DOE/ID/13062--T1

DE93 003285

DEVELOPMENT OF PHOSPHATE-BASED CERAMIC MEMBRANES

Final Report

November 1992

Work Performed Under Contract No. DE-FG07-91ID13062

Prepared for the
U.S. Department of Energy
Under DOE Idaho Field Office
Sponsored by the Office of the Assistant Secretary
for Conservation and Renewable Energy
Office of Industrial Technologies
Washington, D.C.

Prepared by
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Development of Phosphate-Based Ceramic Membranes - Final Report

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ABSTRACT

The primary goal of this research project was to fabricate and characterize microporous ceramic membranes by coating sols that contain nanoparticles onto porous ceramic supports. The resulting modules could be utilized for either gas phase separations or liquid phase separations involving low molecular weight solutes. Fulfillment of this goal required the synthesis of sols containing particles with characteristic dimensions in the range from 2 to 10 nm. Procedures employed to prepare nanoparticulate sols of silica, alumina, and aluminosilicates of various compositions are given. Unsupported ceramic membranes prepared from these sols were characterized by mean pore diameters of <10 Å for silica membranes and ca. 35 Å for aluminosilicate membranes of several different compositions. Although the alumina membranes have not been fully characterized, they display both microporosity (mean pore diameters <20 Å) and mesoporosity (mean pore diameters >20 Å).

Another requirement for successfully completing this project was to coat these nanoparticulate sols onto suitable porous supports. Due to equipment and personnel limitations, only four methods of fabricating supported ceramic membranes could be investigated. Dip coating appeared to give the best performance of all of these techniques and was easily implemented. Deposition of particles within porous supports by permformation was demonstrated, but a viable supported membrane has yet to be fabricated using this technique. Critical point drying studies of membranes were initiated, but progress has been limited by operational problems with the equipment. Slip casting could

not be successfully employed to fabricate a supported membrane that was free from cracks. Although dip coating was the fabrication technique that gave the best results for the systems utilized for this study, other methods of coating nanoparticulate sols onto porous supports might be preferable for other systems. Separate studies should be performed to determine the best coating technique for each combination of sol and support of interest.

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EXECUTIVE SUMMARY

The primary objective of this project was to fabricate microporous supported ceramic membranes for applications involving gas phase separations and separations of low molecular weight materials dissolved in liquid streams. Successful fabrication of these membranes required the synthesis of sols that contained nanoparticles, i.e., particles with characteristic dimensions in the range from 2 to 10 nm, and the coating of these sols on suitable porous supports. All work was performed at the Water Chemistry Program and the Department of Chemical Engineering at the University of Wisconsin - Madison between March 1991 and May 1992. Preparation of sols was based at the Water Chemistry Program, while the studies performed at the Department of Chemical Engineering were focused on fabricating and characterizing modules that utilized nanoparticulate sols.

Research on the synthesis of nanoparticulate sols resulted in the preparation of aqueous sols of silica and boehmite (γ-AlOOH), as well as alcoholic sols of aluminosilicates of various compositions. Unsupported membranes fabricated from the silica sol by evaporation of the solvent were characterized by mean pore diameters of <10 Å. This size is suitable for microfiltration applications. Unsupported alumina membranes displayed a wide distribution of pore sizes and must be further characterized. While many of the aluminosilicate sols did not contain nanoparticles, unsupported membranes fabricated from these sols displayed very impressive thermal stabilities. An 80 mol% Al_2O_3 membrane retained a mean pore diameter of 35 Å when fired at 1200°C for 1 h. Such thermally stable membranes could be useful for separations that must be conducted at high temperatures. The data also indicate that 40 mol% Al_2O_3 membranes would be microporous.

The overall objective of fabricating a microporous supported ceramic membrane was achieved by dip coating porous alumina disks with an alcohol-based nanoparticulate TiO_2 sol. While the resulting modules have displayed some permselectivity for the separation of polyethylene glycol polymers of molecular weight 200 from aqueous solutions, these modules are still being characterized. Several other techniques for fabricating supported ceramic membranes were also studied. Results obtained using a slip casting approach were quite poor. Permformation and critical point drying are still under development. While these latter two methods offer some advantages in making supported membranes, their special requirements in the way of equipment may limit the commercial applicability of these techniques. Of the four methods tested, dip coating appeared to be the most promising.

Dip coating is relatively easy to implement if several factors are incorporated in the experimental design. For one, the porous supports should be saturated with solvent. In addition, the sols employed for dip coating should contain relatively low concentrations of particles. One method of enhancing the performance of both dip coating and permformation was to change the charge of the surface of the support in order to increase the electrostatic attraction force between the particles of the sol and the support. The best method for changing the charge of the support was to adsorb phosphate ions on it. When these factors are implemented, the dip coating of suitable porous supports with nanoparticulate sols can be utilized to fabricate supported ceramic membranes that appear to be useful for separations of aqueous solutions containing low molecular weight materials.

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1. INTRODUCTION

At present, most membranes that are used for industrial separations are fabricated from organic polymer precursors. While current ceramic membrane technology lags behind polymeric membrane technology, ceramic membranes offer several potential advantages over polymeric membranes, particularly for those applications involving use at high temperatures. The robust mechanical and chemical properties of ceramic membranes allow them to be steam or solvent cleaned to permit periodic restoration of permeabilities to values very close to those of the fresh membranes. Ceramic membranes can function at much higher pressures than polymeric membranes and thus are excellent candidates for those applications that employ high pressures and large pressure drops to improve separation efficiencies.

Given these advantages, it is surprising that greater emphasis has not been placed on the development of commercially viable ceramic membranes. This situation exists in part because commercially available ceramic membranes are characterized by relatively large pore sizes. Since organic polymeric membranes with small pore sizes have been available for many years, these membranes dominate the market for industrial membrane technology. Thus, the primary objective of this project was to fabricate supported ceramic membranes with pore sizes that were small enough to allow the resulting modules to be used for microfiltration applications (i.e., gas phase separations and separations of low molecular weight materials dissolved in liquid streams). The work described herein was performed at the University of Wisconsin - Madison between March 1991 and May 1992. This study was a continuation of several years of research into the fabrication and characterization of supported ceramic membranes.

Our approach to fabricating ceramic membranes for microfiltration was to synthesize stable suspensions of metal oxide particles and to coat these suspensions onto porous supports. Once the suspension was placed on the support, the solvent was allowed to dry, thus bringing the particles into close contact with each other. The system was then fired to a high enough temperature to begin to sinter the particles and adhere the coating to the support, while still leaving the coating with a porous structure. If the system was fired at too high a temperature, particle sintering caused the coating to completely densify and produced a non-porous material.

If one assumes that the suspended particles are nearly spherical and form a random close packed structure in the coating during drying, then the size of the pores in the resulting membrane is ca. 20% of the size of the particles. In addition, the membrane is characterized by a porosity of about 33%. Because a microfiltration membrane would require a pore diameter of 1 to 2 nm, the particles needed to prepare such a membrane must be nanoparticles (particles with characteristic dimensions in the range from 2 to 10 nm).

Thus, the first task for this project was to synthesize stable suspensions containing nanoparticles. Our initial efforts to synthesize TiO_2, ZrO_2, and mixed TiO_2-ZrO_2 suspensions were described in an earlier report [1]. These studies have been extended to silica, alumina, and aluminosilicate systems. Our interest in aluminosilicates is due to their potential thermal stability. A major application for ceramic membranes is for separations of gases at temperatures high enough to either decompose conventional polymeric membranes or significantly impair their performance. While membranes fabricated from nanoparticulate sols of pure oxides generally densify when heated to 500°C, membranes prepared from nanoparticulate sols of mixed or doped oxides often remain porous even when heated above 500°C. Thus, the thermal stabilities of aluminosilicate membranes of various compositions are of great interest. These materials may also be useful as catalysts, an application that was not investigated in this study.

All of these suspensions were synthesized by employing the sol-gel process, which involves the controlled hydrolysis of a precursor metal alkoxide or metal salt [2]. In this process, the reactant is first hydrolyzed (either fully or partially) to form Metal-O-H bonds and then individual hydrolyzed molecules condense to form Metal-O-Metal bonds. The condensation reactions cause particle growth to occur and also release water and/or alcohol molecules. (Alcohol would be released if a metal alkoxide was utilized as the precursor.) The sizes of the particles produced during the sol-gel process depend on the relative rates of hydrolysis and condensation. In turn, these rates depend on several processing variables, including processing temperature, solvent, amount of acid or base employed as a catalyst, amount of water in the system and size of the substituent groups on the metal alkoxide. We synthesize nanoparticles by employing conditions that either minimize the rates of hydrolysis and condensation or that cause the initial small particles that are produced to rapidly develop a large charge [1]. In the latter case, the resulting electrostatic repulsion between particles stabilizes the suspension and prevents further particle-particle condensation.

Once the required suspensions have been synthesized, they can be coated onto a suitable support to prepare supported ceramic membranes. Because these coatings are on the order of 1 μm thick, they do not contain enough material to determine the specific surface areas, pore size distributions and porosities of the supported membranes. These properties are estimated by analyzing N_2 sorption isotherms for unsupported membranes and then assuming that these properties will be the same as those of supported membranes that are processed similarly.

Unsupported membranes are prepared by placing a sample of the suspension of interest in a plastic weighing dish and allowing the solvent to evaporate. In many oxide systems, a gel forms as the solvent evaporates. When as much solvent as possible has evaporated at room temperature, the remaining xerogel can be heated to any desired temperature. The pore structure of this unsupported membrane can then be determined from N_2 sorption measurements. By repeating these measurements on unsupported membranes that have been fired under different conditions, the thermal stability of the material can be evaluated. In Section 3 of this report, "Fabrication and Characterization of Unsupported Membranes", we discuss the methods employed to synthesize SiO_2, Al_2O_3, and aluminosilicate suspensions and the characterization data obtained for unsupported membranes prepared from these suspensions.

In order to fabricate a ceramic membrane, the suspension of interest must be coated onto a porous support, dried, and fired under conditions that allow partial sintering of the particles in the membrane to each other and adherence of the particles in the membrane to the support. In addition, these processing conditions must not produce many pinholes or cracks in the membrane or else the performance of the ceramic membrane will be adversely affected. While several techniques are available for coating supports with suspensions, we have utilized dip coating and slip casting as our primary coating methods.

(Manpower and equipment constraints have limited our use of spray coating as a fabrication method.)

Slip casting utilizes the capillary forces that are established between a suspension and a porous support to draw solvent into the pores of the support and deposit the suspended particles on the surface of the support. With this process the thickness of the coating can be increased by increasing the contact time between the suspension and the support. However, if the suspended particles are much smaller than the pores of the support, the particles will be drawn into the support and will not deposit in a coherent layer at the surface. This difficulty can be resolved by placing a sandwich layer on the porous support to produce a surface for deposition that is characterized by a smaller pore size than the original support.

Dip coating requires direct adhesion between the suspended particles and a non-porous support. (Spin coating is a variant of this method that is used quite extensively in the semiconductor industry.) The thickness of the resulting coating depends on several factors including the viscosity of the suspension, which in turn is affected by the concentration of particles in the suspension. In order to mimic a dip coating process with a porous support, the pores of the support must first be filled with an appropriate solvent to prevent the action of capillary forces on the suspension.

Although both processing techniques can be utilized to fabricate ceramic membranes, we prefer to employ dip coating when possible. The coherent separation layer produced during processing should be as thin as possible to minimize its resistance to the flow of permeate through it. In general we obtain better control of the thickness of the coating when we dip coat than when we slip cast. In addition, we often adsorb phosphate to the support to enhance the electrostatic attraction between the suspended particles and the support (thus producing phosphate-based ceramic membranes). This technique is easier to incorporate in a dip coating process than in a slip casting process.

Very thin separation layers have an additional advantage during the drying and firing stages needed to fabricate a ceramic membrane. The primary cause of pinholes and cracks in ceramic membranes is the stresses produced as the solvent is removed from the coating during processing. By employing very thin separation layers, we minimize the amount of solvent that needs to be removed during processing and appear to minimize the number of defects in the final separation layer. An additional source of crack formation in ceramic membranes is mismatches in thermal coefficients of expansion between the membrane and the support. When a very thin membrane is used, the membrane appears to give with changes in the support. In our experience, the thicker a membrane is, the more likely it is to crack during processing.

In Section 4 of this report, "Fabrication and Characterization of Supported Membranes", we describe the results of our studies on utilizing dip coating and slip casting to fabricate ceramic membranes from suspensions that contain nanoparticles. In addition, we also discuss our initial efforts to employ two other fabrication techniques that are designed to minimize crack formation during the processing of supported ceramic membranes. Permformation employs the controlled deposition of particles within the pores of a support to minimize the surface area of the separation layer that must be dried and fired. Critical point drying employs CO_2 held under supercritical conditions as a solvent for drying the membrane so that no solid-liquid interface exists in the pores of the membrane. Thus, no capillary forces are present during drying to cause crack formation.

2. OBJECTIVES

The goal of this research project was to fabricate ceramic membranes that consist of nanoparticles (particles with characteristic dimensions in the range from 2 to 10 nm) and to incorporate such membranes into modules that can be used for either gas phase separations or liquid phase separations involving low molecular weight solutes. In order to attain these ends, our major objectives have been:

1. To define the conditions that are necessary for synthesizing stable sols that are composed of nanoparticles
2. To characterize the properties (e.g., specific surface area, pore size distribution, and thermal stability) of unsupported membranes prepared from such sols
3. To fabricate modules in which ceramic membranes prepared from these sols are formed in situ on various types of porous supports to yield supported membranes
4. To characterize the permselective properties of these modules in laboratory scale challenge tests using model compounds
5. To assess potential applications for these modules
6. To assess industrial manufacturing techniques that are suitable for the fabrication of commercial membrane units.

3. FABRICATION AND CHARACTERIZATION OF UNSUPPORTED MEMBRANES

In order to fulfill the first two objectives of this project, we had to develop techniques for synthesizing sols that contain nanoparticles. Two general approaches, steric hindrance and solubility control, were described in an earlier report [1]. (In a later publication [3], the term controlled nucleation was used instead of the term solubility control because controlled nucleation is a better description of the actual process. In this report, we use the term controlled nucleation to refer to this process.) These methods were applied to the synthesis of both aqueous and t-amyl alcohol based sols that contain nanoparticles of TiO_2, ZrO_2 and mixed TiO_2-ZrO_2 in various proportions [1,4,5].

Further studies have been conducted on the synthesis of nanoparticulate sols, as described herein and in a separate publication [6]. A modification of the controlled nucleation process was employed to synthesize aqueous sols of nanoparticulate SiO_2. Boehmite (γ-AlOOH) sols with characteristic particle sizes in the nanometer range were synthesized by an acidic hydrolysis. Two methods were utilized to study aluminosilicate systems: (a) separate boehmite and silica sols were mixed together in the desired proportions to form membranes and (b) a direct synthesis was obtained by mixing the desired amounts of alkoxide precursors together and hydrolyzing the resulting mixed alkoxide.

After these sols were synthesized, subsamples of the sols were placed in plastic weighing dishes, and as much solvent as possible was allowed to evaporate from the sols under ambient conditions. This process produces a xerogel [2, p. 10] that (once it releases from the plastic dish) is referred to as an unsupported membrane. Very often the capillary forces induced by evaporation cause such severe stresses that the resulting xerogels crack into many small pieces. These pieces are nonetheless useful for characterization of several important properties of the ceramic membranes. The specific surface areas, porosities, and pore size distributions of these samples can all be obtained by way of N_2 sorption measurements. (Pore size distributions can only be obtained for materials with pore diameters >1.5 nm. We calculate pore size distributions based on the Kelvin equation. Because the assumptions underlying this equation are invalid for pores with diameters <1.5 nm, this value limits the applicability of our analyses.) Given this constraint, it is possible to evaluate the thermal stability of a material by analyzing the properties of unsupported membranes that have been fired to different temperatures under different conditions.

By themselves, unsupported membranes are not strong enough to withstand the stresses that are produced in permselective systems employed in process applications. Consequently it is necessary to support these membranes on a stronger material, thereby producing a membrane/support composite that will withstand the stresses imposed by industrial environments. In practice, it will be necessary to fabricate these composite systems in modular form. These composites are prepared by using the precursor sol to form a layer of the ceramic membrane on a stronger porous support material. However, in these supported membranes only a very thin membrane layer (a few microns thick at most) is deposited on the support. Because these thin layers constitute only a very small fraction of the supported membrane system, N_2 sorption measurements on such samples do not yield meaningful results. Hence, we use only unsupported membranes for N_2 sorption studies.

In the remainder of this section we describe the silica, alumina (using alumina in a generic sense to refer to all possible aluminum hydroxides, oxyhydroxides, and oxides that could form in these systems at different temperatures), and aluminosilicate systems that we have studied. Aluminosilicate membranes were synthesized using two different approaches. In one method, separate aqueous sols of boehmite (γ-AlOOH) and silica were mixed, and mixed alumina-silica membranes were fabricated from the mixed sol. In the other method, Al- and Si-alkoxides were mixed together and allowed to react to form a mixed alkoxide. Hydrolysis of the mixed alkoxide and evaporation of the resulting sol gave aluminosilicate membranes. Details of the synthesis procedures utilized are presented, as well as results of the characterization and thermal stability studies that were performed on the various xerogels. Similar studies on the TiO_2, ZrO_2 and mixed TiO_2-ZrO_2 systems are described in Reference 1.

3.1. Silica

The preparation of silica sols by the sol-gel method and the use of these sols to prepare thin films and fibers of silica has been studied extensively because these materials make useful optical fibers and waveguides [2]. There may be fewer applications for silica membranes because of the relatively high solubility of silica in aqueous systems, especially alkaline systems. However, microporous silica membranes should still be useful for gas phase separations at low temperatures and for separations of low molecular weight molecules from organic solvents. We are extremely interested in pursuing these applications because we have had great success in synthesizing microporous silica membranes.

3.1.1. Synthesis

Silica sols were prepared (see Figure 1) by adding 4.5 mL of tetraethyl orthosilicate [TEOS (98%) used as-received from Aldrich] to alkaline water (1 mL of concentrated ammonium hydroxide dissolved in 30 mL of deionized water) at room temperature and stirring vigorously for 1 to 2 h. During this period, the initial two-phase system became a clear, single-phase sol. This sol was then dialyzed against water, using a SpectraPor membrane with a molecular weight cutoff of 3500, to remove the by-product alcohol and most of the ammonia. Dialysis was continued (replacing the water every few hours) until the sol reached a pH value between 8 and 9. Some sols were then acidified to pH 3 by adding nitric acid. Evaporation of either type of sol under ambient conditions produced xerogels that were converted into ceramic membranes by

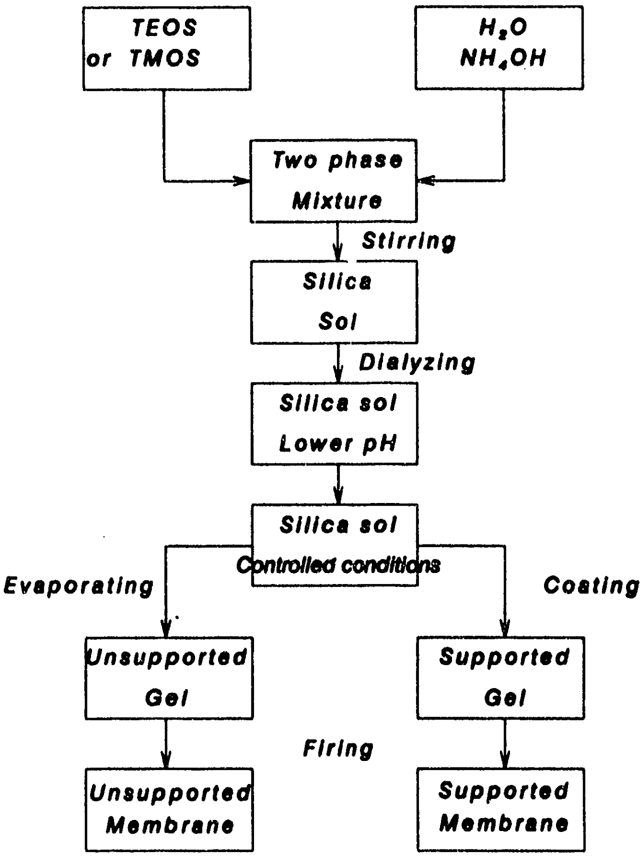

Figure 1. Flow chart of the hydrolysis scheme used in the synthesis of aqueous sols containing nanoparticulate silica.

heating at 2°C/min to temperatures as high as 900°C and holding at the desired temperature for 1 h.

Similar sols were prepared from tetramethyl orthosilicate (TMOS) instead of TEOS by replacing the 4.5 mL of TEOS with 3.0 mL of TMOS, while keeping the amounts of the other reactants the same. When TMOS was employed, hydrolysis proceeded much more rapidly. It was complete in a matter of minutes. Studies of the adsorption of selected gaseous molecules on the unsupported membranes indicated that the hydrolysis of TMOS produced smaller particles than did the hydrolysis of TEOS. However, because TMOS is more toxic than TEOS, most of our characterization studies were performed on sols synthesized from TEOS.

In general, silicon alkoxides are hydrolyzed in alcoholic solvents to ensure that a homogeneous reaction system is present [7-9]. However, the same reactions will occur in the absence of added alcohol if the resulting two-phase mixture is mixed vigorously by either stirring or shaking. Alkaline hydrolyses were utilized for these syntheses so that formation of highly condensed particulate sols would be favored, rather than the linear chain "polymeric" systems produced during acidic hydrolysis of TEOS [2, p. 112]. The rates of these hydrolysis reactions were controlled by adjusting the concentration of ammonium hydroxide (higher concentrations caused more rapid hydrolysis).

Because these hydrolyses were performed in the presence of ammonium hydroxide (a weak base), the resulting sols were characterized by pH values between 10 and 11. (Ammonium hydroxide was employed as a catalyst because ammonium cations are readily removed from the resulting membranes by heating. Sodium or potassium hydroxide could also be employed as a catalyst, but the sodium or potassium cations would remain in the matrix of the membrane after heating, thus affecting the properties of the membrane.) While silica particles are very soluble in the pH region from 10 to 11, the pH is not high enough to dissolve all of the silica particles produced during the hydrolysis. Thus, this synthesis does not completely conform to the conditions required for controlled nucleation syntheses [1,3].

Particles formed under these conditions develop a negative charge that stabilizes the suspension. However, the high solubility of silica in this pH region is conducive to particle growth by Ostwald ripening. Therefore, these high pH sols were dialyzed against water until the pH fell to about 8 in order to decrease the solubility of silica, yet maintain a high negative charge on the particles. Not only does dialysis produce conditions that minimize particle growth, it also removes most of the ammonia and alcohol from the sol. Silica sols stored at pH 8 have remained clear for more than one year, indicating that particle growth in these sols is, in fact, minimal.

3.1.2. Characterization

Some silica sols were dialyzed to pH 8 and then acidified to pH 3. Table I contains data concerning the properties of membranes prepared from these sols and membranes prepared from sols that were dialyzed only to pH 8. Xerogels formed from pH 8 sols exhibited considerable microporosity as well as bimodal pore size distributions after firing. Because many of the pores have diameters of ca. 3.5 nm, these membranes would not be expected to be useful for applications that involve the separation of species with low molecular weights. However, membranes prepared from acidified sols do not display larger diameter pores. Hence, they could be used for such separations. The reason for this differing behavior is still under investigation. We observed that acidified sols turned cloudy after a few days. This observation suggests that the charge on the particles in these sols had decreased and that the particles were slowly aggregating. We also observed much more intense light

Table I. Characteristics of silica membranes prepared under different conditions.

Type	Method of Preparation	pH of the Sol	Porosity (%)	Mean Pore Radius (Å)
Loose packed	Hydrolysis of TEOS in NH_4OH	8 to 12	45 to 50	8, 18
Tight packed	HNO_3 added to above sol	3	33	8

scattering from pH 8 sols than from freshly acidified pH 3 sols. This observation indicates that the pH 3 sols contained much smaller particles than the pH 8 sols. This indication is consistent with the results of the pore size distribution analyses.

Thermal stabilities of these silica membranes were evaluated by measuring the specific surface areas of membranes after sintering at various temperatures. In all cases the membranes were heated to the firing temperature at a ramp rate of 2°C/min and then held at the ultimate firing temperature for 1 h. The results of this study are shown in Figure 2. Note that the curve in

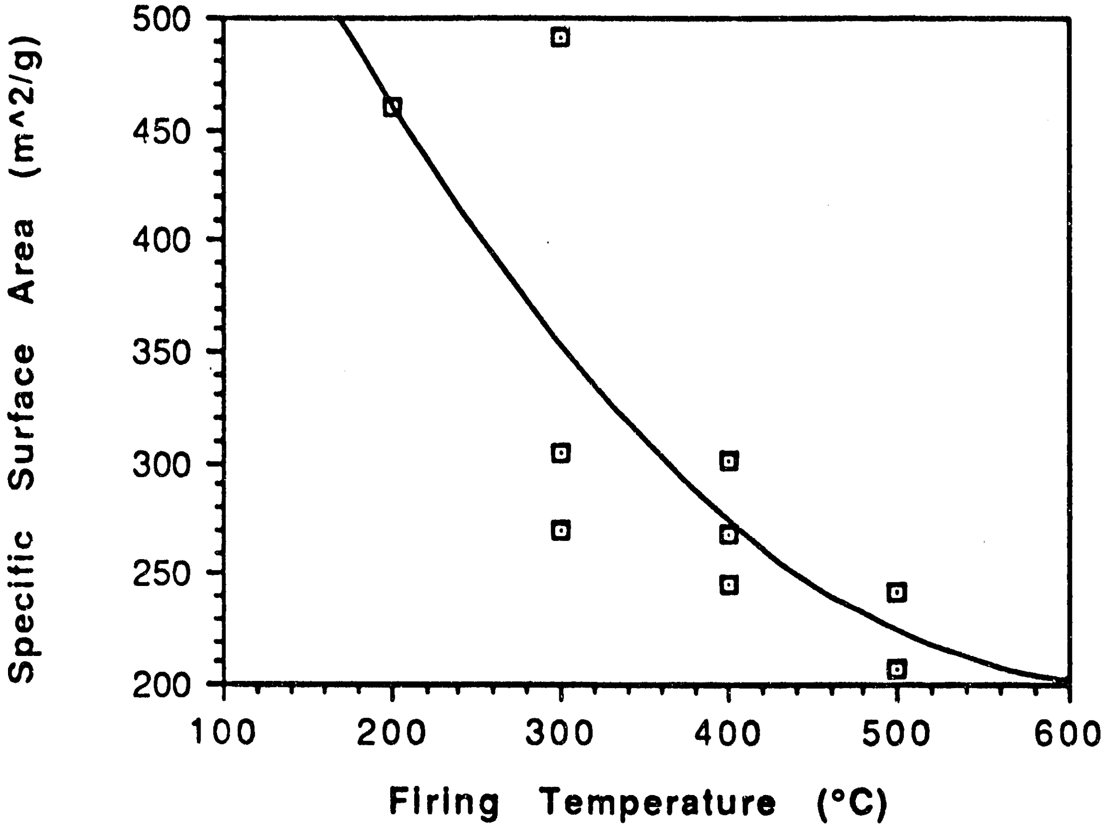

Figure 2. Effect of firing temperature on the specific surface area of silica membranes prepared from acidified sols. All membranes were heated at 2°C/min to the indicated firing temperature and held at this temperature for 1 h.

this figure is intended only to show the trend of the data, not to imply that a specific functional relationship exists between the specific surface area and the firing temperature. Some of the variability in these data points can be attributed to the Brunauer-Emmett-Teller (BET) analysis of the N_2 sorption data that was performed to estimate the specific surface areas of these membranes. Typically, BET analyses of identical samples can display as much as 10% variability. However, the surprisingly high specific surface area obtained for one of the samples that was fired at 300°C suggests that other as yet unknown parameters could also be affecting these measurements.

3.2. Alumina

Because of the relatively high chemical and thermal stabilities of alumina ceramic membranes, they have been the focus of much research interest in the past. In fact, several alumina membrane modules have been marketed for applications involving ultrafiltration (separations of high molecular weight materials). Given this interest in alumina membranes, development of a viable nanoporous alumina membrane is a relatively high priority in our research program.

3.2.1. Synthesis

Boehmite (γ-AlOOH) sols were prepared by acidic hydrolysis. Aluminum tri-sec-butoxide (ATSB, used as-received from Aldrich Chemical Co.) was added (with vigorous stirring) to cold deionized water containing a small quantity of concentrated nitric acid (3.6 L of H_2O and 0.07 moles of HNO_3 per mole of ATSB were used to prepare this sol). Hydrolysis was permitted to proceed for 10 min. The system was then heated to its boiling point and held at that temperature for 2 h. Because the resulting boehmite sol was cloudy, it was centrifuged and the supernatant was decanted. Xerogels prepared from this sol were fired at 2°C/min to 500°C and held at this temperature for 5 h. (These processing conditions were selected because previous studies had indicated that such conditions were sufficient to convert boehmite xerogels to γ-Al_2O_3 membranes [1].)

This synthesis procedure was designed to prepare sols with very small particle sizes. In terms of the theory of homogeneous nucleation of solids in liquid dispersions, hydrolyses performed at low temperatures produce smaller more numerous particles than similar hydrolyses performed at higher temperatures [10]. In the alumina system, acidic conditions increase the rate of hydrolysis of ATSB and lead to formation of smaller nuclei in the sol [11]. However, hydrolysis of ATSB at temperatures below 80°C ultimately produces bayerite (a material that cannot be peptized). By heating the system to the boiling point shortly after hydrolysis, the particles that are produced initially are converted to boehmite (which can be peptized) [12]. Once boehmite particles form, their size is not affected by the addition of nitric acid or by heating [13]. Note that the sols produced by this technique were somewhat cloudy (a condition that indicates the presence of either larger particles or aggregates of particles). This problem was alleviated by centrifuging the suspensions to obtain clear sols.

3.2.2. Characterization

An alumina membrane fabricated from the sol described above was heated at 2°C/min to 500°C and held at this temperature for 5 h. This membrane was characterized by a specific surface area of 200 m^2/g and a porosity of 32.8%. Although a quantitative pore size analysis must still be performed on this material, it is clear that it contained both micropores (mean pore diameters <20 Å) and mesopores (mean pore diameters >20 Å). A preliminary analysis suggested that these mesopores were characterized by a mean pore diameter of 35 Å. X-ray diffraction analysis verified that the membrane was composed of γ-Al_2O_3.

One concern in these systems is the possibility of aging and growth of the boehmite particles constituting the sol. In order to investigate this question, a boehmite sol was aged for three weeks; the γ-Al_2O_3 membranes were prepared from this sol at different times during the aging process and the specific surface area of each membrane was determined. The results of this investigation are presented in Figure 3. Because the specific surface areas of membranes prepared from sols that were aged for different times are constant, this result indicates that the average size of the particles in the sol was not changing. Thus, the sol was very stable.

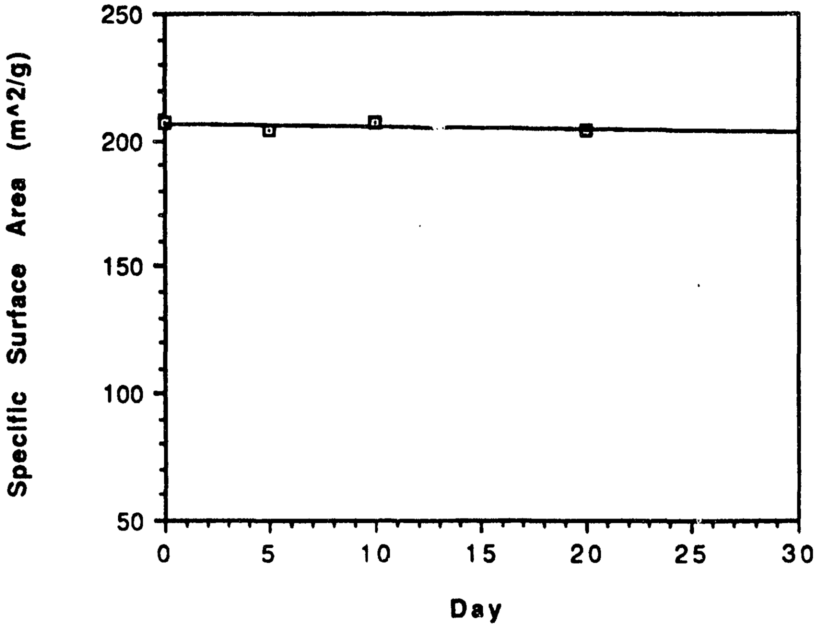

Figure 3. Stability of a boehmite sol as determined by monitoring changes in the specific surface areas of membranes prepared from the sol at different times.

3.3. Mixed Alumina-Silica Membranes Synthesized from Separate Sols

Aluminosilicate membranes are of considerable interest because of their potential stability (i.e., lack of change in the structure of the pores) in high temperature applications. An additional variable, the composition of the membrane, is present in these studies that was not present in the studies of pure silica and pure alumina membranes. Thus, it is possible that increased thermal stabilities would only be observed with certain compositions of aluminosilicate membranes. In this section, we present the results of studies of aluminosilicate membranes prepared by mixing separate silica and alumina sols.

3.3.1. Synthesis

These diphasic membranes were prepared by mixing the boehmite and silica sols described above in different Al_2O_3:SiO_2 ratios. Before mixing, the pH of the silica sol (which is near 8) was adjusted to a value between 3.0 and 3.5 by adding nitric acid. This pH value is similar to that of the boehmite sol. The Al_2O_3-SiO_2 ceramic membranes were obtained by drying the mixed sol at room temperature to form xerogels, which were subsequently heated at 2°C/min to 500°C and held at that temperature for 5 h.

3.3.2. Characterization

Although the particles in the two sols were oppositely charged before they were mixed (boehmite positive and silica negative at a pH between 3.0 and 3.5), no precipitate was produced by mixing the two sols. However, the gelling time for the mixed sol was affected by the composition of the sol. A sol with a 1:1 mole ratio of Al_2O_3 to SiO_2 displayed the shortest gelling time (as short as several minutes). This phenomenon is probably related to the electrostatic attraction forces between the particles.

The effects of the membrane composition on the specific surface areas and mean pore radii of these membranes are shown in Figure 4. The specific surface area decreased linearly as the alumina:silica ratio increased, although the pore radii of all samples remained constant at ca. 17.5 Å. With one exception, the specific surface area and the mol% Al_2O_3 were related by

$$\text{SSA } (m^2/g) = 866.4 - 745.5 \text{ mol\% } Al_2O_3 \qquad r^2 = 0.996 \qquad (1)$$

The one exception was the sample containing 34.5 mol% Al_2O_3, in which the specific surface area was significantly lower than that predicted by the

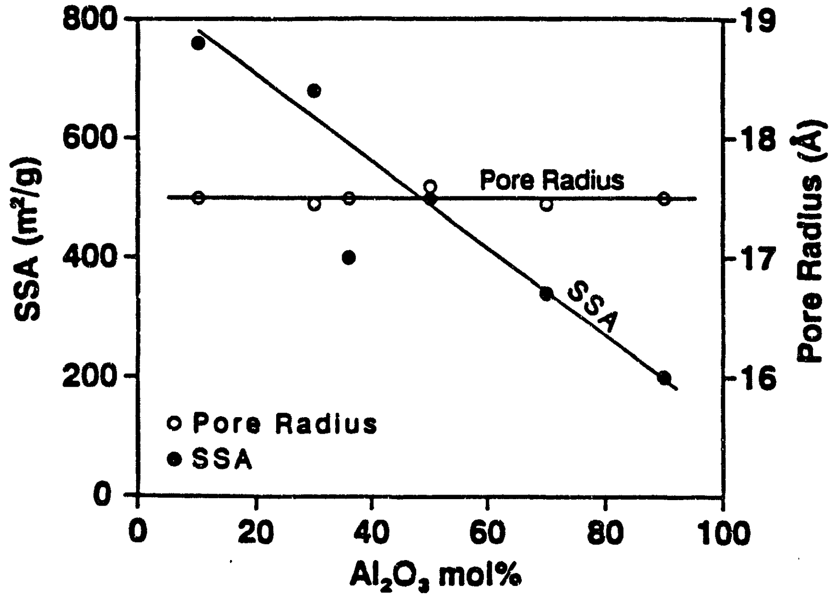

Figure 4. Effect of the composition of mixed alumina-silica membranes on the specific surface areas and mean pore radii of those membranes.

regression equation. This anomaly is unexplained but agrees with the report by Hietala et al. that silica-alumina gels have anomalously low surface areas in the vicinity of 47 wt% Al_2O_3 (34.5 mol% Al_2O_3) [14].

The data in Figure 5 show the effects of firing temperature on specific surface areas and mean pore radii of membranes with a composition corresponding to that of mullite (60 mol% Al_2O_3). When the ultimate firing temperature was <1200°C, the specific surface areas decreased linearly as the firing temperature increased. However, the mean pore radii of all samples remained constant at ca. 17.5 Å, regardless of the ultimate firing temperature. In this temperature range, the specific surface area and the firing temperature (T) were related by

$$\text{SSA } (m^2/g) = 978.1 - 0.8 \text{ T } (^\circ C) \qquad r^2 = 0.976 \qquad (2)$$

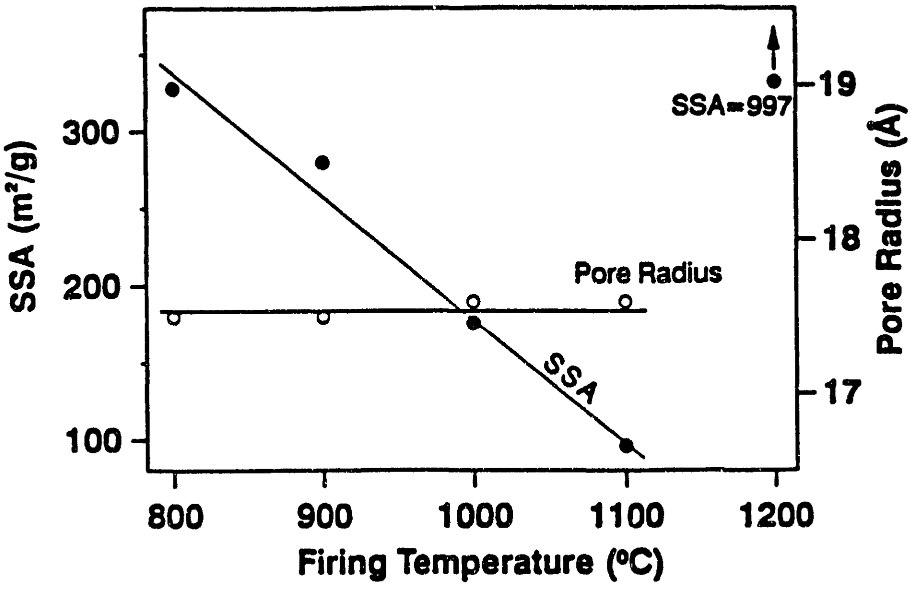

Figure 5. Effect of the firing temperature on the specific surface areas and mean pore radii of membranes composed of 60 mol% Al_2O_3 and 40 mol% SiO_2, the composition of mullite.

At temperatures >1200°C at this composition, Al_2O_3 reacted with SiO_2 to form mullite. This reaction leads to a significant increase in the specific surface area, as shown by the apparently anomalous point in the upper right of the figure. Paradoxically, opening of the pores was also observed [9].

X-ray diffraction spectra of mixed Al_2O_3-SiO_2 membranes were characterized by two distinct features: a very wide peak attributed to very poorly crystallized silica and several sharp peaks arising from γ-Al_2O_3. These spectra indicated that the mixed membranes were diphasic and consisted of separate alumina and silica particles, the presence of which persisted above 1200°C.

3.4. Aluminosilicate Membranes Synthesized from a Mixed Alkoxide

In the previous section, we described studies performed with aluminosilicate sols prepared by mixing sols of pure silica and pure alumina in the desired mole ratios. In this section, we describe similar studies performed with aluminosilicate sols prepared from mixed alkoxides.

3.4.1. Synthesis

Aluminosilicate sols were prepared in which molecular- or atomic-scale mixing of alumina and silica could occur and from which a single-phase solid could be produced. Before mixing, water was removed from the reactants (ATSB, TMOS and 2-butanol) by drying them over anhydrous sodium sulfate (TMOS was used for these studies rather than TEOS because TMOS is more reactive than TEOS). Solutions of TMOS (at varying concentrations in 2-butanol) and ATSB (0.28 M in 2-butanol) were mixed in the desired Al:Si molar ratios and allowed to equilibrate for 1 h. A separate solution was prepared that contained a small amount of H_2O and concentrated HNO_3 dissolved in a quantity of 2-butanol that was equal to the total amount of 2-butanol used to prepare the TMOS and ATSB solutions. The acidified 2-butanol was slowly dropped into the mixed alkoxide system at room temperature. The final solution, containing 1 mole of H_2O and 0.07 moles of HNO_3 per mole of total alkoxide (TMOS + ATSB), was aged at room temperature for at least 2 h. This process produced a clear sol that was slowly dried at room temperature over a period of 3 weeks to form xerogels (this process was modified from the procedure given in Reference 6, in which a centrifugation step was included in order to obtain a clear sol).

Ceramic membranes were formed by either of two heat treatments of these xerogels. In initial studies, xerogels were heated at 2°C/min to the desired temperature and held at that temperature for either 1 h or 5 h. Because ceramic membranes subjected to this treatment generally displayed very low porosities, later studies employed a modified protocol for heat treatment (heat at 2°C/min to 150°C, heat at 0.1°C/min to 400°C, heat at 2°C/min to the desired higher temperature, and hold at the desired temperature for 5 h). Because this modified treatment scheme produced membranes with much higher porosities, this revised heating protocol is recommended for use in further studies.

This firing protocol is designed to minimize a problem that arises when we either prepare xerogels from alcoholic sols or use alcoholic sols to coat supports. In either case the resulting material should be heated at a rate that is sufficiently slow to allow any adsorbed alcohol molecules to vaporize without being trapped within either the xerogel or the coating. Otherwise, subsequent pyrolysis of the alcohol may form carbon deposits in the xerogel or coating. These deposits in turn can lead to irreproducible behavior of the product. In the worst case, such deposits could actually block the pores of the membrane.

After being subjected to the modified treatment described above, the unsupported aluminosilicate membranes were transparent but were characterized by a reddish color. This color suggests that some pyrolysis of butanol may have occurred within the membranes even when they were subjected to this modified heat treatment. However, there are other possible explanations for this observation (e.g., reactions between the alcohol and nitric acid within the pores of the membranes on heating or contamination from the furnace).

3.4.2. Characterization

This material was more extensively characterized than were the previous materials. The charge on the surface of the suspended particles was monitored by measuring the electrophoretic mobility of the particles. This measurement provided one indication that true aluminosilicate particles were present in the suspension rather than silica-coated alumina particles. In the former case, a change in the composition of the mixed alkoxide should produce a significant change in the isoelectric pH. In the latter case, one would expect little variation in the isoelectric pH of the particles (the pH at which the particles display zero mobility, indicating a neutral surface) as the composition of the mixed alkoxide was changed. Laser light scattering studies were utilized to determine particle size distributions in the synthesized sols. Specific surface areas of unsupported membranes were determined after firing to 500°C. Finally, thermal stability studies were performed on unsupported membranes containing a high alumina content. These membranes had displayed high specific surface areas after being fired to 500°C.

3.4.2.1. Isoelectric Points

When ATSB and TMOS are mixed in butanol, these two alkoxides can react with one another, undergoing chemical modification. The mechanisms and products of these reactions are currently under study. However, the addition of water to this system causes the resultant products to immediately hydrolyze. A general equation for the overall reaction can be written as

$$x\ \mathrm{Al(OC_4H_9)_3} + y\ \mathrm{Si(OCH_3)_4} + (2x + 4y)\ \mathrm{H_2O} \rightarrow$$
$$[\mathrm{AlO(OH)}]_x[\mathrm{Si(OH)_4}]_y + 3x\ \mathrm{C_4H_9OH} + 4y\ \mathrm{CH_3OH} \qquad (3)$$

Although TMOS is more reactive than TEOS, it is not clear that TMOS is sufficiently reactive to form a mixed alkoxide after exposure to ATSB for only 1 h. If a mixed alkoxide was not present, one would expect that hydrolysis of the more reactive ATSB under acidic conditions would first form an aluminum hydroxide. Slow hydrolysis of TMOS would produce a coating of silica on the aluminum hydroxide particles. This possibility can be tested by studying the variation with pH of the electrophoretic mobilities of particles that are synthesized using different ATSB:TMOS ratios. If silica-coated aluminum hydroxide particles were formed, they should behave much like pure silica particles even if the amount of SiO_2 in the alkoxide solution is varied.

This hypothesis was tested by synthesizing xerogels from alkoxide solutions that contained different ratios of ATSB to TMOS. These xerogels were crushed to a fine powder and suspended in aqueous solutions at different pH values. Electrophoretic mobilities of the resulting sols were measured using a PenKem System 3000. Data obtained in this study are plotted in Figure 6.

These data suggest that aluminosilicate particles of varying compositions, rather than silica-coated aluminum hydroxide particles, are actually being formed in these systems. As shown in Figure 7, the isoelectric point (the pH at which the particles have zero mobility) of the particles decreases regularly as the amount of aluminum in the particles decreases, as would be expected for particles of mixed compositions. In addition, the electrophoretic mobility curves for the particles of mixed composition all appear quite different from the curve for pure silica particles. This observation suggests that the particles of mixed composition are not coated with a layer of silica.

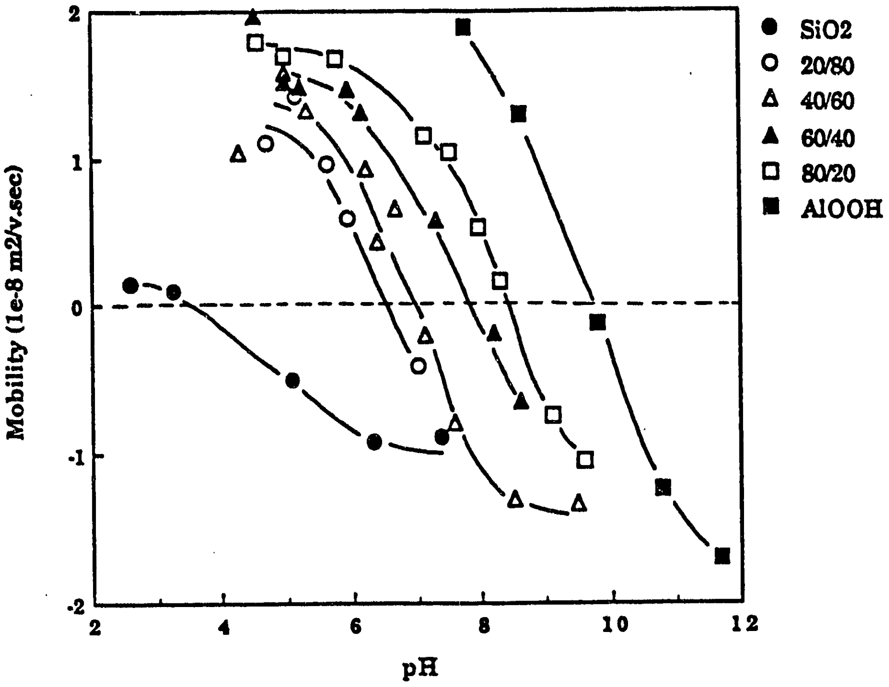

Figure 6. Variation of electrophoretic mobility with pH for sols prepared from crushed xerogels of mixed aluminosilicates of various compositions. The boehmite and silica sols used in this study were synthesized by techniques described earlier in this report.

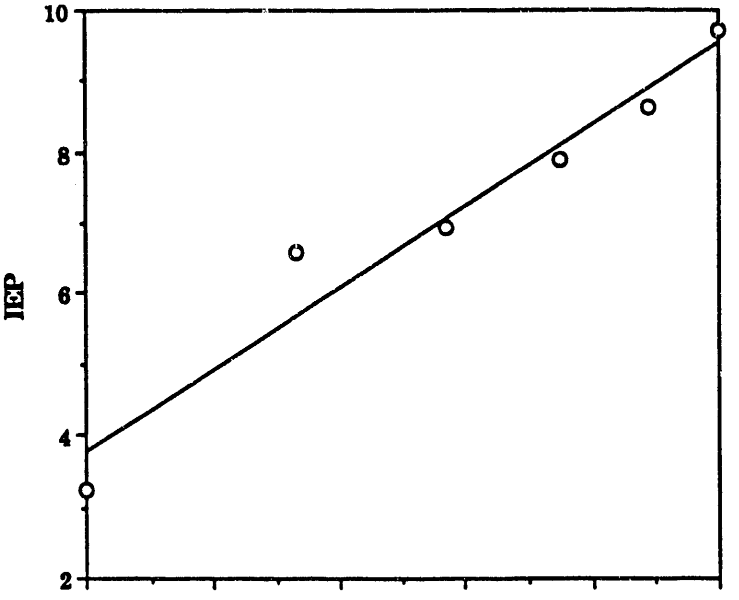

Figure 7. The isoelectric points (IEP) of silica, boehmite, and aluminosilicate suspensions as a function of the aluminum content in the precursor alkoxide solution.

3.4.2.2. Particle Sizes

The sizes of the particles in these aluminosilicate sols were estimated through dynamic light scattering studies. Particle size distributions for four aluminosilicate sols of different compositions (Figure 8) were determined from the correlation curves obtained from each sol. Figure 9 displays the average particle diameters in each sol, as calculated from the size distributions shown in Figure 8.

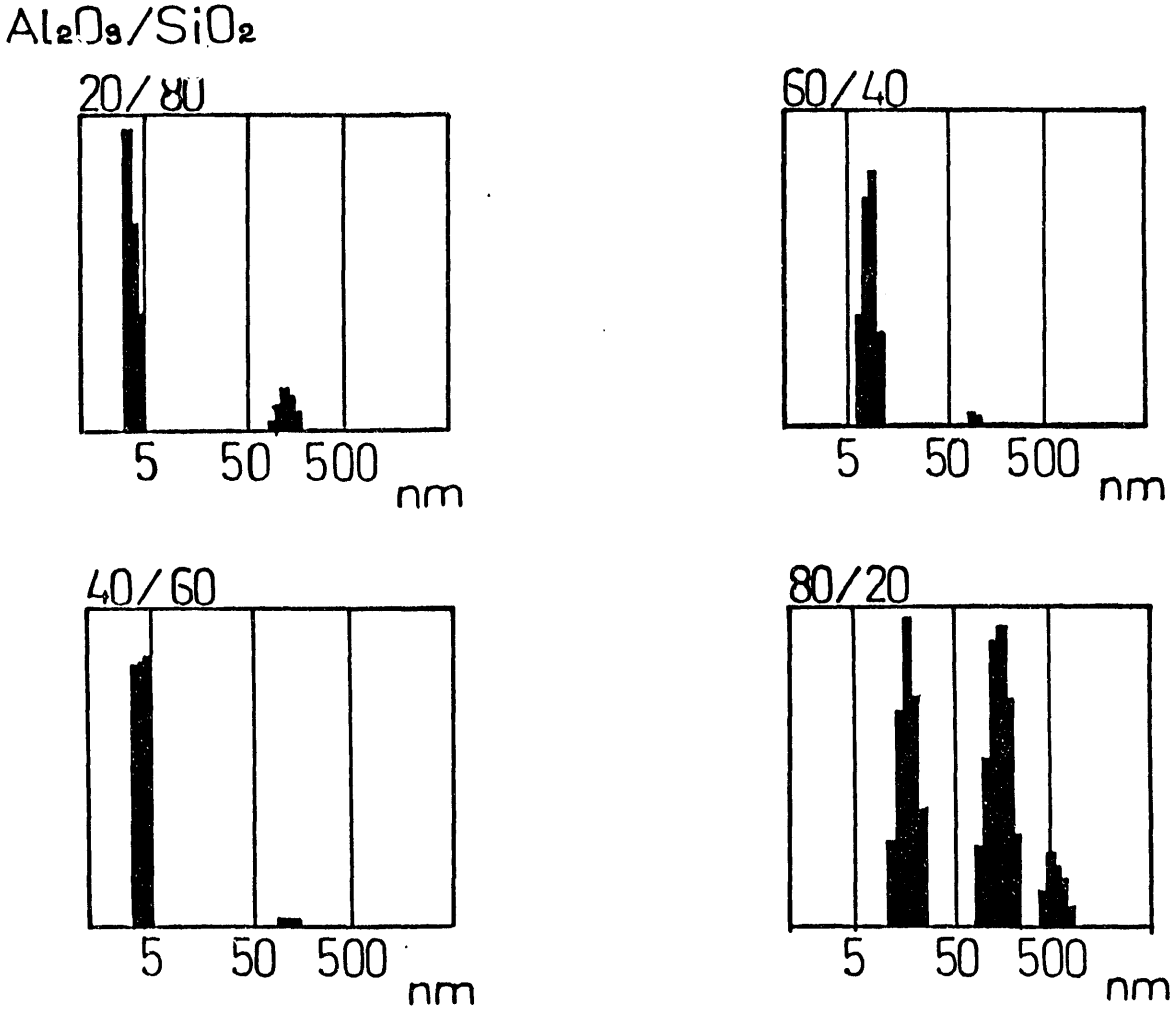

Figure 8. Particle size distributions of aluminosilicate sols with different compositions.

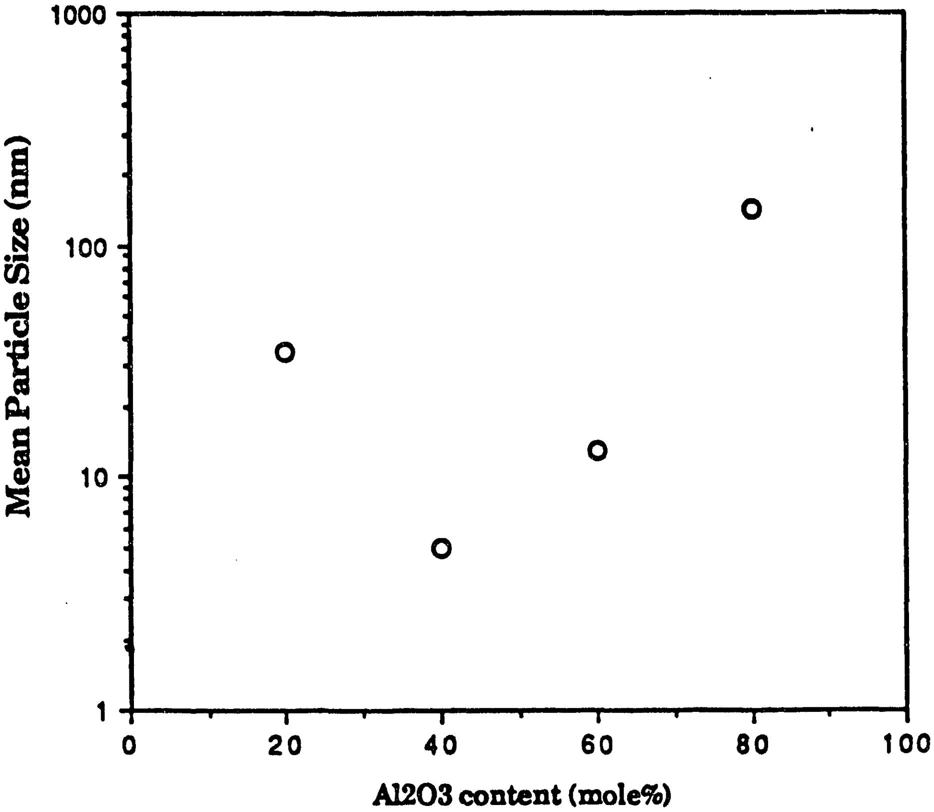

Figure 9. The effect of alumina content on the mean diameters of particles in aluminosilicate sols of varying composition.

Based on the data shown in Figures 8 and 9, it is clear that the particle size in the sol depends on the alumina content of the precursor alkoxide solution. A solution with a concentration of ATSB corresponding to 80 mol% Al_2O_3 produced relatively large particles with a broad size distribution. Solutions with a concentration of ATSB corresponding to 60 mol% Al_2O_3 or less produced smaller particles with fairly narrow size distributions. The reason for this behavior is not known.

3.4.2.3. Thermal Stabilities

Xerogels were prepared from the four different aluminosilicate sols used in the experiments described above by allowing the solvent to evaporate at room temperature over a three week period. Unsupported ceramic membranes were fabricated from these xerogels by heating them at 2°C/min to 500°C and holding the membranes at that temperature for 5 h. The specific surface areas, porosities and pore size distributions of these membranes were estimated from N_2 sorption data. Figure 10 presents the specific surface areas and porosities obtained for these membranes.

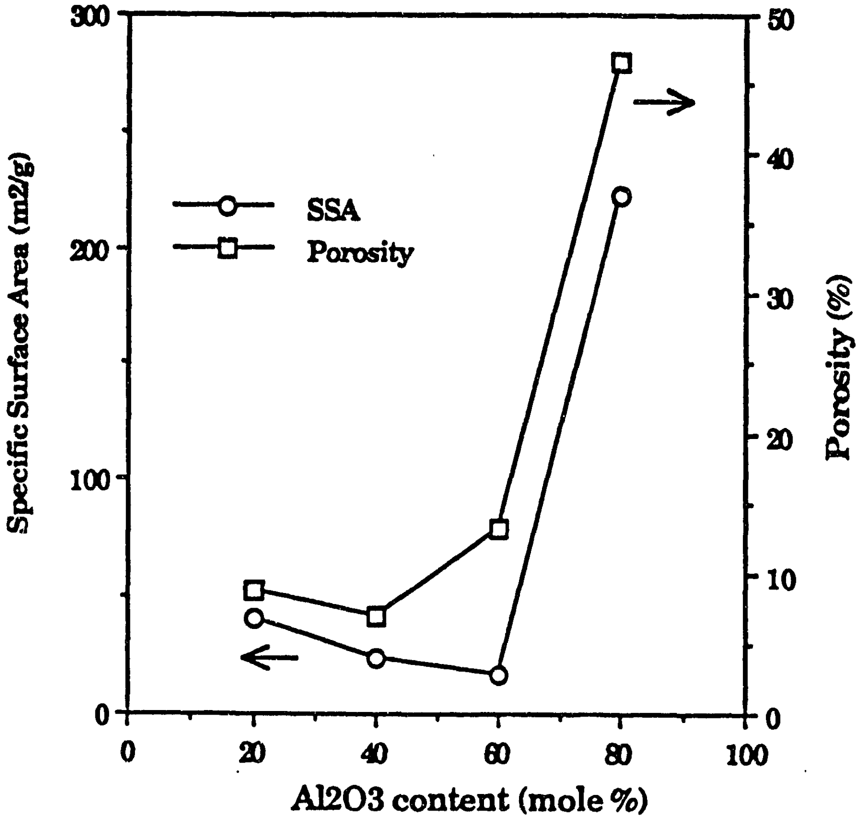

Figure 10. The effect of alumina content on the specific surface areas and porosities of aluminosilicate membranes.

The data shown in Figure 10 indicate that membranes containing 80 mol% Al_2O_3 were characterized by the highest specific surface areas and porosities of any of the membranes tested. However, this result for the specific surface area is unexpected given that the precursor sol for the 80 mol% Al_2O_3 membrane had the largest particle size and the broadest size distribution of any of the aluminosilicate sols. One would expect the 80 mol% Al_2O_3 membrane to have the largest pore size, and thus the smallest specific surface area, of any of the membranes. The high porosity of the 80 mol% Al_2O_3 membrane is probably related to the broad size distribution of the particles in the precursor sol. This broad distribution could have hindered close packing of the particles as the xerogel was formed, thus leading to a high porosity.

The low specific surface areas and porosities of the other membranes can be explained if the pore sizes in these membranes are very small. In this case, considerable butanol could be trapped in the membranes even under the slow firing conditions used to fabricate the membranes. Pyrolysis of this butanol with the concomitant deposition of carbon would block the pores of the membranes and cause the observed low specific surface areas and porosities. This hypothesis would also explain the observation that the fired membranes were black (or very dark red, see discussion on p. 27 concerning similar membranes fired at a slower heating rate). A thermogravimetric study performed on a 60 mol% Al_2O_3 xerogel indicated that 50% of the weight of the xerogel was lost on heating to 500°C. This large weight loss suggests that considerable amounts of butanol are present in the xerogels.

The extremely low porosities of membranes containing ≤ 60 mol% Al_2O_3 make them unsuitable for use as permselective materials. However, the response of the 80 mol% Al_2O_3 membranes to further heating was monitored. Figure 11 presents the specific surface areas and porosities of such membranes after they were heated to the indicated temperatures at 2°C/min and held at these temperatures for 5 h. Even when heated to 1200°C, these membranes retained a reasonable porosity and some exposed surface area. However, further study of the long-term thermal stability of these membranes is needed. In particular, information concerning the effects of heating the membranes for several days would be of interest.

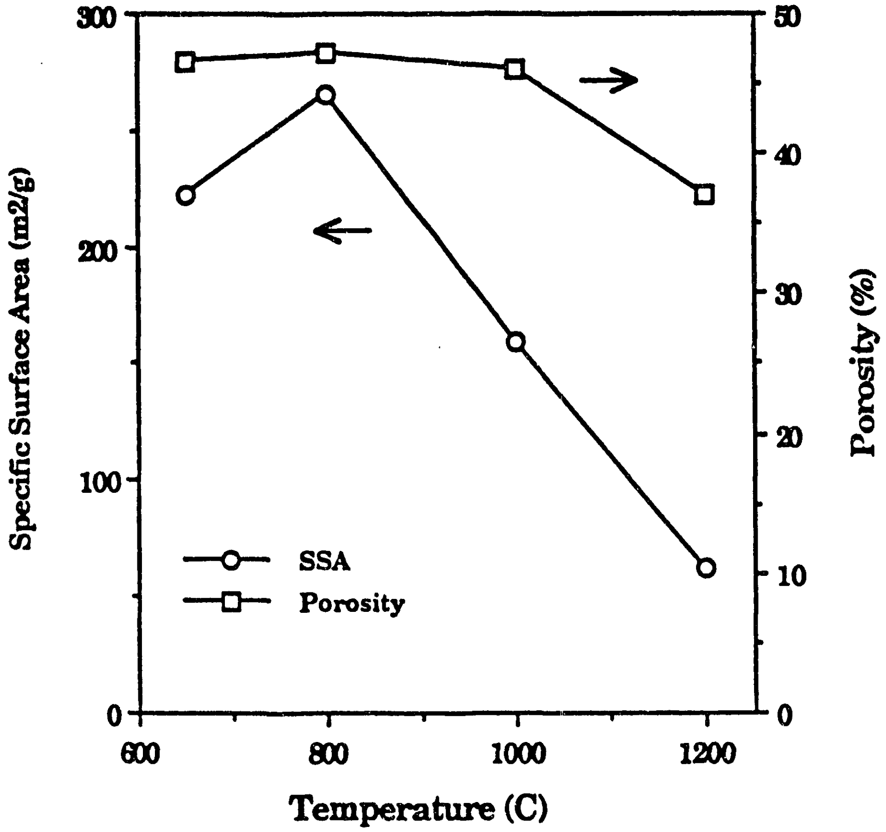

Figure 11. The effect of firing temperature on the specific surface areas and porosities of membranes containing 80 mol% Al_2O_3.

Pore size distributions were also obtained for samples of the 80 mol% Al_2O_3 membranes that were fired at different temperatures for 1 h. Figure 12 depicts the pore size distributions calculated from both the adsorption and desorption branches of the N_2 sorption isotherms for a membrane that was heated to 500°C. Figure 13 presents similar data for a membrane heated to 1200°C. The pore sizes of these membranes were not significantly affected by heating to 1200°C for 1 h, as in both cases the mean pore diameters of the membranes appear to be ca. 3.5 nm. Although such pore sizes are too large to be practicable for use in performing gas phase separations at high temperatures, the thermal stability of this material is quite good. Thus, studies of methods for fabricating materials with similar compositions but smaller pore sizes appear to be warranted.

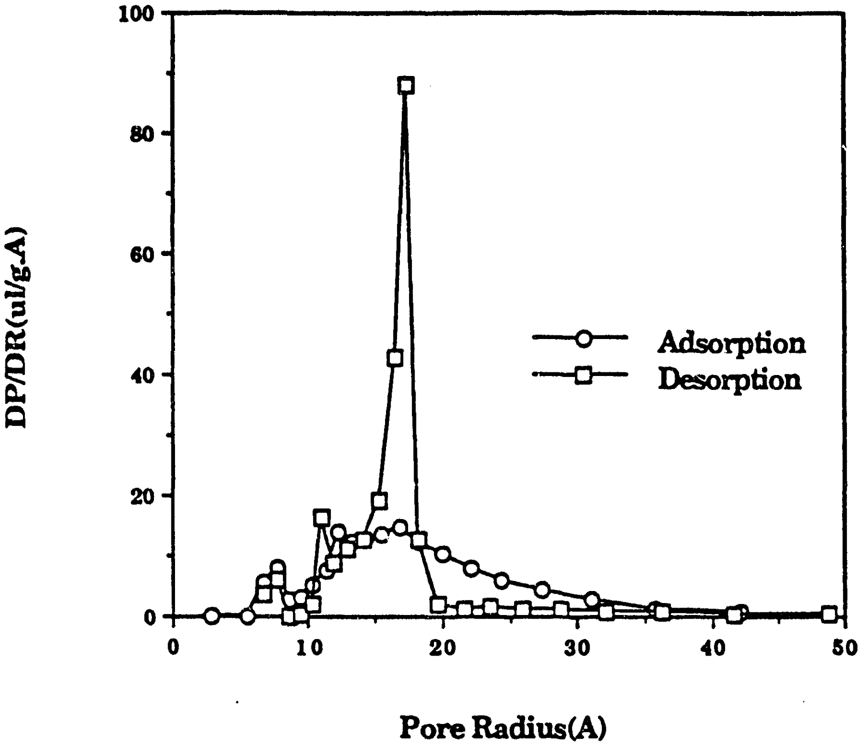

Figure 12. Pore size distributions for an 80 mol% Al_2O_3 membrane that was fired at 500°C for 1 h.

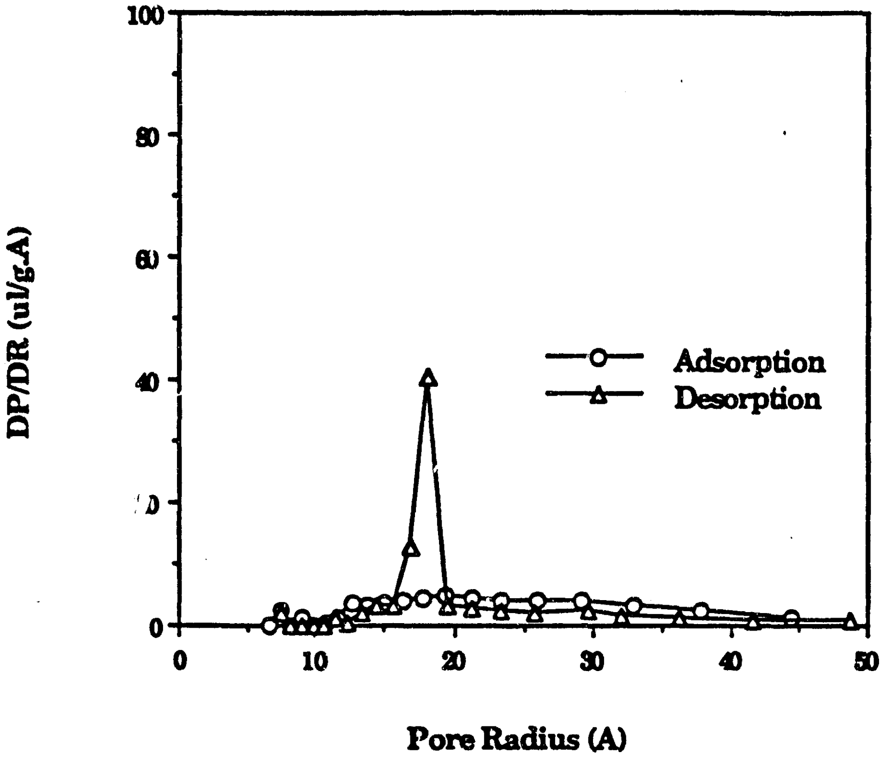

Figure 13. Pore size distributions for an 80 mol% Al_2O_3 membrane that was fired at 1200°C for 1 h.

As discussed earlier, the pyrolysis of organic solvents in the pores of the membranes can be minimized by heating the membranes sufficiently slowly to allow most of the solvent to escape. The pore size distribution depicted in Figure 14 was obtained for a 9.4 mol% Al_2O_3 membrane that was heated at 2°C/min to 150°C, heated at 0.1°C/min to 400°C, heated at 2°C/min to 500°C, and held at 500°C for 5 h. While the mean pore size of this membrane was similar to that of the 80 mol% Al_2O_3 membrane (ca. 3.5 nm pore diameter), the specific surface area measured for this membrane was 640 m^2/g. This value suggests that the slower heating protocol does indeed reduce the amount of pyrolysis of butanol in the pores of these membranes. In addition, this membrane was characterized by a reddish color, rather than the black color observed in membranes of similar composition that had been heated more rapidly.

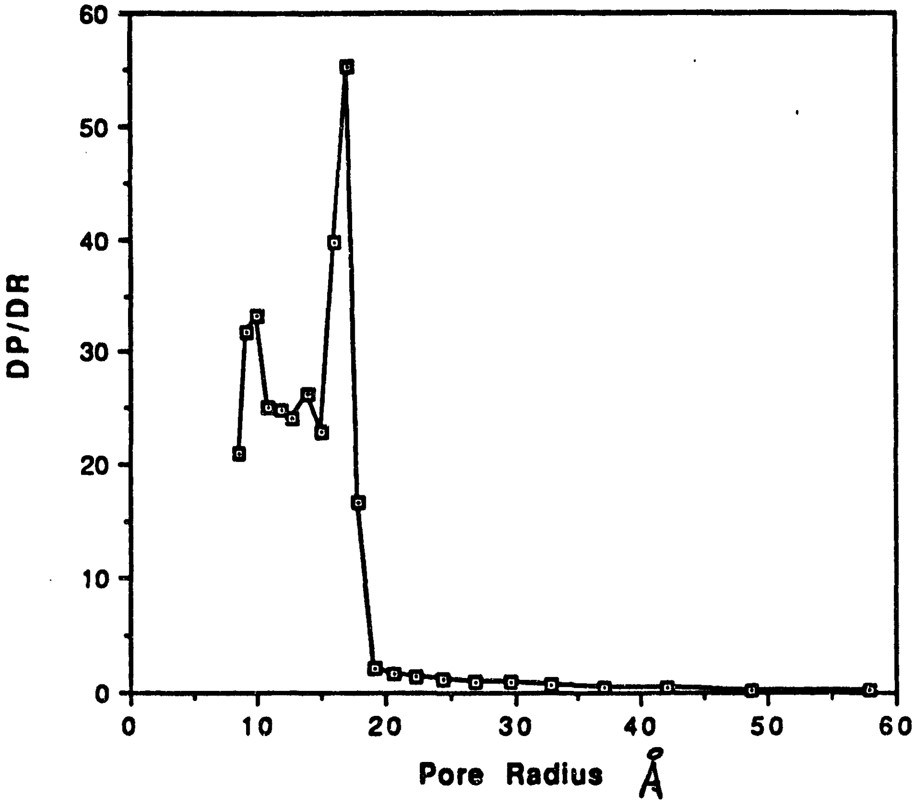

Figure 14. Pore size distribution of a 9.4 mol% Al_2O_3 membrane slowly heated to 500°C (firing protocol given on previous page) and held at 500°C for 5 h.

Although the mean pore diameter of this membrane is larger than desired for a microporous membrane, this relatively large pore diameter is expected based on the data presented in Figures 8 and 9. It appears that microporous aluminosilicate membranes might well be fabricated by synthesizing sols with compositions near 40 mol% Al_2O_3, forming xerogels from these sols, and employing the slow sintering protocol described on the previous page to prepare unsupported membranes. Experiments are currently being performed to determine if this hypothesis can be verified.

3.5. Summary

Many applications of ceramic membranes involve separations of materials with low molecular weights, often at high temperatures. An ideal ceramic membrane for such applications would be chemically inert to the species present in the system, would have uniformly sized pores with small pore diameters (ca. 1 nm), and would not undergo morphological changes when exposed to temperatures up to 1000°C. While we have not yet fabricated an individual membrane that satisfies all of these criteria, we have synthesized membranes that separately fulfill each of these criteria.

The TiO_2 and ZrO_2 membranes [1,4,5] and the aluminosilicate membranes should be chemically inert under most operating conditions. Alumina membranes would be expected to deteriorate if exposed to strongly acidic conditions [1]. Given the fairly high solubility of amorphous silica in aqueous systems (especially under alkaline conditions), the use of silica membranes in aqueous systems would have to be tested on an individual basis. Such membranes may be more appropriate for use with organic solvents or for gas phase separations.

To date, the membranes that best fulfill the requirement of having small pore sizes are the amorphous silica membranes, some of which appear to have mean pore diameters <10 Å. These materials are being tested for their utility for gas phase separations. Some tests have also been performed with supported TiO_2 membranes fabricated from nanoparticulate TiO_2 sols. These membranes appear to be permselective and have displayed permeabilities that are comparable to the permeabilities of commercially available organic membranes that are used for reverse osmosis separations. Alumina membranes may also be useful for these applications, but their mean pore diameters must be better characterized before viable applications for these membranes can be determined. The mean pore diameters of the aluminosilicate membranes synthesized to date have all been near 3.5 nm. Such pore sizes would not be effective in separating materials that have low molecular weights. However, there is evidence suggesting that slow sintering of aluminosilicate membranes containing ca. 40 mol% Al_2O_3 might result in a microporous material.

We have been able to fabricate membranes with good thermal stabilities only in mixed oxide systems. The best examples of such systems are the aluminosilicate membranes described above. These membranes are thermally stable when exposed to 1200°C for short periods. Mixed TiO_2-ZrO_2 membranes are also stable when exposed to 700°C for short periods [1]. The thermal stability of alumina membranes with small pore sizes has not yet been investigated. Other materials typically deteriorate when heated to 500°C for short periods.

The best materials we have fabricated to date for separations of low molecular weight molecules are amorphous silica membranes. However, these membranes are not suitable for high temperature applications and are not likely to have good chemical stability in aqueous systems. Our best materials for high temperature applications are aluminosilicate membranes. These membranes should be relatively inert in most systems, but their pore sizes are so large at present that such membranes would be useful only for applications involving ultrafiltration.

4. FABRICATION AND CHARACTERIZATION OF SUPPORTED MEMBRANES

Unsupported ceramic membranes are too weak to withstand the pressures generated during use in permselective applications. A common solution to this problem is to support the membranes on a stronger porous material. Although several methods are available for casting membranes on porous supports, each method has particular characteristics that affect its utility for a given application. Because our interest in the present project lies in fabricating supported ceramic membranes for microfiltration applications, we need to prepare membranes that contain neither cracks nor pinholes. In addition, the membranes must adhere well to the support material when exposed to a variety of operating conditions.

Techniques are available to help achieve acceptable adhesion between the support and the permselective layer responsible for the separation. If an aqueous suspension of oxide particles is being coated on a porous oxide support, both the particles in the sol and the exposed surfaces of the support will be charged. The signs and magnitudes of these charges are largely governed by the pH of the suspension. We have obtained good adhesion by manipulating the pH of the suspension so that the particles in the sol and the surfaces of the support bear opposite charges. In cases where this approach is unsuccessful, it is possible to change the charge on the support by *a priori* adsorption of various ionic species on this material (e.g., phosphate ions). One can also adsorb species on the support that will chemically bind to the particles in the sol (e.g., small amounts of organic binders such as polyvinyl alcohol). However, the amount of organic binder used must be carefully controlled. If too much binder is used, defects will form in the structure of the membrane when the composite is fired and the binder is burnt out.

Once the separation layer has been deposited on the support, the solvent (and any organic binders) must be removed from the membrane and the membrane must then be sintered. The capillary stresses that are produced as the solvent evaporates can lead to the formation of cracks in the membrane as it is dried. Cracks can also form during sintering if there is a mismatch between the coefficients of thermal expansion of the membrane and the support. Our experience indicates that both these causes of crack formation can be minimized by using very thin separation layers (i.e., thicknesses of 1 μm or less). (Thin membranes have another advantage in that they offer less resistance to the flow of permeate through the membrane than do membranes that are several microns thick.) Thus, the fabrication technique to be employed should be one that favors the formation of thin membranes.

Because we have experienced difficulties in slip casting thin membranes of uniform thicknesses, we no longer utilize this technique for fabricating membranes for microfiltration. (However, at least one research group with experience in slip casting utilizes this approach to prepare microporous supported membranes [15].) We prefer to fabricate these membranes by dip coating. Two other techniques (permformation and critical point drying) are also being investigated as possible methods for manufacturing supported ceramic membranes for microfiltration applications. While we have utilized spin coating to cast films on non-porous supports [1], we have not attempted to spin coat porous supports.

4.1. Dip Coating

In a typical dip coating process, a *non-porous* support material is immersed in a sol and, on withdrawal, particles adhere to the support. In order to mimic the behavior of a non-porous support and to minimize the potential for imbibition of the sol by the support, we wet porous supports with either water or alcohol (depending on the composition of the sol) before dipping. This technique for fabricating supported membranes has been shown to be a coating process rather than a slip casting process [1].

To date, we have prepared only one type of nanoparticulate supported membrane by dip coating, namely 0.02 μm Anodisc™ alumina membranes (Anotec Separations Co.) coated with a nanoparticulate TiO_2 sol dispersed in t-amyl alcohol [16]. Figure 15 summarizes the method used for preparing these membranes. First the supports were placed in a solution of phosphate ions in order to render the charge on the surface of the supports more negative. Next, the supports were placed in t-amyl alcohol for 30 min. Immediately upon removal from the alcohol, the supports were immersed in a 0.05 M TiO_2 sol. After 20 s, the supports were slowly removed from the sol, and any excess sol was shaken from the surface of the supports. The supported membranes were then dried in ambient air for 1 h and fired at 200°C for 1 h (ramp rate: 1°C/min).

A scanning electron photomicrograph of the top surface of an Anodisc™ support is shown in Figure 16. This micrograph indicates that pores on this surface are uniformly distributed across the surface of the membrane and that they are ca. 0.02 μm in diameter. This value agrees well with information provided by Anotec.

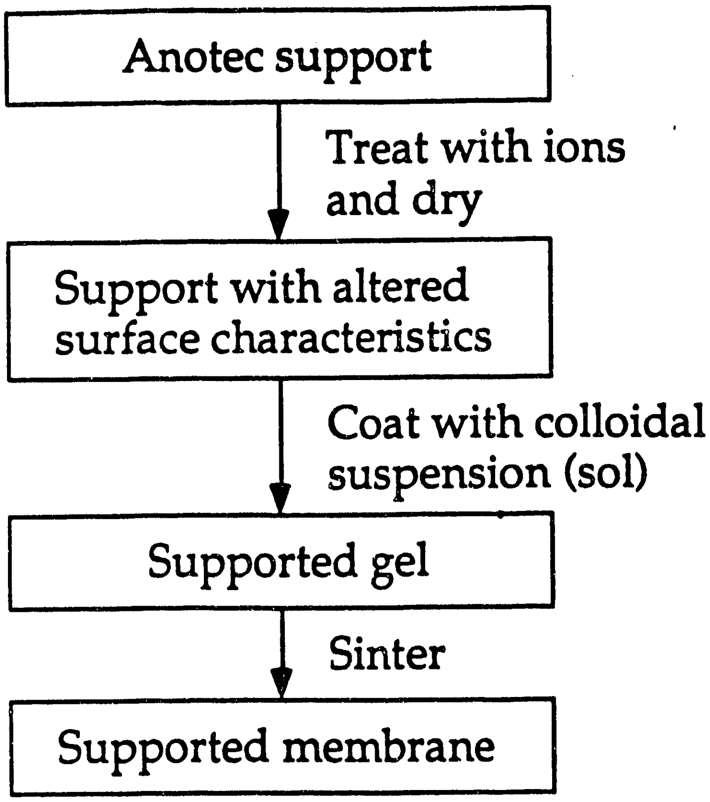

Figure 15. Flow diagram of the procedure used for depositing nanoparticles on an Anotec support.

Figure 17 is an electron photomicrograph of the top surface of an Anotec support that was coated with a 0.05 M titania sol using the procedure given on the previous page. Inspection of this figure indicates that the support is completely covered by a membrane and that this membrane is free from flaws. Comparison of Figures 16 and 17 indicates that the pores that were evident in the uncoated support have been totally covered by the membrane.

Figure 18 is an electron photomicrograph of a fracture edge of the same membrane shown in Figure 17. Inspection of Figure 18 indicates that the thickness of this membrane is <1 μm. Because this membrane is also free from flaws, this information supports the contention that the stresses produced in supported membranes as they dry can be limited by fabricating thin membranes.

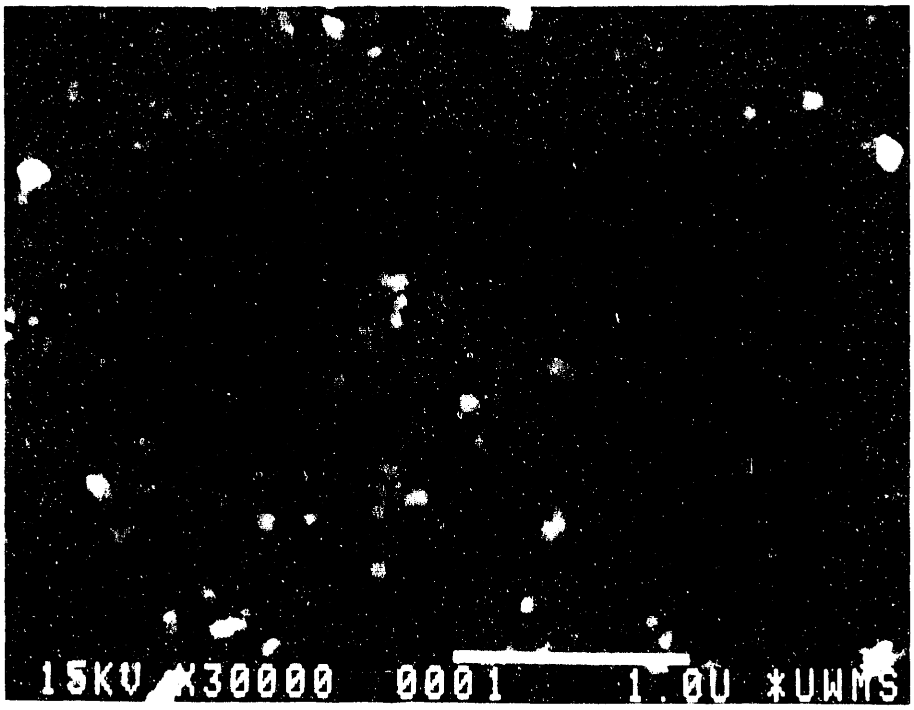

Figure 16. Electron photomicrograph of an Anotec support.

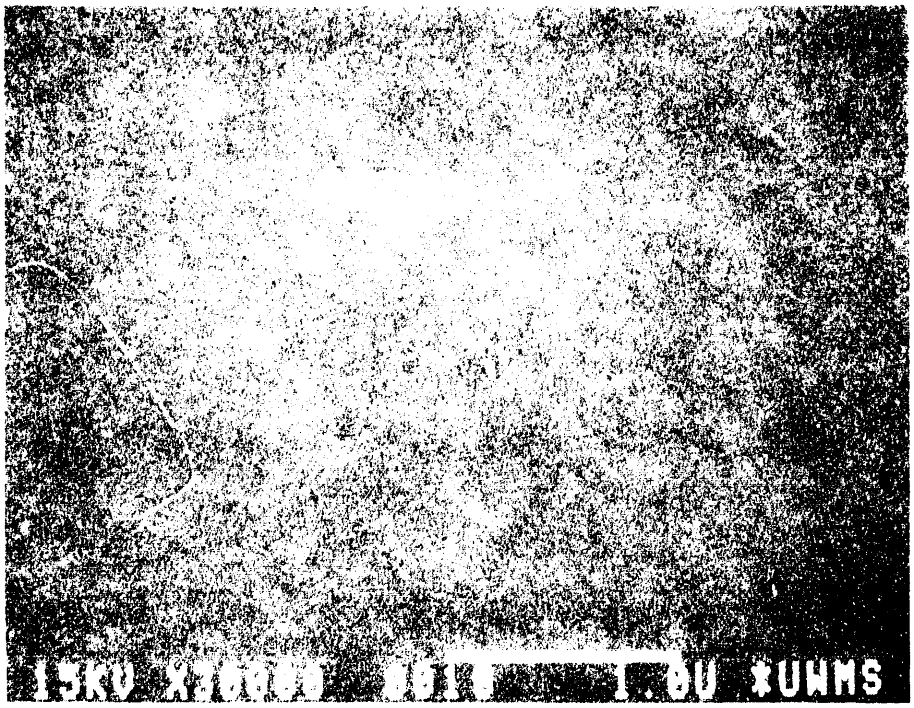

Figure 17. Electron photomicrograph of an Anotec support that has been coated with a 0.05 M TiO_2 sol of 50 Å particles.

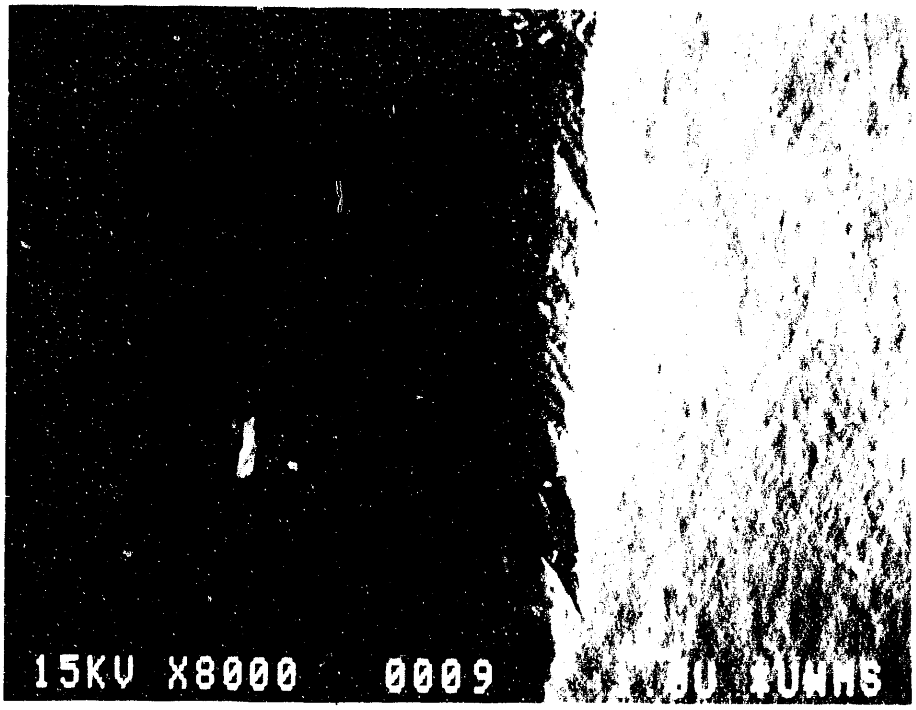

Figure 18. Electron photomicrograph of a fracture edge of an Anotec support that has been coated with a 0.05 M TiO_2 sol of 50 Å particles.

One method of minimizing the thickness of these coatings is to prepare them from sols that contain a low concentration of particles. This rationale explains our use of a 0.05 M TiO_2 sol to fabricate these membranes rather than a sol with a higher concentration of particles. Attempts were also made to slip cast TiO_2 sols into dry Anotec supports. This process produced thicker coatings that cracked readily. Hence, slip casting was not considered further as a technique for fabricating supported ceramic membranes.

Our success in fabricating a flaw-free supported membrane may be attributable, in part, to the enhanced attraction between the support and the membrane that was obtained by prior adsorption of phosphate ions on the support. This treatment of the support lowered the positive charge on its surface, thereby decreasing the electrostatic repulsion forces between the positively charged sol particles and the support. Furthermore, once the sol particles were deposited on the support, the particles were held more strongly than in the case where its surface charge had not been altered. This increased interaction between the membrane and the support material may also minimize the stresses that develop as the membrane dries and gels.

Only limited testing of the permeabilities and permselectivities of these supported membranes has been performed. While they reject polyethylene glycol with molecular weight 200 dissolved at the 0.01% (w/w) level in aqueous solution, their permselectivities must still be quantified. The permeabilities of these membranes appear to be comparable to the permeabilities of commercially available reverse osmosis membranes. However, these membranes are too fragile to withstand the operating pressures that are employed in commercial reverse osmosis systems.

It is possible that alcoholic TiO_2 sols will not be appropriate for use in some applications because the particles sinter at too low a temperature. Unsupported TiO_2 membranes prepared from alcoholic sols were observed to lose porosity when fired above 300°C for 30 min [1]. If sintering of TiO_2 particles closes down the resulting membranes, their performance could be improved by doping the particles with small amounts of other metal oxides that enhance the thermal stability of these membranes. The addition of 1 mol% V_2O_5 to TiO_2 particles increased the temperature at which microporosity of the unsupported membranes was lost by as much as 100°C.

Aluminosilicate membranes (which maintain porosity when sintered at temperatures as high as 1200°C) would also be useful candidates for use in these studies once the pore sizes of these membranes can be reduced to the micropore region. However, the effects of varying the sintering conditions on the behavior of aluminosilicate membranes with different compositions must be evaluated more thoroughly than has been possible to date. In addition, it usually requires considerable effort before a good coating of a given sol can be obtained on a given support. Even with our experience in fabricating supported membranes by way of dip coating, we typically require two to four months of relatively intensive effort to develop a good protocol for preparing a particular supported membrane system.

4.2. Permformation

Permformation is a process in which the deposition of particles from a suspension occurs within the pores of a support. This deposition must be carefully controlled if a coherent separation layer is to be formed. However, once such a separation layer has been deposited, the small pore size of each pore should help to minimize the stresses produced as the separation layer is dried and fired. Thus, our goal in this study is to design and demonstrate a semi-automated permformation process for fabricating defect-free supported ceramic membranes under reproducible conditions.

4.2.1. Theory

Permformation occurs in three stages: internal deposition, chemically-induced gelation, and controlled dehydration. The permformation process is conducted in the apparatus depicted in Figure 19. This particular *permformer system* was designed to operate with a tubular support.

In the internal deposition stage of this process, an aqueous sol passes through the wall of the support by way of capillary action, as depicted in Figure 20. When the interior surface of the support is reached, a drying gas (stream 1 in Figure 19) causes the carrier solvent to evaporate. Over time, the colloidal particles concentrate at the interior surface within the mouths of the pores, forming a gel. An advantage of this process is that it restricts gelation to the pores contained within the surface of the support, rather than allowing gelation to occur across the entire interior surface of the support. As a result, the effective planar dimensions of the individual

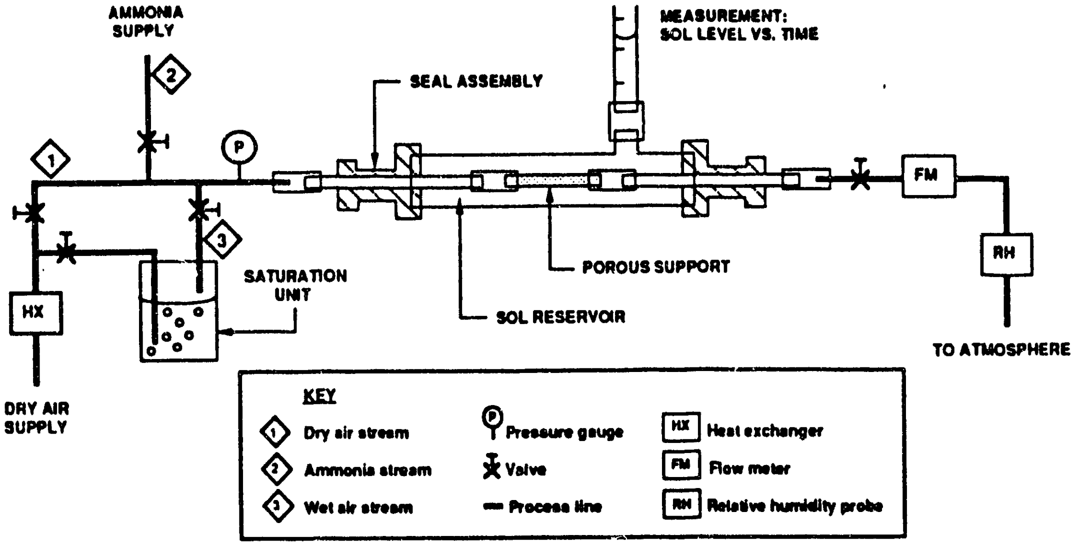

Figure 19. Schematic diagram of the permformer system.

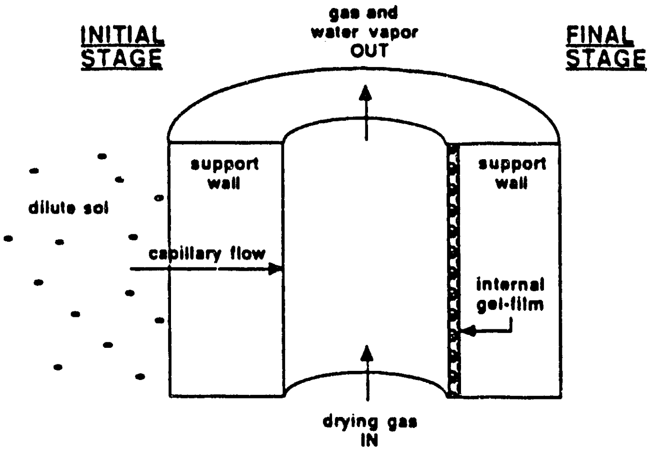

Figure 20. Schematic diagram of the internal deposition stage of permformation.

gels and the associated distortional stresses are diminished. Currently, the only fully operational phase of the permformation process is the internal deposition stage. All of the results obtained to date pertain to this stage.

The other stages of permformation (gelation and drying) are still under development. In the chemically-induced gelation stage, we will destabilize and aggregate the concentrated colloid that has been deposited in the wall of the support by applying a sudden, calculated increase in pH. This shift in pH toward the isoelectric point of the sol particles will be accomplished by inclusion of anhydrous ammonia gas (stream 2 in Figure 19) in the air stream and subsequent dissociation of ammonium ions in the film of sol particles. This approach permits direct control over the thickness of the resultant gel-film by way of variations in the concentration of particles in the sol, the rate of evaporation of the solvent, and the time at which ammonia is added.

The final stage (drying) is designed to produce a crack-free membrane by replacing the dry air stream with a stream of air saturated with water vapor (stream 3 in Figure 19). This humidified air stream allows us to dry the gel in a controlled manner. With the current design of the permformer system, the sol must be drained from the annular reservoir around the support, after which the reservoir is opened to the atmosphere. This process reverses the direction of evaporation.

In the drying configuration, the menisci of the fluid that remains in the pores of the support would slowly retreat from the exterior (outer) surface of the support toward the gel-films. No evaporation would occur at the interior, gelled surface; therefore, the potential for disturbance of the films is minimized. After the support is fully drained, the films are fully dehydrated by gradually lowering the humidity level of the drying stream to ambient conditions with the aid of a monitoring system to control relative humidity. Subsequent firing of the dehydrated gel is expected to produce crack-free ceramic membranes of uniform thickness.

4.2.2. Characterization

Prototype permformed ceramic membranes have been analyzed by scanning electron microscopy (SEM) to characterize the physical surface features of the composite membrane-support structure. In tandem, energy dispersion X-ray spectroscopy (EDX) was used to map the elemental composition of the surface. Studies of the permeabilities and permselectivities of permformed membranes will be conducted once suitable materials are fabricated.

Two separate studies of the internal deposition stage of the permformation process have been performed. Table II outlines these studies, which are referred to as the initial and revised studies. In both cases, porous alumina support tubes (Alcoa Separations Technology, now a division of U.S. Filter) were employed in permformation experiments involving either a silica sol or an iron oxide sol. A solution of ammonium phosphate was utilized before the permformation step to modify the surface charge of the support. Figure 21 is a scanning electron photomicrograph at 30X magnification of a cross section of

Table II. Materials and experimental conditions used in the initial and revised studies of the internal deposition process in permformation.

Study	Material Deposited	Concentration of Sol (M)	pH	Pore Diameter of Support	Treatment of Support
Initial	Goethite	0.001	4	0.2 μm	Entire support was phosphated
Initial	Silica	0.1	9	0.2 μm	Support was not phosphated
Revised	Iron Oxide	0.2	4	50 Å	Only internal surface of support was phosphated
Revised	Silica	0.1	9	50 Å	Only external surface of support was phosphated

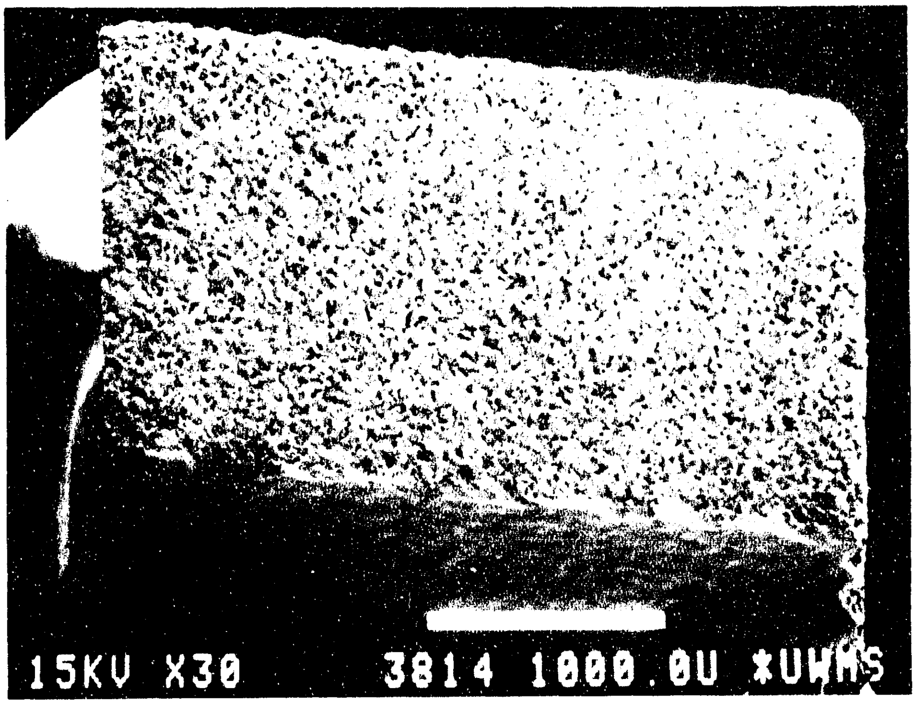

Figure 21. SEM photomicrograph of a cross section of an alumina support with a mean pore size of 50 Å.

the alumina support that was employed in the revised study. Three slip cast layers of alumina, added by the manufacturer, form the 50 Å layer and are evident in the lower portion of the SEM image.

For the reasons described in the previous discussion of dip coating, phosphate was utilized in the initial study to enhance adhesion between the sol particles and the surface of the support by modifying the electrical charge of the surface of the wetted support. In this instance, adsorption of phosphate was achieved by exposing the alumina support to an ammonium hydrogen phosphate solution ($[(NH_4)_2HPO_4] = 0.5$ M, pH $\approx$ 4) for a period of 18 h.

For the goethite (α-FeOOH) and alumina system at pH 4, the support was phosphated so that it would develop a negative surface charge under these conditions, thus enhancing the attraction between the support and the positively charged goethite particles. For the initial silica and alumina system at pH 9, the support was *not* phosphated. Thus, the support would retain a positive surface charge under these conditions and attract the negatively charged silica particles.

SEM imaging combined with EDX analysis of the membranes formed during the initial internal deposition study indicated that (in the case of both silica and goethite) almost all of the sol particles had deposited prematurely on the exterior surface of the support tube. Virtually none of the particles had actually passed through the wall of the support and deposited at the interior surface.

This premature deposition was attributed to two possible causes. First, there is a tendency for the local particle concentration to increase as the sol passes into the entrances of the pores at the exterior surface. This increased concentration can destabilize the particles and lead to aggregation or gelation. Second, the general phosphate treatment promoted the electrostatic attraction between the particles of the sol and the exterior surface of the support. This increased attraction would favor deposition of the particles on the outer surface of the support.

Thus, the revised study was designed to achieve enhanced adhesion only between the sol particles and the inner (bore) surface of the support by way of selective modification of the electrical charge of the surface of the wetted support. This selective modification was achieved by preferentially adsorbing phosphate ion to either the interior or exterior surface of the support based on the type of sol used. Contact was made between the desired support surface and an ammonium hydrogen phosphate solution ($[(NH_4)_2HPO_4]$ = 0.1 M, pH ≈ 4) for a period of 30 to 80 s.

For the revised iron oxide and alumina system, only the interior surface of the alumina support was phosphated and the exterior surface was left unphosphated. Therefore, the surface charge attraction was selectively enhanced at the interior surface and remained low at the exterior surface. For the revised silica and alumina system, only the exterior surface of the support was phosphated. Under these conditions, the surface charge attraction was greatly reduced at the exterior surface and was maintained at its unmodified, low level at the interior surface.

The conditions of the revised study are illustrated in Figure 22, in terms of the electrophoretic mobility vs. pH curves for the two sol/support

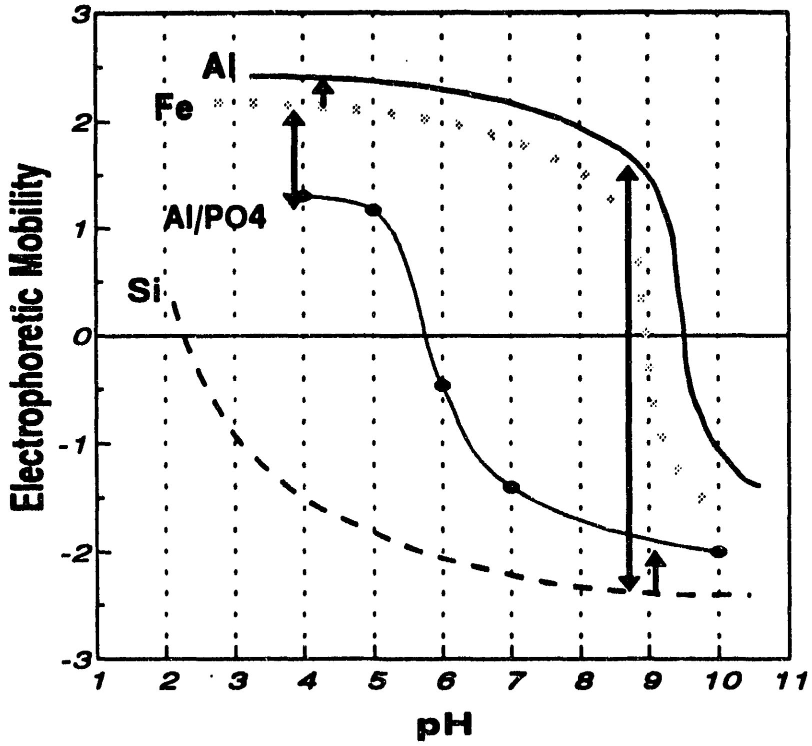

Figure 22. Revised conditions of electrostatic attraction following selective phosphation of alumina supports.

systems. The large double-headed arrows indicate relatively high charge attraction at the interior surfaces, and the small single-headed arrows indicate relatively low attraction at the exterior surfaces.

Under the revised conditions of selective phosphation, the internal deposition was dramatically improved. SEM imaging and EDX analyses of the ceramic membranes made under the revised conditions indicated that little or no premature deposition had occurred. Instead, the sol deposited internally on the inner surfaces of the support as desired, although not in a completely coherent layer. The deposition of iron oxide was patchy, but the deposition of silica was encouragingly uniform.

Figure 23 is an SEM photomicrograph at 300X magnification of the alumina support after selective phosphation and internal deposition of silica. The silica forms a distinct internal membrane layer, about 100 μm thick, immedi-

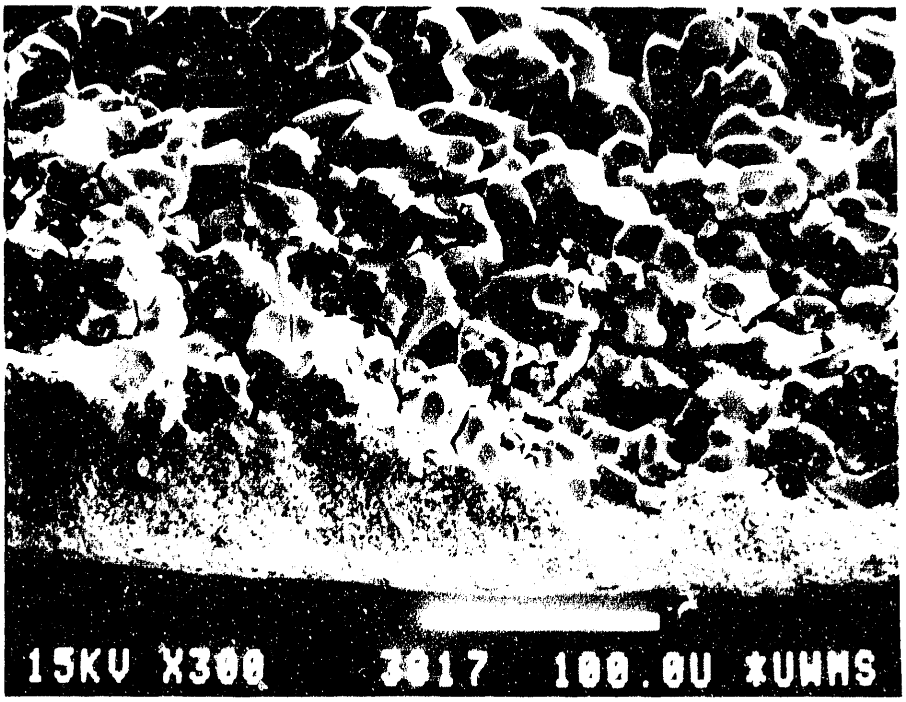

Figure 23. SEM photomicrograph of a silica layer that was deposited internally in an alumina support (300X).

ately behind the slip cast alumina layers. This deposition is evidenced by the cracked material in the alumina interstices. Figure 24 is a 600X magnification image of the same section that provides clearer detail.

A system has also been designed and built that will allow the permformation of disk-shaped porous supports. While this system has not been successfully operated yet, we believe that its design is sound. The primary problem is that although the system has been used to deposit nanoparticulate ZrO_2 sols in porous silver supports, there is poor adhesion between the ZrO_2 particles and the supports. These supports are now being pretreated to enhance their reactivity with ZrO_2 particles (e.g., by exposure of the silver supports to nitric acid).

Figure 24. SEM photomicrograph of a silica layer that was deposited internally in an alumina support (600X).

4.3. Critical Point Drying

The capillary forces that cause cracks to form in gels as they dry arise at the interface between the solvent that is held in the gels and the surrounding air. One way to avoid the formation of cracks in gels is to dry them at the critical point conditions for the solvent. No gas-liquid interface exists under these conditions, so no capillary forces are present. Thus, gels that are dried in this manner are free of cracks.

However, the applicability of this technique is somewhat limited. One major difficulty is that the conditions required to reach the critical points of many common solvents are rather extreme (e.g., the critical point of water lies above 200 atm and 370°C). Processing of some of our ceramic materials at such a high temperature might well cause an undesired transition in the crystalline form of the material or in the properties of the resulting membranes.

Rather than invest in the expensive equipment that is necessary for safe operation under such conditions, many researchers have employed carbon dioxide as a solvent for critical point drying and extraction. Because the critical point of carbon dioxide is ca. 70 atm and 31°C, it is much easier to operate with carbon dioxide than with water for this application. However, if one uses carbon dioxide as the solvent for the critical point drying of aqueous gels, one finds that all the water is not removed from the gel because water is not infinitely soluble in carbon dioxide at the critical point of carbon dioxide. This problem is typically solved by replacing the water in the sample with another fluid that is fully miscible with both water and carbon dioxide (e.g., ethanol or amyl acetate). The moisture in the sample is removed by exposing the sample in a step-wise manner to a graded series of solutions from 10% replacement solvent - 90% water up to the pure replacement solvent. An important question in working with gels prepared from aqueous sols is whether the replacement of the water in the gel with another solvent will destabilize the gel and cause major changes in the properties of the resulting membranes.

Another possible advantage (or a possible difficulty) in applying critical point drying to fabricate ceramic membranes for separations is that materials produced by critical point drying have very high porosities, often in excess of 80%. Such high porosities can lead to high permeabilities through the membranes, which is a very desirable feature. However, high porosities are likely to be associated with large pore sizes in the membranes, a characteristic that detracts from their performance as microfilters. The capillary forces that develop in gels during conventional drying appear to aid in tightly packing the particles together. Because these capillary forces are absent in critical point drying, one would expect that membranes formed by this process would exhibit looser packing of particles than would be observed in membranes formed by conventional drying processes. However, critical point drying would be very advantageous if it could be utilized to fabricate microporous ceramic membranes with high porosities.

Thus, the use of critical point drying to prepare ceramic membranes is of interest in spite of the operational difficulties in using the technique. To date, however, we are still developing the methods needed to successfully fabricate ceramic membranes by means of critical point drying using carbon dioxide. Hence, there is as yet no characterization data available for evaluating the utility of this approach.

4.4. Summary

Of the three techniques currently under investigation for preparing supported ceramic membranes (dip coating, permformation, and critical point drying), only dip coating can be considered to be operational. However, dip coating has proven to be quite useful in fabricating thin films of ceramic membranes. In order to avoid a slip casting process, we saturate the porous support with solvent before dip coating. In some cases, we also modify the charge on the surface of the support by adsorbing species such as phosphate ions on the support. Charge modification is utilized in order to enhance the electrostatic attraction between the support and the particles in the sol. Thin membranes are desired because they are more resistant to the formation of cracks during the drying process and because they minimize the resistance of the membrane to the flow of permeate through that membrane. Thin coatings of particles can be obtained by employing sols that have relatively low concentrations of particles (ca. 0.05 M) for dip coating.

Dip coating (as we utilize it) will likely remain a batch technique. However, dip coating is relatively inexpensive to implement, with the major cost being the design and fabrication of a holder for the supports. In principle, this holder could handle many supports simultaneously. Because processing times are fast, a large number of coated supports could be fabricated in a day. If drying under ambient conditions is feasible, the thin films that are applied by dip coating should dry within a matter of hours. Thus, the major concern in implementing this method is to determine whether cracks form during processing of the coated supports.

Results of the revised permformation study indicate that internal deposition within tubular supports is a promising technique for fabricating ceramic membranes. Planned developments in the method of internal deposition that should improve control over surface charge attraction include refinement of the technique of selective phosphation and a more rigorous protocol for precleaning the supports. It should also be possible to reduce the thickness of the membrane by optimizing process parameters such as the concentration of the sol, the duration of the deposition process, and the rate of evaporation.

In theory, permformation has two advantages over dip coating in industrial applications: it provides better control over the deposition of sols and it minimizes crack formation in the deposited membranes. However, the present permformer system requires more expensive monitoring equipment and longer processing times than dip coating. It is not yet known if permformation can be used to process large quantities of supports at a time. Further experience in implementing permformation as a method of fabricating ceramic membranes is required to determine whether its advantages outweigh its disadvantages.

Critical point drying studies are only in their initial phase because of operational difficulties encountered to date. Thus, no characterization data are available for ceramic membranes that have been fabricated by this process. Because membranes produced by this method should have high permeabilities, it will be interesting to compare the mean pore sizes and pore size distributions of such membranes with those of membranes produced from identical sols using conventional drying methods.

Commercial application of critical point drying to prepare ceramic membranes may be limited by the relatively large equipment costs and safety concerns associated therewith, especially where the direct removal of water is involved. In addition, this method can process only small quantities of supports at a time, although processing times may be comparable with those needed to prepare ceramic membranes by dip coating. If microporous ceramic membranes with high porosities can be fabricated by critical point drying, the economic value of such membranes may be high enough to justify the associated costs.

5. CONCLUSIONS

The primary objective of this project was to fabricate a microporous supported ceramic membrane for use in gas phase separations and separations of low molecular weight solutes in liquid phase systems. This objective was achieved by dip coating porous alumina disks with an alcohol-based TiO_2 sol that contained nanoparticles. In order to form the TiO_2 membrane, the coated support was dried under ambient conditions and fired at 200°C. This membrane appears to be permselective and displays permeabilities that are comparable to those of commercially available reverse osmosis membranes. However, this supported TiO_2 membrane is not strong enough to withstand the pressures employed in commercial reverse osmosis systems.

While this particular system allows one to evaluate the performance of ceramic membranes in applications involving microfiltration, it is not likely that this system could be commercially utilized because of the inherent fragility of the support. In addition, there are likely to be applications for which a titania membrane is not suited. Thus, our studies are continuing in two directions: (a) to synthesize nanoparticulate sols of several different oxides, including mixed oxide systems that could be expected to display enhanced thermal stabilities and (b) to develop alternative techniques for placing ceramic membranes on supports that are suitable for industrial use. The permselectivities and permeabilities of the resulting modules will also be characterized.

Aqueous sols that contain nanoparticles of SiO_2 have been synthesized. However, the particles in these sols grow relatively rapidly, so the sols must be used within three days of synthesis in order to fabricate microporous membranes. Pore sizes in these membranes are too small to be characterized by analysis of N_2 sorption data using the Kelvin equation. Other techniques indicate that these membranes can be synthesized with average pore diameters of <10 Å. Although membranes with such small pore diameters are prime candidates for use in microfiltration, the relatively high solubility of amorphous silica in aqueous systems may limit the applications of this material.

The pore size distributions of alumina membranes that were fabricated from aqueous boehmite sols have not yet been characterized. It is known that these membranes display both microporosity (mean pore diameters <20 Å) and mesoporosity (mean pore diameters >20 Å), with indications that the mean diameters of the mesopores are ca. 35 Å. Thus, these alumina membranes represent an improvement over commercial alumina membrane modules. These modules can be obtained with nominal pore diameters between 4 and 5 nm.

To date, we have been unable to fabricate aluminosilicate membranes with pore sizes that are small enough to be useful for microfiltration. Typical mean pore diameters for these membranes are 35 Å. However, these membranes display impressive thermal stabilities. The mean pore diameter of an 80 mol% Al_2O_3 membrane was still 35 Å after the membrane was fired at 1200°C for 1 h. Research continues on fabricating membranes with smaller pore sizes from these materials. There are indications that ca. 40 mol% Al_2O_3 membranes would be microporous. We also noted that, when these membranes were prepared from butanol-based sols, a very slow firing protocol had to be employed to avoid pyrolysis of the solvent within the pores of the membranes. When pyrolysis occurs, the resultant membranes are very dark and have almost no porosity.

Three different methods of fabricating supported ceramic membranes are under investigation. A fourth method (slip casting) has given such poor results that we no longer employ it to prepare membranes. At present, dip coating appears to be the best of the three fabrication techniques. It is relatively easy to implement, requiring only that the porous support be filled with solvent and that the sols employed contain low concentrations of particles. In certain cases it is also helpful to modify the charge on the surface of the support to enhance the electrostatic attraction between the support and the particles in the sol.

The other two techniques (permformation and critical point drying) are still in early stages of development. While each of these techniques offers certain advantages over dip coating as a fabrication method for preparing ceramic membranes, critical point drying requires an expensive investment in equipment and is likely to be difficult to implement for processing large quantities of supports simultaneously. The present design of the permformer system also requires relatively expensive monitoring equipment and can only process a single porous support at a time. However, as more experience is gained in implementing permformation as a processing technique, it may be possible to scale up the permformer system so that several supports can be processed simultaneously with minimal monitoring of the system. This outcome would considerably improve the economics of employing permformation to fabricate supported membranes. To date, there is not enough information available about permformation to allow one to predict its potential utility for industrial processing.

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