

NOTE

On the Loss of Hydraulic Permeability in Ceramic Membranes

The properties of inorganic membranes are dependent on the surface chemistry of the material, which in turn are affected by parameters such as temperature, pH, and chemisorption of molecules. For both silica and γ -alumina membranes, a significant reduction in water hydraulic permeability was observed after heat treatment or exposure to organic solvents. For silica membranes, the water permeability reduction due to heating at 140°C has been attributed to the removal of physically adsorbed water, which exposes hydrophobic surface patches covered by isolated hydroxyl groups. In the case of γ -alumina membranes strong adsorption of a wide range of organic compounds can result in significant permeability loss. © 1996 Academic Press, Inc.

INTRODUCTION

The use of silica and alumina membranes for separation processes has expanded during the past decade, mainly in the areas of biotechnology, environmental control, and gas separation (1). As the applications of ceramic membranes diversify, it is expected that these membranes will be exposed to a wide range of organic solvents and subjected to various types of pre- and post-treatments involving heating and solvent washing. However, the structure and chemistry of these surfaces, which directly affect membrane separation properties, are sensitive to temperature and pH. Similarly, various organic compounds can chemisorb onto the surface of these inorganic oxides (2), which can alter the surface chemistry and membrane performance.

Given the complexity of the silica and alumina surfaces, it is instructive to briefly outline some of the major characteristics which have bearing on the permeability behavior of these ceramic membranes. A fully hydroxylated silica surface contains 4.6 silanol groups ($\equiv\text{Si}-\text{OH}$)/ nm^2 (3). However, the silanol groups are not equidistant and this results in two distinct types of silanol groups: paired (H-bonded) silanol groups, where two hydroxyl groups are close enough together to form a hydrogen bond, and isolated silanol groups with a separation distance between oxygen atoms greater than 0.3 nm (4, 5). The silica surface also contains physically adsorbed water which initially adsorbs by forming clusters around surface silanol groups (6, 7). The majority of this water is removed from the surface by vacuum at room temperature, with less than a monolayer remaining up to approximately 200°C (8–10).

Among the various forms, γ -alumina has been the most widely studied because of its importance as a catalyst support (11) and for adsorption of both inorganic and organic compounds (12). In the lattice of γ -alumina, five different OH configurations have been identified in which different coordination with both aluminum and oxygen are involved (12–14). Alumina surfaces are also known to have acidic sites associated with Al^{3+} cations not hydroxylated. All these sites, to different degrees, can be viewed as being potentially reactive. For example, alcohol chemisorption can occur (15–20) due to hydrogen bonding with surface oxygen atoms and also due

to either aluminum ions or surface hydroxyls and can result in the formation of a surface alkoxide.

The purpose of this note is to illustrate the effects of heat treatment and chemisorption of organic molecules on the permeability characteristics of porous silica and γ -alumina membranes, respectively. In both cases, a significant reduction in hydraulic permeability was observed, which has been attributed to alteration of the membrane surface. Plausible reasons for the permeability loss for both cases, along with the appropriate regeneration procedures, are discussed.

EXPERIMENTAL

Materials

The silica membranes used in this study were isotropic porous silica membranes (Microporous Glass, MPG-AM, Asahi Glass Inc., Tokyo, Japan), which are low surface area (2–10 m^2/g) silica glasses. The alumina membranes were made of a porous γ -alumina layer deposited onto a ceramic support (Membralox, U.S. Filter, Warrendale, PA, USA). The present study was conducted with flat silica disk membranes of pore size of 3000 Å and tubular alumina membranes of 100 Å pore size. Powdered activated γ -alumina (Alfa), 96%, was supplied by Johnson Matthey (Ward Hill, MA). The surface area of this alumina powder was 158 m^2/g with an average pore diameter of 54 Å as determined by BET analysis (Autosorb-1, Quantachrome Inc., Sysset, NY). Finally, the deionized and distilled water used for the permeability measurements was filtered through a 0.2 μm sterilized capsule filter before all filtration experiments.

Permeability Measurements

The permeability of the membranes was determined from simple flow rate–pressure drop measurements where the permeability was determined from Darcy's law (i.e., $Q = k\Delta P/\mu L$, where k is the permeability, Q is the flow rate, ΔP is the pressure drop, μ is the fluid viscosity, and L is the thickness of the membrane). Prior to the permeability measurements with the silica membrane, the membrane was suspended in an agitated 1.0% (v/v) HCl solution (hereafter referred to as the acid treatment) for 3 h. The membrane was subsequently rinsed with water and the original permeability was measured. The membrane was then dried overnight at 140°C (under vacuum), followed by remeasurement of the water permeability. The membrane was removed from the cell, immersed in water (with agitation) overnight and then the water permeability was remeasured. Finally, the membrane was subjected to the acid treatment procedure and subsequent determination of the water permeability. For alumina membranes, permeability tests for water and five different organic solvents (ethanol, 1-propanol, 1-butanol, cyclohexane, and toluene) were conducted in the dead-end filtration mode. Unless otherwise noted, the membrane was dried overnight at 110°C after each test in order to remove physically adsorbed solvent.

Adsorption Tests for γ -Alumina

Approximately 1 g of powdered γ -alumina was soaked in 50 ml of solvent for 2 h (with agitation). The suspension was filtered and dried

TABLE 1
Hydraulic Water Permeability for a 3000 Å
Pore Size Silica Membrane

| Membrane conditioning | $k_w \times 10^{12}$ (cm ²) |
|-----------------------------------|---|
| Original (after acid treatment) | 10.1 |
| After heat treatment ^a | 0 ^b |
| After H ₂ O treatment | 0 ^b |
| After acid treatment | 10.1 |

^a Heat treatment at 140°C (vacuum).

^b No permeate flow at a transmembrane pressure of 68.9 kPa.

overnight at 110°C under vacuum. The amount of adsorbed solvent was determined by thermogravimetric analysis (TGA). All TGA samples were first held at 100°C until no weight loss was observed, and then heated at a rate of 15°C/min to 500°C. This temperature was sufficient to remove any chemisorbed organic compounds utilized in this work (19, 20).

RESULTS AND DISCUSSION

Silica Membranes

A demonstration of the effect of different membrane conditioning procedures on the hydraulic water permeability of a silica membrane is provided in Table 1. The uncertainty in the measured permeability values for this 3000 Å pore size membrane was estimated to be ±3.2%. The membrane became impermeable to water at a transmembrane pressure of 69 kPa after vacuum drying at 140°C for a period of 16 h. Immersion of this reduced-permeability membrane in water for 24 h failed to recover a measurable permeability. However, the original water permeability was recovered after repeating the acid treatment step.

The drastic loss of water permeability due to the mild heat treatment is believed to be due to *dehydration* of the membrane surface. Removal of physically adsorbed water exposes the high concentration of isolated hydroxyl groups for these amorphous, low surface area silica membranes. It has been demonstrated that patches of isolated hydroxyl groups are hydrophobic since water molecules adsorb via one hydrogen bond, a process which has a low enthalpy of adsorption compared to hydrophilic patches of hydrogen-bonded silanol groups (4, 22, 23). For hydrophilic patches, water adsorption occurs by the formation of two hydrogen bonds between the water molecule and the silanol groups.

Restoration of the original water permeability requires rehydration of the silica surface. Assuming water adsorption is limited to H-bonded silanol groups, then the remaining part of the surface, where only isolated silanol groups exist, would remain dehydrated. The large observed reduction in hydraulic water permeability reflects the limited amount (<5%) of paired silanol groups that would be present on these low surface area, large pore size membranes (24).

Complete rehydration of the silica surface can occur provided the concentration of H-bonded silanols is sufficient. The acid treatment step leads to the formation of a positive net charge of the silica surface due to the following reaction:



For silica, the point of zero charge occurs at approximately pH 2.0 (25). Therefore, the acid treatment step (pH 1.7) results in the formation of ionized silanol groups ($\equiv\text{Si}-\text{OH}_2^+$) on the membrane surface. These positively charged hydroxyl groups are similar to H-bonded silanol groups, enabling water adsorption to occur at these surface sites.

Permeability reduction due to surface dehydroxylation is unlikely to be a factor for the silica membrane since dehydroxylation of the silica surface begins at about $190 \pm 10^\circ\text{C}$ (11) which is well above the drying temperature employed in this work. Furthermore, rehydroxylation is known to be catalyzed in a basic media, occurring very slowly for $\text{pH} < 5$ (25). Permeability due to the primary electroviscous effect (26) can also be discarded as the source of permeability reduction since the membrane surface charge, which is a function of pH, was the same for all permeability measurements.

It is interesting to note that in earlier work mild heat treatment did not reveal any permeability reduction for organic solvents, indicating that only water was affected (21). As was shown by Castro *et al.* (1991), heat treatment of silica membranes was effective in removing adsorbed organics which would have caused measurable permeability reduction. This behavior is in marked contrast to the effect of organic solvents on the permeability of alumina membranes as described below.

Alumina Membranes

The experimental hydraulic permeabilities obtained for the γ -alumina membrane with solvents of different polarity are given in Table 2. After permeability measurements with the organic solvents, the hydrophilic character of the membrane changed and the membrane became impermeable to water at transmembrane pressures up to 172 kPa. Attempts to recover the hydrophilicity by acid treatment were unsuccessful.

A second set of measurements was carried out to determine the influence of heating and solvent exposure on permeability. Heating a fresh membrane at 110°C overnight did not alter the original hydraulic water permeability (Table 3). The loss of hydraulic water permeability after exposure to organic solvents (see Tables 2 and 3) is attributed to irreversible adsorption of the organic compounds. This hypothesis is supported by the fact that alcohols are capable of chemisorbing onto acidic alumina sites to form alkoxides at low temperature. This chemisorbed layer imparts a hydrophobic character to the membrane (27) and reduces the pore size. Although physically adsorbed alcohol can be removed by heating, the alkoxides remain stable at temperatures up to 300°C (19).

An evaluation of the loss of permeability due to the adsorption of a nonpolar organic and permeability recovery by heating was carried out with cyclohexane. The cyclohexane permeability of this new membrane (Table 3) was 65% higher than that reported in Table 2. However, it should be noted that the cyclohexane permeability presented in Table 2 was obtained after measurements with alcohols. Therefore, chemisorption of alcohols would have reduced the original nominal pore size of the membrane, resulting in the lower cyclohexane permeability reported in Table 2.

The loss of water hydraulic permeability, after exposure of the membrane

TABLE 2
Hydraulic Permeabilities for Various Solvents
Using a 100 Å Pore Alumina Membrane

| Solvent ^a | $k \times 10^{12}$ (cm ²) ^b |
|----------------------|--|
| Water | 1.20 |
| Ethanol | 0.78 |
| 1-Propanol | 0.37 |
| 1-Butanol | 0.49 |
| Cyclohexane | 0.51 |
| Toluene | 0.50 |
| Water | 0 ^c |

^a Tests made sequentially; membrane was dried at 110°C prior to each test.

^b In the range 0–83 kPa of transmembrane pressure.

^c No permeate flow at a transmembrane pressure of 172 kPa.

TABLE 3
Hydraulic Permeabilities for a 100 Å Pore Size Alumina Membrane

| Membrane conditioning | Solvent | $k \times 10^{12}$ (cm ²) | Equivalent pore diameter (Å) ^a |
|----------------------------|-------------|---------------------------------------|---|
| Original | Water | 1.22 | 100 |
| Drying overnight at 110°C | Water | 1.22 | 100 |
| Drying overnight at 110°C | Cyclohexane | 0.84 | — |
| Drying overnight at 110°C | Water | 0.97 | 89.2 |
| Drying two days at 110°C | Water | 0.99 | 90.1 |
| Drying overnight at 110°C | Cyclohexane | 0.42 | — |
| Drying overnight at 110°C | Water | 0.73 | 77.3 |
| Heating overnight at 150°C | Water | 0.83 | 82.5 |
| Heating overnight at 500°C | Water | 1.33 | 104.4 |

$$^a d_E = d_{\text{ORIG}} \left(\frac{k}{k_{\text{ORIG}}} \right)^{1/2}$$

to cyclohexane, was not reversed after drying the membrane overnight at 110°C. In fact, after the first and second cyclohexane permeability tests the water permeability decreased by about 25 and 33%, respectively (or equivalent to a radius pore reduction of approximately 6 Å after each cyclohexane exposure). Drying at 150°C provided a small recovery of the water permeability. The above results support the suggestion that cyclohexane is also capable of chemisorbing onto the alumina surface. Finally, we note that heating at 500°C resulted in a water permeability that was 9% higher than that of the virgin membrane, indicating complete removal of chemisorbed compounds and some possible alteration of the pore structure.

The chemisorption hypothesis was evaluated by batch adsorption measurements with powdered γ -alumina. The virgin alumina powder dispersed in water. In contrast, alumina exposed to organic solvents formed aggregates in water, due to the hydrophobicity associated with chemisorbed organics. Thermogravimetric analysis revealed adsorption capacities of 1.9×10^{-4} mol/g and 1×10^{-4} mol/g for toluene and cyclohexane, respectively. Based on 2-propanol adsorption (14), alumina possesses approximately 10^{18} sites/m², regardless of the alumina type. Assuming that the number of adsorption sites for cyclohexane is similar, the adsorption capacity of the powdered alumina should be about 2.6×10^{-4} mol/g. The lower measured adsorption capacity could be attributed to different adsorption sites, diffusional limitations associated with the small pore size of the γ -alumina powder, or steric hindrance effects for the slightly larger toluene and cyclohexane molecules. However, it is believed that the above adsorption capacities are sufficiently high to impart hydrophobic characteristics to the alumina surface, and thus reduce the hydraulic water permeability.

CONCLUSIONS

The hydraulic permeabilities of inorganic membranes depend on the pore surface chemistry. It has been demonstrated that low surface area silica membranes are affected by heat treatment, even at 140°C. Removal of physically adsorbed water by mild heat treatment (140°C) results in a significant reduction in the hydraulic water permeability. The original hydraulic water permeability can be restored by acid treatment because at low pH the isolated (nonhydrogen bonded) silanol groups are positively charged, making them equivalent to the H-bonded silanol groups.

Heat treatment of γ -alumina membranes does not appear to reduce the hydraulic water permeability. However, the γ -alumina surface is highly reactive toward organic compounds, including alcohols, aromatics, and cyclohexane. Chemisorbed organics increase the hydrophobicity of the surface and reduce the effective pore membrane diameter of the membrane. Heat treatment of the alumina membrane, at temperatures above 400°C, can be effective in removing chemisorbed organics to regenerate the membrane.

However, one must be cautious since the membrane pore structure may be affected at high temperatures.

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