Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Peterson, R. A. , Webster, E. T. , Niezyniecki, G. M. , Anderson, M. A. and Hill Jr., C. G.(1995) 'Ceramic Membranes for Novel Separations', Separation Science and Technology, 30: 7, 1689 — 1709
To link to this Article: DOI: 10.1080/01496399508010370
URL: http://dx.doi.org/10.1080/01496399508010370

SEPARATION SCIENCE AND TECHNOLOGY, 30(7-9), pp. 1689-1709, 1995

CERAMIC MEMBRANES FOR NOVEL SEPARATIONS

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ABSTRACT

A number of advances have been made in the fabrication and performance of supported ceramic membranes. Improvements in techniques for the synthesis of particulate sols containing particles in the range of 4 to 10 nm in diameter are discussed. Several deposition techniques for the fabrication of supported ceramic membranes via sol-gel technology are examined, including slipcasting, filtration, coating, and permformation.

Supported titania membranes have been fabricated and both liquid phase permselectivity and gas phase permeability experiments have been performed. Results of the liquid phase separations indicate that these membranes are characterized by a molecular weight cutoff value of approximately 200. Gas phase permeabilities reveal that Knudsen diffusion is not the only mechanism of transport through these membranes.

INTRODUCTION

During the past decade, significant advances have been made in ceramic membrane technology. For example, there have been significant reductions in the molecular weights of solutes which can be rejected by ceramic membranes. Ten years ago, the ceramic membranes employed for gas phase separations were typically based on the use of Knudsen diffusion as the primary mechanism of transport. However, currently available ceramic membrane technology permits one to utilize not only Knudsen diffusion, but also surface activated transport as vehicles for bringing about molecular separations.

This paper deals with both these improvements in ceramic membrane technology and the techniques which are employed in fabricating the current generation of membranes. One of the primary improvements in the fabrication of ceramic membranes via sol-gel technology involves advances in the methods used to produce the precursor sol employed in fabricating the final product.

Other changes have been made in the fabrication protocol typically employed to produce ceramic membranes. A decade ago, slipcasting was the primary method of depositing membranes on support materials. Today, in addition to slipcasting, a variety of other techniques are employed. These alternative techniques include coating, filtration deposition and permformation. These new methods have facilitated the development of flaw free ceramic membranes which are capable of novel separations.

Commercial Development of Ceramic Membranes

In 1982, the only commercially available inorganic membranes characterized by pore diameters of less than 10 nm were glass membranes (1). These membranes were typically fabricated from Vycor glass. However, at that time sol-gel techniques for fabricating ceramic membranes were well known and γ-alumina membranes characterized by pore diameters of approximately 40 Å had been developed by Keizer et. al. (1). However, commercialization of these membranes was not immediate. By 1988, ultrafiltration membranes made of either γ-alumina or zirconia were available from Ceraver (2). Today, a number of inorganic membranes which are characterized by pore diameters of 200 Å or less are available. Table 1 indicates the chemical compositions and mean pore diameters of some commercially available membranes (3). Except for the glass membranes, the ceramic membranes listed in Table 1 are fabricated via sol-gel techniques. The balance of this paper will focus on membranes produced by sol-gel technology.

Current Status of Ceramic Membranes

The membranes listed in Table 1 are of primary interest because of the sizes of the pores contained within these membranes. When particulate sols are employed to produce ceramic membranes, the size of the pores is dictated by the size of the particles in the sol from which the membrane is fabricated. Hence, if one wishes to fabricate membranes whose pores are characterized by very small diameters, it is necessary to employ a sol which contains very small particles. Smaller particles produce smaller pores. It should be noted that while various authors have reported the preparation of a number of supported membranes whose pore diameters are smaller than those of the membranes listed in Table 1, none of these membranes is currently available commercially (4).

SYNTHESIS OF SOLS

While ceramic membranes can be fabricated using a number of techniques, the method of interest here is based on sol-gel technology. Sol-gels can be classified into two general categories, polymeric and particulate sols. Our efforts at the University of Wisconsin have focused on the use of particulate sols to prepare ceramic membranes. Figure 1 is a brief summary of the steps involved.

TABLE 1. COMMERCIALLY AVAILABLE INORGANIC MEMBRANES

Manufacturer	Membrane Material	Diameter of Pores in the Membrane
U.S. Filter	ZrO_2	200 Å
U.S. Filter	Al_2O_3	50 Å
Alcan/Anotec	Al_2O_3	200 Å
Gaston County Filtration Systems	ZrO_2	40 Å
Rhone-Poulenc/SFEC	ZrO_2	40 Å
TDK	ZrO_2	~100 Å
Schott Glass	Glass	100 Å
Fuji Filters	Glass	40 Å

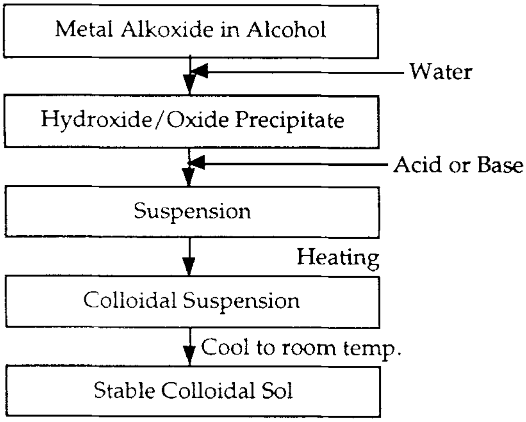

FIGURE 1. Procedure for producing particulate sols.

The initial step in the production of particulate sols is hydrolysis of the metal alkoxide (5). Complete hydrolysis yields metal hydroxides or hydrous metal oxides (6). The metal hydroxides are then peptized to form a stable colloidal sol. Peptization involves addition of acid or base to the solution, thereby altering the electrostatic interactions that are responsible for stabilization of the sol (7). The electrostatic double layer formed around each of the particles serves to repulse other like charged particles and prevents particle aggregation from occurring. When this surface charge is sufficiently large, one obtains a stable sol.

The procedure for preparation of stable sols begins with a solution of a metal alkoxide dissolved in alcohol. The alkoxide is then hydrolyzed with water. This hydrolysis reaction is followed by a condensation reaction. The relative rates of the hydrolysis and condensation reactions determine the size of the particles which are produced. If the hydrolysis reaction is fast relative to the condensation reaction, then the final particle size will be large. By contrast, when the rate of the hydrolysis reaction is slow relative to that of the condensation reaction, the resultant particles are small. The goal of our research efforts has been to fabricate sols which contain relatively small particles (i.e., particles with characteristic dimensions in the 3 to 10 nm range). This goal has been achieved by decreasing the effective rate of the hydrolysis reaction. Changes in the effective rate of hydrolysis were brought about by controlling the kinetics of the reaction and/or controlling the concentrations of the products of the hydrolysis reaction which are available to undergo subsequent condensation reactions.

The preparation of titania sols will be used to indicate the manner in which these two different methods are employed for controlling the effective rate of the hydrolysis reaction. For titania sols, the hydrolysis reaction can be written as:

$$Ti(OR)_4 + xH_20 = Ti(OH)_x(OR)_{4-x} + xHOR$$

Subsequent condensation reactions of the $Ti(OH)_x(OR)_{4-x}$ species lead first to the formation of oxo-bridged species and ultimately to the formation of amorphous or crystalline TiO_2.

The kinetics of the hydrolysis reaction can be controlled by altering the properties of the reactants. For example, by employing larger substituent groups in the metal alkoxide, one can reduce the rate of the hydrolysis reaction. When the alkoxide group is an isopropoxide, the rate of the hydrolysis reaction is significant relative to the rate of the condensation reactions. Thus a large amount of the precursor will be completely hydrolyzed before the intermediate partially hydrolyzed species have an opportunity to undergo condensation reactions. The intermediate hydrolysis products [e.g., $Ti(OH)_3(OR)$] are very reactive and rapidly undergo reactions which lead to the formation of a precipitate, thereby forming relatively large particles. However, if 2-methyl-2-butoxide groups are substituted for the isopropoxide groups in the metal alkoxide, one obtains a further degree of control over the rate of hydrolysis. The bulkier 2-methyl-2-butoxide moieties sterically hinder the hydrolysis reaction, thereby decreasing the rate of this reaction. Partially hydrolyzed products [e.g., $Ti(OH)(OR)_3$] condense to form smaller, stable particles. For values of x less than or equal to four, these sols are relatively stable. When the molar ratio of water to the alkoxide precursor becomes larger than four, the sol becomes unstable. This approach to preparing stable sols can be employed not only for the preparation of titania sols, but also for the preparation of zirconia sols.

The solubility of titania increases dramatically as one decreases the pH. The high solubility of titania allows one to produce solutions in which all of the titania present is in dissolved form. This situation is achieved when the pH of the solution is below a value of 2. Thus, even though excess water is present in such solutions and the titanium alkoxide precursor is completely hydrolyzed, none of the potentially resultant titania is available to participate in condensation reactions because it dissolves as soon as it is formed. If one then increases the pH, the solubility of titania will decrease. When the solubility of titania in the solution is less than that corresponding to the concentration of titania which would be produced by complete hydrolysis of the alkoxide precursor, the excess titania species will become available to participate in condensation reactions. If the pH is increased rapidly, the amount of titania which becomes available to undergo condensation reactions will be large, and these reactions will produce relatively large particles. However, if the pH of the solution is increased slowly and with sufficient care, the rates of the condensation reactions can be closely controlled. This control permits one to produce particles which are characterized by relatively small diameters.

Several metal oxides exhibit high solubilities at both low and high pH values. Thus, one can, in principle, achieve comparable results (with respect to the dimensions of the sol particles) by dissolving metal oxides in a solution characterized by a high pH. This general technique for controlling the size of the particles of the sol can be employed for producing a variety of oxides, including titania, zirconia, silica, alumina and iron oxide.

These two methods of controlling the size of the final particles have been employed in preparing stable colloidal sols containing a variety of metal oxides. Table 2 indicates some of the metal oxides which we have employed in colloidal form to prepare ceramic membranes. The colloidal sols are divided into two groups. The first group consists of those sols which were prepared via a controlled hydrolysis route. The most important parameter in the preparation of sols via this route is the chemical nature of the alkoxide group which is resident on the metal before the hydrolysis reaction takes place. For both cases cited in Table 2, the alkoxide group employed was 2 methyl-2-butoxide. The sol particles generated via this approach are characterized by diameters of approximately 8 nm. (The size of the particles was determined by light scattering measurements.) Unsupported membranes fabricated from these sols were characterized by pore diameters of 15 Å. The average diameters of the pores in the membranes produced from these sols were determined via nitrogen adsorption (BET) measurements.

The second category of sols is that for which the condensation reaction is the limiting step. In all of the cases listed, the rates of the condensation reaction are controlled by dissolving the precursor metal alkoxide or metal salt in an aqueous solution. For the indicated chemical species, this dissolution can frequently be accomplished under either acidic or basic conditions. The conditions under which the particular metal alkoxide or metal salt was dissolved are indicated in Table 2, as are the sizes of the sol particles and the pores in the resultant membrane.

The indicated protocol permits one to produce sols from a variety of different materials. The sols are characterized by particles which are 10 nm or less in diameter. In addition, the diameters of the pores of membranes fabricated from these materials are typically less than 20 Å. The pore radii are significantly lower than those of the membranes which were prepared by sol-gel techniques a decade ago.

Etienne et. al. (8), have described an alternative method for fabricating zirconia particles which are approximately 6 nm in diameter. Membranes fabricated from these sols were characterized by pore diameters of less than 20 Å. The fabrication technique employed by Etienne et. al., also involves dissolving the metal oxide in an acid solution.

Burggraaf and co-workers (9-11) have indicated that alumina membranes can be improved without employing extensive control of the reactions involved in the preparation of the sol. They reported that alumina membranes with pore diameters as small as 25 Å can be prepared using traditional sol-gel techniques. The mathematical model of the pore structure which has been employed by Burggraaf et. al., in the determination of the average pore diameter is significantly different than that previously employed in the characterization of alumina membranes. These researchers assumed that the pores in the alumina membranes were slit-shaped rather than cylindrical.

The methods indicated above are based on use of the particulate route for the preparation of colloidal sols. It is also possible to employ a polymeric route wherein the gel is formed by a polymerization reaction involving oxygen linkages between metal atoms. Using this approach, Brinker (12) has fabricated silica membranes which are characterized by pore diameters of less than 15 Å and Guizard et. al. (13), have prepared mixed silica-organic membranes which are characterized by pore diameters of less than 15 Å. It should be noted, however, that both of these types of membranes are of limited utility because of their instability in the presence of water (14).

TABLE 2. CHARACTERISTICS OF MEMBRANES AND THE SOLS FROM WHICH THEY WERE FABRICATED

Controlled Hydrolysis			
Oxide	Alkoxide Group	Particle Size (diameter)	Pore Size (diameter)
Titania	2 methyl-2-butoxide	~8 nm	15 Å
Zirconia	2 methyl-2-butoxide	~8 nm	15 Å
Controlled Precipitation			
Oxide	Solubilized in Acid or Base	Particle Size (diameter)	Pore Size (diameter)
Alumina	Acid	~10 nm	20 Å
Iron Oxide	Acid	3 - 4 nm	< 10 Å
Silica	Base	3 - 4 nm	< 10 Å
Titania	Acid	~ 8 nm	15 Å
Zirconia	Acid	~ 8 nm	15 Å

DEPOSITION OF SOLS

In order for the sols described in the previous section to be of use, it is necessary to place the sols on a support material in order to form a membrane with the requisite mechanical strength. This section describes the methods by which the membrane is formed initially. The most common method of depositing a membrane is slipcasting (14); however, a number of alternative deposition techniques are available, including filtration deposition, coating, and permformation.

Slipcasting

Slipcasting involves placing a dry support into the sol. The suspension is then imbibed into the pores of the support. As the suspension is drawn into the support, the concentration of the sol particles at the surface of the support increases. When this concentration increases to a sufficient degree, the sol becomes unstable. The sol then transforms into a porous gel layer. While liquid can still pass through this layer, the sol particles are stopped at the gel-solution interface and become part of the gel network. In this fashion, the thickness of the gel layer is increased. This mechanism is very similar to the mechanism that produces concentration polarization in conventional membrane separation processes such as reverse osmosis and ultrafiltration. The thickness of the gel formed by this procedure varies with time in a manner which obeys the relation:

$$h = K\sqrt{t} \qquad (1)$$

where h is the thickness of the membrane, K is a constant dependent on the characteristics of the sol, and t is the time of contact between the support and the suspension.

In order for slipcasting to be effective, it is necessary that the initial concentration of particles in the suspension be sufficiently large that destabilization and formation of a gel layer will occur when the suspension becomes more concentrated. In addition, it is important that the porous substrate possess the proper characteristics. First, the pores of the substrate must be sufficiently large that transport of the liquid phase into the porous material occurs readily. Rapid transport of the liquid allows the gel layer to form before the sol particles can diffuse away from the liquid-support interface. Second, the volume of the void regions in the support material must be sufficiently large that the support does not become saturated with solution before a gel layer of adequate thickness has been formed. Typically, microfilters are used as the support materials.

There are a number of variables that determine the ultimate thickness of a membrane formed by slipcasting. For example, this thickness will depend on the concentration of the sol and the rate at which the support is removed from the sol. In this process it is essential to accurately control the viscosity of the sol. If the sol is too viscous (greater than 1 poise), the thickness of the cast layer will vary from the top to the bottom of the sample. If the solution is not sufficiently viscous (less than 0.1 poise), the sol particles will be imbibed into the pores along with the solvent. Slipcasting typically yields a membrane thickness of ca. 5 microns. However, upon drying and sintering, these cast membranes are frequently flawed by cracks which must be repaired by casting additional, thinner layers on top of the original membrane.

Slipcasting forces the sol particles into intimate contact with the support material. In this fashion, electrostatic repulsion forces between the sol particle and the support material can be overcome. This forced intimate contact affords better adhesion of the resultant membrane to the support.

Filtration

A second membrane deposition technique, viz., filtration has been developed from the principles of slipcasting (15). In this method, a pressure difference is imposed across the support material. This pressure difference causes the suspension to flow through the pores of the support material. However, as in the slipcasting process, the sol particles are largely excluded from entering the support. Again, when the concentration of sol particles becomes sufficiently large, a gel layer is formed. The parameters that control the thickness of a membrane formed via this method are the pressure drop, the sol concentration, the size of the suspended particles and the size distribution of the pores of the support. The advantage of this method is that the forces arising from the pressure applied to bring the sol particles into contact with the support material are larger than the capillary forces used in slipcasting. In addition, this method is applicable for use with support materials which do not have sufficient bulk to permit slipcasting to be employed.

Coating

Coating involves the same basic phenomena as slipcasting. In this approach, however, the pores of the support are filled with solvent prior to immersion in the sol. This technique effectively inhibits capillary action. Hence the sol is retained on the external surface of the support by viscous forces and surface tension effects. The system can then be modeled as a non-porous rod being removed from a solution. If the rate of removal is held constant and end effects are neglected, the thickness of the fluid adhering to the rod can be related to the velocity of removal, the radius of the cylindrical rod, the viscosity and surface tension of the fluid, and the gravitational constant. By appropriate choice of the experimental conditions, one can cause the thickness of the applied coating to increase or decrease (16). Experimentation has been carried out wherein cylindrical rods were removed from glycerol mixtures at a constant rate. The thickness of the resulting film was measured using a laser. The light scattered by the film was measured and correlated with the film thickness. These experiments indicated that for a low velocity of removal, the film thickness was linearly dependent on the velocity of removal. However, as the rate of removal increased, the thickness asymptotically approached a constant value (17).

It should be noted, however, that the above analysis neglects an important phenomenon that has been observed on many occasions. Immediately upon removal from the solution, the solution begins to flow down the side of the rod causing an increase in the thickness of liquid film at the bottom of the rod. This situation may eventually lead to the formation of droplets at the bottom of the rod, which then drip off (18). This drainage leads to coatings of inconsistent thickness. If the initial thickness is sufficiently thin, problems arising from drainage can be nearly eliminated. The solution to this problem usually requires withdrawing the support from the solution at low speed and the use of a suspension characterized by low values of viscosity and surface tension. The presence of solid particles in the sol adds an additional complication relative to the case of a pure solution. By increasing the concentration of the sol, one not only usually increases the viscosity and the surface tension of the fluid, but also increases the number of particles deposited per unit volume. Small variations in the concentration of the sol can greatly influence the thickness of the deposited film.

Permformation

The technique which we refer to as *permformation,* is a method for depositing sol particles within the pores at the surface of a support (19). In the permformation process, an aqueous colloidal suspension (sol) of metal oxide particles passes through the wall of a porous, tubular support. This transport is depicted in Fig. 2. The sol is assumed to flow under capillary pressure from the outside surface of the tube (above which the sol forms a hydrostatic head) to the inside surface of the tube (over which a stream of dry air passes).

When the front of sol flowing under capillary pressure reaches the inside surface of the support, the solvent (water) portion of the sol evaporates into the stream of dry air. As the solvent evaporates, the colloidal particles are deposited. Over time, the colloidal particles concentrate within the individual pores near the inside surface of the support. When the concentration of particles in the pores reaches a critical value, gelation occurs.

The result of the physical phenomena which take place during internal deposition is the formation of a film of aggregated particles (i.e., the gel-film) in the pores near the inside surface of the support. Geometric and material balance considerations indicate that the mean thickness of this gel-film (h) is given by the relation

$$h = -\frac{D_i}{2} + \sqrt{\frac{D_i^2}{4} + \frac{C_{sol}\Delta V_{sol} M_p}{L\pi\phi(1-\varepsilon)\rho_p}} \qquad (2)$$

where C_{sol} is the molar concentration of the sol; ΔV_{sol} is the volume of sol which evaporates over the course of the internal deposition process; L is the length of the support; D_i is the inner diameter of the support proper; ϕ is the porosity of the support at the inside surface; ε is the porosity of the gel-film; M_p is the molecular weight of the oxide monomer which comprises the gel; and ρ_p is the mass density of the gel. Except for ε and ρ_p, which must be estimated (e. g., on the basis the properties of dry, unsupported membranes of the same composition), all of the aforementioned variables can either be measured directly or determined from the periodic table.

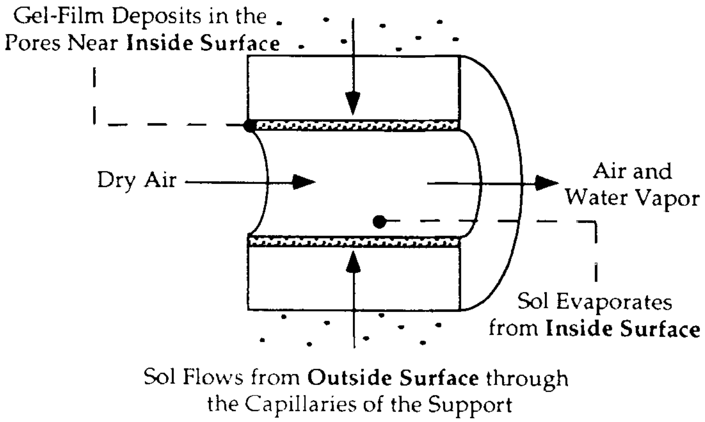

FIGURE 2. Schematic representation of the mechanisms involved in the process of internal deposition of sol particles on a porous support.

In terms of a reduction in the potential deleterious effects of any defects which might be present in the finished membrane, an important advantage is gained when the gel is formed within the porous structure of the support rather than on the surface of the support. The latter situation is usually encountered when coating or slipcasting techniques are employed. A number of researchers have postulated mechanisms by which fracture might occur (20-27). According to one model of fracture (28), defects form when microscopic flaws propagate through the gel. The stress which develops at the tip of a microscopic flaw, σ_c, is proportional to the macroscopic stress, $\sigma_{x,z}$, via the relation

$$\sigma_c = \sigma_{x,z}\sqrt{\pi c} \tag{3}$$

where c is the length of the flaw prior to propagation. Microscopic flaws are able to propagate only when the stress produced by the flaw (σ_c) exceeds the critical stress-intensity factor (K_{Ic}) of the gel. In this way, K_{Ic} represents the strength, or resistance, of the gel to fracture.

Equation 3 predicts that, once the crack begins to propagate, c increases, and the crack grows catastrophically with increasing σ_c. When the gel forms within the pores of the support, the distance available for propagation of the flaw is equivalent to the diameter of an individual pore. With traditional surface-coating techniques, the entire inside surface of the support tube is available for propagation of the crack. Thus, the process of internal deposition produces physical conditions under which the propagation of flaws is arrested before the defects can achieve catastrophic dimensions.

SEPARATIONS

Membranes have been fabricated from the various sols described in Table 2. In addition, all of the deposition techniques described above have been employed in fabricating ceramic membranes. The fabrication protocol which yields the best, most consistent results is that which involves use of the coating technique to deposit a titania sol prepared via the controlled hydrolysis route on an Anotec support.

The support materials employed are Anotec Anodiscs. These supports are commercially available materials which are characterized by mean pore diameters of 0.02 μ. The sol employed consists of suspensions of TiO_2 (0.05 M) in amyl alcohol. The titania particles are formed from titanium tetra 2-methyl, 2-butoxide and are roughly 50 Å in diameter. The resultant unsupported membranes have mean pore diameters of less than 20 Å as determined by nitrogen adsorption (BET) measurements. TEM micrographs indicate that the mean pore diameter is perhaps as small as 15 Å.

To date, we have achieved our greatest success in fabricating flaw-free membranes from colloidal particles with dimensions in the nanometer range by using nanoparticulate TiO_2 sols to coat Anotec Anodiscs. After dipping the supports into the sol, we allow the membrane to dry on the support for a period of 24 hours and then fire the resultant material at 200 °C for 1 hour. At firing temperatures in excess of 300 °C there are marked decreases in both the porosity and the specific surface area of the membrane. These losses can be attributed to the transformation of the structure of the TiO_2 from anatase to rutile. The result of this fabrication protocol is a flaw-free membrane, approximately 0.2 microns thick. (The thickness of the membrane has been determined via visual inspection of electron-photomicrographs.)

Liquid Phase Separations

Initial liquid phase permselectivity experiments were performed using aqueous solutions of polyethylene glycol. The results of these experiments are shown in Figure 3. The permselectivities for other membranes have also been plotted to serve as points of reference (13). Inspection of the data in Figure 3 indicates that the molecular weight cut-off for the TiO_2 membranes supported on Anotec disks is significantly lower than those of other available ceramic membranes.

Gas Phase Permeabilities

A second set of experiments focused on measurements of the permeability of a supported titania membrane to various gases. These experiments are described below.

Figure 4 depicts the permeabilities of the titania membrane to propylene and nitrogen as functions of the average pressure. Results for an alumina membrane reported previously by Ulhorn (29) are also included in Figure 4. Since the permeabilities of the two membranes are significantly different, the results are displayed using two different vertical axes. The relatively high permeability of the membranes to propylene has been attributed to multilayer diffusion and capillary condensation. It should be noted, however, that for the titania membranes the onset of multilayer diffusion takes place at much lower relative pressures than it does for alumina membranes. This phenomenon has been attributed to the smaller pore diameter of the titania membrane (15 Å versus 40 Å for the alumina membranes) (30).

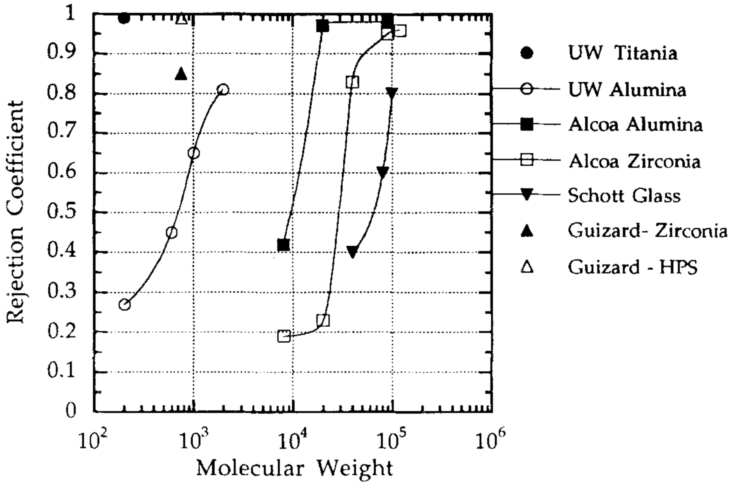

FIGURE 3. Rejection as a function of molecular weight for various membranes.

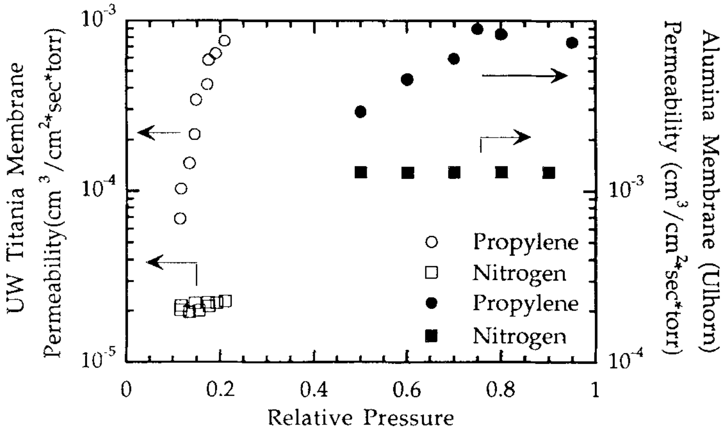

FIGURE 4. Permeability of titania and alumina membranes to nitrogen and propylene.

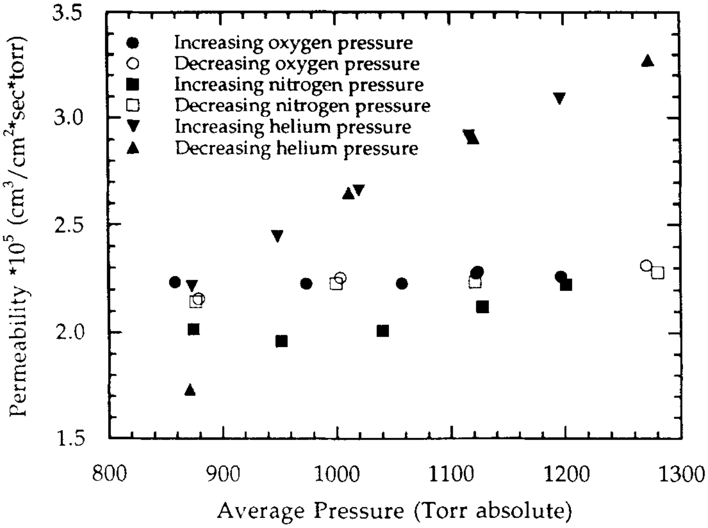

FIGURE 5. Permeability of a titania membrane to various gases.

Additional experiments were performed using the same titania membrane employed in the previous experiment. The results shown in Figure 5 indicate that the permeabilities of the membrane to nitrogen, oxygen, and helium increase to some extent with increasing pressure. These results indicate that the transport mechanism for these membranes is not simple Knudsen diffusion, but rather, that the transport of these gases through these membranes involves some form of surface transport (30).

CONCLUSIONS

The ceramic membranes commercially available at present are characterized by pore diameters of approximately 40 Å. However, sol-gel techniques can be employed to produce membranes which are characterized by pore diameters as small as 10 Å. Supported membranes of these types have been characterized for both liquid and gas phase applications. Data for liquid phase separations indicate that these supported membranes are characterized by molecular weight cut-off values which are nearly two orders of magnitude lower than those of commercially available membranes. In addition, gas phase permeability experiments with these same types of ceramic membranes indicate that the mechanism of transport through these membranes involves not only Knudsen diffusion, but also surface transport.

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