.* 1992, 47, 3925.
- Nam, S. W.; Gavalas, G. R. Stability of H₂ Permselective SiO₂ Films Formed by Chemical Vapor Deposition. *AIChE Symp. Ser.* 1989, 85, 68.
- Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1986; p. 85.
- Raymont, M. E. D. Make Hydrogen from Hydrogen Sulfide. *Hydrocarb. Process.* 1975, 54 (7), 139.
- Ritala, M.; Leskelä, M.; Nykänen, E.; Soininen, P.; Niinistö, L. Growth of Titanium Dioxide Thin Films by Atomic Layer Epitaxy. *Thin Solid Films* 1993, 225, 288.
- Shelby, J. E. Molecular Solubility and Diffusion. In *Treatise of Materials Science and Technology*; Academic Press: New York, 1979; Vol. 17.
- Sun, Y. M.; Khang, S. J. Catalytic Membrane for Simultaneous Chemical Reaction and Separation Applied to a Dehydrogenation Reaction. *Ind. Eng. Chem. Res.* 1988, 27, 1136.
- Suntola, T.; Simpson, M. *Atomic Layer Epitaxy*; Blackie, Glasgow, 1990; p. 1.
- Tsapatsis, M.; Kim, S.; Nam, S. W.; Gavalas, G. R. Synthesis of H₂ Permselective SiO₂, TiCl₄, Al₂O₃, and B₂O₃ Membranes From the Chloride Precursors. *Ind. Eng. Chem. Res.* 1991, 30, 2152.

- Tsapatsis, M.; Gavalas, G. R. A Kinetic Model of Membrane Formation by CVD of SiO_2 and Al_2O_3 , *AIChE J.* **1992**, 38, 847.
- Tsapatsis, M.; Gavalas, G. R. Structure and Aging Characteristics of H_2 Permeative SiO_2 -Vycor Membranes. *J. Membr. Sci.* **1994**, 87, 281.
- Usui, A. Study of Self-limiting Growth Mechanism in Chloride ALE. *Thin Solid Films* **1993**, 225, 53.
- Yoldas, B. E. Alumina Gels that Form Porous Transparent Al_2O_3 . *J. Mat. Sci.* **1975**, 10, 1856.

Table 1 Membrane permeance to H₂ and N₂ before deposition, after deposition, and after hydrothermal treatment by flow of 10% H₂O-N₂ at atmospheric pressure and 700°C for one day. The SiCl₄ dosage per cycle was 0.62 μmol/cm² for Membrane 1 and 0.33 μmol/cm² for Membrane 2.

Permeance at 700°C (cm ³ (STP)/cm ² -min-atm)						
	<u>Before deposition</u>		<u>After final cycle</u>		<u>After hydrothermal treatment</u>	
	N ₂	H ₂	N ₂	H ₂	N ₂	H ₂
Membrane 1	0.131	0.473	0.0046	0.413	0.0026	0.405
Membrane 2	0.135	0.505 ^a	0.0013	0.456	0.0006	0.420

^a estimated by the Knudsen ratio H₂:N₂ = 3.74

Table 2 Permeance of membranes deposited on the inner surface before and after hydrothermal treatments.
The dosage of SiCl_4 per cycle was $0.28 \mu\text{mol}/\text{cm}^2$.

Permeance ($\text{cm}^3(\text{STP})/\text{min atm cm}^2$)										
	Reaction T (°C)	Measure- ment T (°C)	after <u>Deposition</u>		after <u>Treatment 1</u>		after <u>Treatment 2</u>		after <u>Treatment 3</u>	
			N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2
Membrane 3	700	700	0.0039	0.38	0.0011	0.37	0.00049	0.34	0.00042	0.33
		600	0.0036	0.37	0.00073	0.35	0.00021	0.31	0.00015	0.30
		450	0.0019	0.33	0.00041	0.29	0.00016	0.23	0.000094	0.21
Membrane 4	800	800	0.0013	0.37	0.00099	0.37	0.00053	0.34	0.00033	0.34
		600	0.00046	0.34	0.00038	0.33	0.00025	0.30	0.00018	0.28
		450	0.00020	0.28	0.00026	0.27	0.00018	0.20	0.00015	0.19

Treatment 1: 5 days at 500°C under 7 atm N_2 and 3 atm H_2O .

Treatment 2: 10 days at 500°C under 7 atm N_2 and 3 atm H_2O .

Treatment 3: 15 days at 550°C under 7 atm N_2 and 3 atm H_2O .

Table 3 The permeance of deposit layers excluding the resistance of Vycor tube. The SiCl_4 dosage per cycle was $0.28 \mu\text{mol}/\text{cm}^2$.

Permeance ($\text{cm}^3(\text{STP})/\text{min atm cm}^2$)										
	Reaction T (°C)	Measure- ment T (°C)	after <u>Deposition</u>		after <u>Treatment 1</u>		after <u>Treatment 2</u>		after <u>Treatment 3</u>	
			N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2
Membrane 3	700	700	0.0041	1.74	0.0012	1.57	0.00049	1.15	0.00042	1.04
		600	0.0037	1.33	0.00074	1.13	0.00021	0.76	0.00015	0.70
		450	0.0019	0.82	0.00041	0.62	0.00016	0.40	0.00009	0.34
Membrane 4	800	800	0.0013	1.65	0.00099	1.58	0.00053	1.18	0.00033	1.16
		600	0.00046	0.99	0.00038	0.93	0.00025	0.72	0.00018	0.63
		450	0.00020	0.56	0.00026	0.51	0.00018	0.32	0.00015	0.29

Treatment 1: 5 days at 500°C under 7 atm N_2 and 3 atm H_2O .
 Treatment 2: 10 days at 500°C under 7 atm N_2 and 3 atm H_2O .
 Treatment 3: 15 days at 550°C under 7 atm N_2 and 3 atm H_2O .

Table 4 Permeance of membranes¹ produced by one-sided (simultaneous flow) deposition before and after hydrothermal treatments.

Reaction T (°C)	Measure- ment T (°C)	Permeance (cm ³ (STP)/min atm cm ²)							
		after <u>Deposition</u> ²		after <u>Treatment 1</u>		after <u>Treatment 2</u>		after <u>Treatment 3</u>	
		N ₂	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂	H ₂
750	750	0.002	0.40						
	600			0.006	0.25	0.0001	0.12	0.0001	0.11

¹Selected data from Table I in (Tsapatsis and Gavalas, 1993).

²Deposition by continuous flow of 0.027atm SiCl₄ and 0.13atm H₂O for 5 minutes.

Treatment 1: 2 days at 550°C under 7 atm N₂ and 3 atm H₂O.

Treatment 2: 9 days at 500°C under 7 atm N₂ and 3 atm H₂O.

Treatment 3: 21 days at 500°C under 7 atm N₂ and 3 atm H₂O.

Table 5 Activation energy for H₂ permeance of Membranes 3 and 4 before and after hydrothermal treatments in kJ/mol).

	after <u>Deposition</u>	after <u>Treatment 1</u>	after <u>Treatment 2</u>	after <u>Treatment 3</u>
Membrane 3	17.3	21.5	24.6	25.8
Membrane 4	20.1	20.8	24.5	25.8

Treatment 1: 5 days at 550°C under 7 atm N₂ and 3 atm H₂O.

Treatment 2: 10 days at 550°C under 7 atm N₂ and 3 atm H₂O.

Treatment 3: 15 days at 550°C under 7 atm N₂ and 3 atm H₂O.

Table 6 Parameters used in the calculations.

$D_{\text{eff}}(\epsilon_0) = 2.32 \times 10^{-2} \text{ cm}^2/\text{min}$	$C_{\text{bo}} = 8.77 \times 10^{-7} \text{ mol/cm}^3$
$k = 3.7 \times 10^8 \text{ cm}^3/\text{mol min}$	$v_s = 49.2 \text{ cm}^3/\text{mol}$
$m_0 = 1.6 \times 10^{-10} \text{ mol/cm}^2$	$V = 12.5 \text{ cm}^3$
$S(\epsilon_0) = 3.0 \times 10^6 \text{ cm}^2/\text{cm}^3$	$A = 33.0 \text{ cm}^2$
$L = 0.11 \text{ cm}$	$\epsilon_0 = 0.3$
	$r_0 = 16.65 \text{ \AA}$

Figure 1 Schematic diagram of the reactor system. 1: bubbler with heating element and temperature controller; 2: furnace with temperature controller; 3: quartz tube reactor; 4: fixed volume gas collection bulb; 5: 3-way valve; 6: 4-way valve; 7: on-off valve; 8: pressure transducer connected to microcomputer.

Figure 2 Permeance of H₂ and N₂ versus cycle number at 700°C for SiCl₄ dosage of 0.62 μmol/cm² for Membrane 1 (▲) and 0.33 μmol/cm² for Membrane 2 (■). (Δ) and (□) indicate the permeance changes after 1 day of hydrothermal treatment at 700°C under 0.1 atm H₂O and 1 atm of N₂.

Figure 3 Permeance of H₂ and N₂ versus cycle number for the reaction at 700°C (Membrane 3, ●) and 800°C (Membrane 4, ◇) for SiCl₄ dosage of 0.28 μmol/cm² per cycle. The points marked by I indicate the end of intermediate hydrothermal treatments. (◇) and (○) indicate the permeance changes after 5 days of hydrothermal treatment at 550°C under 3 atm H₂O and 7 atm of N₂.

Figure 4 EMA linescan of a tube cross section containing TiO_2 layers deposited at 700°C using TiCl_4 dosage of $0.37\mu\text{mol}/\text{cm}^2$ per cycle.

Figure 5 Calculated deposit density profiles after each cycle of deposition at 700°C. The SiCl₄ dosage was 0.33 μmol/cm² per cycle.

Figure 6 Calculated final deposit density profiles for different SiCl_4 dosages.

Figure 7 Calculated permeance versus cycle number for different SiCl_4 dosages (—). The full squares (■) show the experimental permeance obtained using SiCl_4 dosage of 0.33 $\mu\text{mol}/\text{cm}^2$ per cycle.

Figure 8 Calculated permeance versus cycle number for SiCl_4 dosage of $0.33 \mu\text{mol}/\text{cm}^2$ and for different pore size distributions. (---) : single pore size ($20\text{\AA}$ in radius, void fraction 0.3); Curves A, B, and C : pore size distributions with radii $25\text{\AA}$, $20\text{\AA}$, and $10\text{\AA}$ and void fractions 0.083, 0.20, 0.017 (A), 0.042, 0.25, 0.008 (B), and 0.017, 0.28, 0.003 (C). The full squares (■) show the experimental permeance obtained using SiCl_4 dosage of $0.33 \mu\text{mol}/\text{cm}^2$ per cycle.

Figure 9 Calculated deposit density profiles for various initial surface concentrations of -OH groups.

Chapter 2

MEMBRANE CHARACTERIZATION

*The material in this chapter has been published in
the Journal of Membrane Science 87, 281 (1994).*

Reprint removed for separate cycling. et

Chapter 3

TGA STUDY OF KINETICS OF SiO₂ CVD

*The material in this chapter has been published in the
Journal of Colloid and Interface Science 161, 6 (1993).*

*Reprint removed for separate
cycling. At*

Chapter 4

MEASUREMENTS OF MEMBRANE PERMEABILITY

~~Reprint removed~~

Introduction

Membrane layers deposited by reactions of gaseous precursors in porous supports are spatially nonuniform. The nonuniformity is simply the result of the concentration gradients established by the depletion of the reactants inside the porous support. The nonuniform structure causes a permeability profile $P(x)$ so that the overall permeance Q of the deposit layer is given by the integral

$$\frac{1}{Q} = \int_0^{\delta} \frac{dx}{P(x)}$$

where δ is the layer thickness. It is evident that a measurement of the overall permeance Q cannot reveal the pointwise permeability of the deposit layer. From the fundamental standpoint, however, it is important to determine the pointwise permeability as a function of the extent of reaction and other parameters of CVD. Measurement of the permeability P requires spatially uniform layers. Such layers can be prepared by the alternating CVD procedure described in Chapter 1 with the following modification. Each of the successive periods of reaction with SiCl_4 and with H_2O must be extended sufficiently to permit complete conversion of all the available surface groups. The self-limiting nature of these reactions ensures a spatially uniform deposit layer until such time as SiCl_4 diffusion becomes extremely slow and activated.

Experimental

Measurement Procedure

The basic experimental setup is shown in Figure 1. A porous Vycor tube is placed vertically within a larger quartz tube and enclosed in an electrical furnace. The upper end of the Vycor tube is sealed while the lower end is connected to a differentially pumped inlet of a quadrupole mass spectrometer (UTI 100C) not shown in the figure. The support tube is subjected to alternating CVD with SiCl_4 and H_2O flows introduced as

shown in Figure 1. A small section of Vycor tubing--identical material to that of the support tube--is suspended from a digital recording microbalance (CAHN D-200) to provide a continuous mass measurement during CVD.

After the completion of each reaction cycle (reaction with SiCl_4 followed by reaction with H_2O) the permeance of the Vycor tube to different gases is measured using the MS. This measurement is complicated by the fact that the pressure inside the Vycor tube decreases from cycle to cycle as the permeation resistance of the tube increases. The differentially pumped system utilizes a controlled addition of another gas to maintain a relatively constant pressure and a small constant flow of Ar to serve as an internal standard.

Preparation of the Support Tube

Consider the difficulties were encountered with the preparation of Vycor tubes sealed at one end and welded to nonporous tubing at the other end. The tubes would invariably break during the prolonged heating needed in the experiments. In an effort to improve the strength of the tubes, the glass blower's welding was replaced with a glass seal. After some optimization of the sealing procedure, the tubes could maintain their integrity for several hours of alternating CVD at 500°C . After 8-12 hours, however, the tubes cracked.

An effort was made to replace reaction with SiCl_4 and H_2O with TEOS (tetraethyl silicate) pyrolysis at a lower temperature about 300°C . The latter reaction is not self-limiting and it proved impractical to achieve spatially uniform deposition.

In view of these difficulties we were able to carry out spatially uniform deposition only up to 6-8 cycles of reaction with SiCl_4 and H_2O . The limited results obtained are given in the next section.

Results and Discussion

Kinetic Experiments

Figure 2 shows the TGA trace for the first two cycles of silylation and hydrolysis resulting in approximately 2% weight gain per cycle. The sample used in this experiment was a small Vycor tube segment (0.5 mm ID, 0.7 mm OD, 0.5 cm length, 40 Å mean pore diameter). Figure 3 shows the cumulative weight gain for the same sample over eight complete cycles of silylation and hydrolysis. As noted earlier, both silylation and hydrolysis are self-limiting reactions, i.e. they continue until all surface sites have fully reacted and then stop.

Pore Modification Experiments

Figure 4 shows the decline of the permeance of several gases (measured by the MS) as a function of weight gain (measured by the TGA). Using the density, surface area and porosity of Vycor we estimate the average thickness (thickness of a uniform layer of the same mass) of the deposit layer as 0.4 nm at 14% weight gain. Thus, the mean pore radius would be reduced from 0.22 nm to 0.18 nm. Assuming diffusion in the Knudsen regime, the diffusion coefficients based on the mean pore diameter should have declined by 18%. The experimental results in Figure 3 show that the permeances suffered a much larger decline, 25-50% (the smallest decline was observed for the smaller molecule, hydrogen). This important result shows for the first time that chemical vapor deposition of SiO₂ does not produce a smooth deposit layer but generates local growths, or lumps, which cause steeper decline of the diffusion coefficient than a smooth layer of equal mass would.

To appreciate the results of Figure 4 better, Figure 5 compares the flux of SF₆ and CH₄ normalized by the flux of N₂ and the molecular weights of these molecules versus weight gain. If diffusion was in the Knudsen regime throughout, the normalized fluxes would be equal to unity. The measured fluxes show modest deviations from Knudsen

diffusion even at 0% weight gain and the deviations increase slowly with weight gain. It must be noted that these deviations are not due to surface diffusion which is negligible at 500°C.

In conclusion, the diffusion coefficient and permeability of mesoporous materials about 4-5 nm diameter show modest deviations from their Knudsen values. Moreover, as solid product accumulates on the pore surface the diffusion coefficient declines rapidly because of the lump like geometry of the deposit.

Our efforts to continue CVD of SiO₂ beyond 14% mass gain were unsuccessful because the tube invariably developed cracks or was completely shattered after about 6-8 cycles of silylation and hydrolysis. The cause of this disintegration of Vycor is not known but is evidently due to some form of chemical corrosion and stresses as a result of the reaction and the accumulation of solid material.

Deposition System

Figure 1. TGA system showing the porous Vycor tube placement in the TGA furnace.

Silica Deposition in Porous Glass

Figure 2. The first (—) and second (···) cycle of alternating silylation and hydrolysis at 500°C of a porous Vycor sample, 1 mm thick.

Absolute Weight Change of Vycor During Silica Deposition

Figure 3. Cumulative weight gain during successive silylation and hydrolysis cycles at 500°C of a porous Vycor sample, 1 mm thick.

Variation of Permeance with Deposition

Figure 4. Permeance of several gases at 500°C versus weight gain during alternating reactants deposition of SiO₂.

Deviation of Permeances from Knudsen Results

Figure 5. Normalized permeance ratios $CH_4:N_2$ and $SF_6:N_2$ at $500^\circ C$ versus weight gain during alternating reactants deposition of SiO_2 .

Chapter 5

MATHEMATICAL MODEL OF CVD

The material in this chapter has been submitted to the AIChE Journal.

Preprint removed for separate cycling. At

Chapter 6

CONCLUSIONS

Conclusions

1. Hydrogen permselective silica layers were deposited on porous Vycor tubes by a series of alternating reactions with SiCl_4 and H_2O . Comparison of the membranes prepared by this alternating deposition with those prepared in our earlier work by one-sided deposition revealed the following differences. Immediately after deposition both types of membranes have approximately the same permeance, $0.3\text{--}0.4 \text{ cm}^3/\text{cm}^2\text{-min-atm}$ at 600°C . Upon prolonged hydrothermal treatment, 3-4 weeks at $500\text{--}550^\circ\text{C}$ under 3 atm of H_2O vapor, however, the membranes prepared by alternating deposition suffer much smaller decline in permeance (20-30% vs. 70-80%) and have better $\text{H}_2:\text{N}_2$ selectivity (2000 vs. 1000). These results strongly suggest that the membranes prepared by alternating deposition are thinner and initially denser. Both types of membranes reach approximately equal densities after prolonged hydrothermal treatment. Approximately one half of the permeation resistance of the membrane is due to the support, hence, using thinner or more permeable (multi-layered) supports can increase the permeance to about $0.6 \text{ cm}^3/\text{cm}^2\text{-min-atm}$. This is considered as the best permeance that can be achieved with this type of preparation protocol. In subsequent work in our laboratory the deposit layer permeance (net of the support) was increased further to about $2 \text{ cm}^3/\text{cm}^2\text{-min-atm}$ using a carbon barrier technique but the stability of these thinner membranes was not tested.
2. Results of thermogravimetric measurements and transmission electron microscopy show that at the end of deposition the deposit layer contains a sizable fraction of trapped porosity. The formation of this trapped porosity is due to the disruption of pore connectivity before complete pore filling. The trapped porosity enhances the permeance of the deposit layer to a level several times higher than that of a

completely dense layer of equal thickness. A CVD model using tools from percolation theory was developed to explain the formation of trapped porosity.

3. The mechanism and kinetics of SiO_2 deposition on porous Vycor glass by alternating reaction with SiCl_4 and H_2O were studied at 400-600°C using a thermogravimetric analyzer. The Si-OH (silanols) groups that react with SiCl_4 can be approximately classified as isolated and vicinal or paired, the latter being more abundant. After reaction of the first silanol of a pair with SiCl_4 , the second silanol can either combine with a second gaseous SiCl_4 or condense with the already attached $-\text{SiCl}_3$ group. The competition between these two sterically hindered and slow reactions controls the overall extent of silylation. A simple kinetic model postulating two types of silanols and including the reaction with SiCl_4 , the hydrolysis and the condensation steps was formulated and used to determine the relevant rate parameters. Even at 500°C the reactions are limited by external mass transfer and pore diffusion.
4. Permeability measurements with spatially uniform deposit layers reveal that the deposit does not develop in a smooth layer-by-layer fashion but by the growth of lumps centered around the initial silanol groups on the support surface. As a result of this nonuniform growth, the decline of permeability is steeper than would be the case for a smooth layer-by-layer deposition. The implications of the lump-like mode of growth have not been included yet in our modeling efforts.