Pore Modification in Porous Ceramic Membranes With Sol-Gel Process and Determination of Gas Permeability and Selectivity

F. Nihal Tüzün, Ersel Arçevik*

Summary: The aim of the study was to investigate the variation in total surface area, porosity, pore size, Knudsen and surface diffusion coefficients, gas permeability and selectivity before and after the application of sol-gel process to porous ceramic membrane in order to determine the effect of pore modification. In this study, three different sol-gel process were applied to the ceramic support separately; one was the silica sol-gel process which was applied to increase porosity, others were silica-sol dip coating and silica-sol processing methods which were applied to decrease pore size. As a result of this, total surface area, pore size and porosity of ceramic support and membranes were determined by using BET instrument. In addition to this, Knudsen and surface diffusion coefficients were also calculated. After then, ceramic support and membranes were exposed to gas permeation experiments by using the CO_2 gas with different flow rates. Gas permeability and selectivity of those membranes were measured according to the data obtained. Thus, pore surface area, porosity, pore size and Knudsen diffusion coefficient of membrane treated with silica sol-gel process increased while total surface area was decreasing. Therefore, permeability of ceramic support and membrane treated with silica sol-gel process increased, and selectivity decreased with increasing the gas flow rate. Also, surface area, porosity, pore size, permeability, selectivity, Knudsen and surface diffusion coefficients of membranes treated with silica-sol dip coating and silica-sol processing methods were determined. As a result of this, porosity, pore size, Knudsen and surface diffusion coefficients decreased, total surface area increased in both methods. However, viscous flow and Knudsen flow permeability were detected as a consequence of gas permeability test and Knudsen flow was found to be a dominant transport mechanism in addition to surface diffusive flow owing to the small pore diameter in both methods. It was observed that silica-sol processing method had lower pore diameter and higher surface diffusion coefficient than silica-sol dip coating method.

Keywords: Membrane; Permeability; Selectivity; Sol-Gel

Introduction

Inorganic membranes have a great potential in wide range of practical applications including water desalination, ultrafiltration in food industries, waste water treatment and gas separation owing to their excellent chemical and thermal stability.

Inorganic membranes are usually classified into two types with respect to the presence of micropores;

1) Non-porous membrane
2) Porous membrane

Non-porous membranes, which have a dense separative layer show high selectivity

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Department of Chemical Engineering, Hitit University, Çorum 19030, Turkey
E-mail: nihaltuzun@yahoo.com

but low permeance. On the other hand, the porous membranes with micropores of a few 10 nm possess much higher permeance and relatively lower selectivity than the polymeric membranes.[1]

Porous ceramic membranes have received increasing attention over recent decades due to their unique ability to operate under extreme environments and operating conditions. The continuous improvement of the development and manufacturing of these materials resulted in increased commercial applications of ceramic membranes in recent years. Ceramic membranes are technically important in separation and filtration as well as in catalytic reactions, because of their high thermal and chemical stability, long life time and good defouling properties in comparison with polymeric membranes.[2,3] Many researchers have reported on the synthesis and microstructure development of ceramic membranes and their application.[4] A major difficulty during the fabrication of a ceramic porous membrane is the combination of sufficiently high throughput and sufficiently high species selectivity. Since the flow rate through a membrane is inversely proportional to the membrane thickness.[5] There are various ways to prepare such membranes depending on the material-type used and the required structural characteristics (porosity, pore size, thickness).[6] Sol-gel, hydrothermal treatment, and chemical vapor deposition, encapsulating active molecules in host porous matrices are well-known synthesis methods in the preparation of membranes.[5] Silica fabricated by the sol-gel process is known to have high surface area and microporosity.[7–9] The sol-gel process refers to the controlled hydrolysis and polymerization of tetraethylorthosilicate(TEOS) in a water-alcohol solution.[10,11] The solution goes through an irreversible sol-gel transition. The resulting gel can be dried to a rigid silica-like material. The form of the silica may be a fiber, a thin film or a monolithic shape.[12] Synthesis parameters are also modified and optimized to control material properties. One of the important factors in the membrane separation process is the optimal compromise between permeance and selectivity.[13]

The important mechanisms of gas separation via a porous membrane are Knudsen flow and surface diffusion. Knudsen flow occurs when the mean free path of the gas molecule is sufficiently larger than the pore diameter and the collisions between the permeating gas molecules and the pore wall are dominant. Gas flux due to Knudsen flow is inversely proportional to the square root of molecular weight. Thus, the ideal separation factor defined as the permeability ratio of two different permeating gases is inversely proportional to the square root of the molecular weight ratio, if the separation is driven mainly by Knudsen flow. Moreover, surface diffusion becomes important as the pore size becomes as small as the permeating gas molecules, since physicochemical interactions between the pore wall and the permeating molecules become pronounced. It is thus important to reduce the pore size to nanometer scale without pinholes or cracks.[14]

In this study, sol-gel method, silica-sol dip coating method and silica-sol processing were applied to the macroporous ceramic support to enable the pore modification in the membranes and provide the gas permeability of those membranes.[15]

Experimental Part

Three different sol-gel process were applied to ceramic support to observe the pore modification; one was the silica sol-gel process applied to increase the porosity. In this process, the reactants were acidic water-alcohol mixture and TEOS. Distilled water and ethyl alcohol were mixed at 298 K (with 4:1 molar ratio) by vigorous stirring. Small amount of hydrochloric acid was added as a reaction catalyst into the water-alcohol mixture. The inner region of the cylindrical support was filled with the acidic water-alcohol mixture while the outer side in contact with TEOS with 98% purity (Aldrich). Then, TEOS and acidic water-alcohol mixture diffuse into the inside of the porous ceramic support counter-currently and reacts in the vicinity of the interface between the two layers of the support. As the reaction proceeded for 20 min, the silica sols were formed and partly gelled simultaneously in the intermediate layer of the support. By circulating water, temperature of the reactor was maintained at 353 K to accelerate the hydrolysis and poly-condensation reactions. After the reactions were completed, drying the membrane in atmospheric condition was followed by calcination out at 673 K. This procedure was repeated three times. At the end of this procedure, total surface area and pore surface area of ceramic support and membrane were detected with BET instrument by using nitrogen. Besides, porosity and pore size were determined and Knudsen diffusion coefficients were also calculated according to Equation (1). Then, ceramic support and membrane treated with sol-gel process were placed in a stainless steel cell and they were exposed to gas permeation experiments by using CO_2 gas with the flow rates of 5, 10, 12.5, 15 and 18 lit/min. The feed pressure and the pressure difference over the membrane were measured by using pressure transducers. A permeate pressure of 0.01 bar was achieved. As a consequence of this, gas permeability and selectivity of ceramic support and membrane were determined with respect to Equation (2) and Equation (3) respectively.

$$D_{A,KN} = 97\, r \left(\frac{T}{M_A}\right)^{\frac{1}{2}} \qquad (1)$$

The other two methods; silica sol dip-coating method and silica sol processing were also applied to the ceramic support separately in order to decrease the pore size.

In silica sol dip-coating method, TEOS (Aldrich), distilled water and ethyl alcohol were mixed at 298 K (with 1:4.7:3.8 molar ratio) with vigorous stirring. Small amount of nitric acid was added as a reaction catalyst into the water-alcohol mixture. Then, both end parts of the cylindrical support were sealed and dipped into this solution. One day drying in atmosphere was followed by calcination in an electric furnace. Temperature was raised to 773 K at which the membrane stayed for about 3 hours. The dipping and calcination were repeated 3 times.

In silica sol processing, a solution of TEOS, H_2O, C_2H_5OH and HNO_3 (in the ratio 1:1: 26:11.76) was refluxed at 353 K for 2 hours. A sample of the solution was diluted with C_2H_5OH (1:18) and the membrane dipped (with ends sealed to prevent the solution from coating the inner side of the tube) for a few seconds. It was then dried at 393 K for 3 hours and calcined at 673 K for 3 hours. The dipping was repeated a second time with the dilution being 1:180.

After the application of both methods to the ceramic support separately, surface area and pore size of membranes were measured by Micromeritics BET surface area measurement and adsorption-desorption isotherm of BET instrument respectively in terms of nitrogen and porosity values of membranes were also calculated. After then, quality of membranes were tested by CO_2 gas with the flow

$D_{A,KN}$: Knudsen diffusion coefficient T : temperature
r : pore radius MA : molecular weight of gas

$$F = Q/X^{*}\Delta P \qquad (2)$$

F : permeability coefficient (mol/Pa. m. s) Q : gas flow rate (mol/s)
X : thickness of the membrane (m) ΔP : pressure difference (Pa)

$$\alpha = P_p/P_f \qquad (3)$$

α : selectivity P_p : permeate side pressure (Pa) P_f : feed side pressure (Pa) rates of 5, 10, 12.5, 15 and 18 lit/min at room temperature. As a result of this, permeability, selectivity, Knudsen and surface diffusion coefficients of the membranes were obtained and compared with the ceramic support. Surface modification of ceramic support and membranes was detected by using LEO 440 model computer controlled digital scanning electron microscope as well.

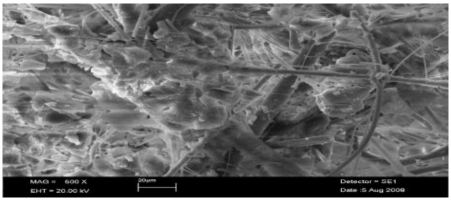

Figure 2.
Surface modification of membrane after the application of sol-gel process.

Results and Discussion

Surface modifications of ceramic support and membranes prepared with sol-gel process were obtained by using digital scanning electron microscope. SEM micrograph of ceramic support is demonstrated in Figure 1. After applying the sol-gel process, total surface area, pore surface area and porosity of membrane were detected by means of BET surface area measurement instrument.

Comparison of the results attained from support and membrane showed that porosity of membrane increased and total surface area decreased due to the rise in the pore surface area as observed from SEM micrographs in Figures 1 and 2.

Other variables calculated with respect to the results obtained from BET instrument were mean pore radius and Knudsen diffusion coefficient. When the results were evaluated, it was found that mean pore diameter and Knudsen diffusion coefficient of membrane was greater than the ceramic support. It was determined that results were compatible with literature values and sol-gel process increased the mean pore diameter and total pore surface area owing to the surface modification, Knudsen diffusion coefficient also increased in terms of rising in the pore diameter. Results attained are observed in Table 1.

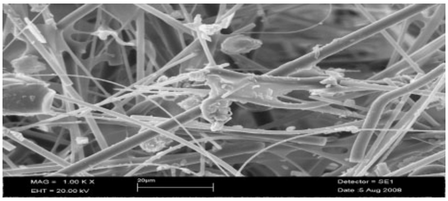

Figure 1.
SEM micrograph of ceramic support.

One of the important factors in the membrane separation process is the optimal compromise between permeance and selectivity, since selectivity decreases as the permeance increases. For example, although the permeance of a polymeric membrane is very low, the selectivity is high due to the so-called solution-diffusion mechanism. However, the mechanism of gas separation by a porous alumina membrane or Vycor glass, is closely related to the membrane pore size relative to the permeate molecule size, as well as other physical and chemical properties of the membrane and the permeate species.[6]

During the study, ceramic support and membrane were placed into permeation testing system and applied to CO_2 gas. Then, permeance and selectivity were determined by means of the average pressure values as observed in Figures 3 and 4. Permeance increased and selectivity decreased continuously as given in Figures 5 and 6 with increasing the gas flow rate in both ceramic support and membrane. Results showed that acceptable values were attained according to literature for both of them.[6]

In the second step of this study, silica-sol dip coating method and silica-sol processing were applied into the ceramic support separately. Surface modifications of membranes are shown in Figures 7 and 8 respectively.

Table 1.
Comparison of the structural properties for ceramic support and membrane.

	Ceramic Support	Membrane
Amount of sample (gr)	0.0818	0.0793
Thickness (X, m)	0.002	0.002
Permeability coefficient (F, mol/Pa·m·s)	0.0033	0.0036
Porosity (ε)	0.218	0.513
Total surface area (m^2)	0.37	0.06
Pore surface area (m^2)	0.0233	0.0254
Knudsen diffusion coefficient (D_{KN}, m^2/s)	0.00252	0.0256
Pore radius (μm)	10	101.57

Surface diffusion has an importance in both methods due to the smaller pore size and the concentration gradient of adsorbed CO_2 gas on the pore wall. Since, the adsorption of gas molecules on the pore wall is important, and molecules adsorbed on the porous solid surfaces may have considerable mobility. This gives rise to an additional contribution to gas transport.[16–18] The surface diffusion rates are determined by the surface diffusion coefficient and adsorption equilibrium, both of which are related to the interactions between adsorbates and pore surfaces.[19] Surface diffusion coefficients were calculated as given in Equation (4).

$$K = \frac{F.\Delta P}{\ell(1-\varepsilon)\Delta y} \tag{4}$$

$K:$ surface diffusion coefficient (cm^2/s) $F:$ permeability coefficient (mmol/Pa·m·s)

$\Delta P:$ pressure drop $\varepsilon:$ porosity $\ell:$ density of membrane (g/cm^3)

$\Delta y:$ concentration gradient (mmol gas adsorbed/g membrane)

When the results obtained from silica-sol dip coating and silica-sol processing methods were compared, it was determined that porosity, pore diameter, Knudsen and surface diffusion coefficients decreased, whereas, total surface area increased after the application of both methods. Results are observed from Tables 2 and 3. However, lower pore diameter was attained in silica-sol processing than silica-sol dip coating method. As a result of this, higher surface diffusion coefficient was also observed in silica-sol processing method.

Gas permeability tests of membranes prepared with silica-sol dip coating and silica-sol processing methods were performed with gas permeation testing system. In Figures 9 and 10, CO_2 permeability is represented at 298 K as a function of average pressure (Pav) for silica-sol dip coating and silica-sol processing methods respectively.

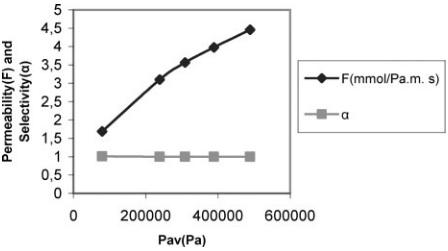

Figure 3.
Variation of Permeability and Selectivity with Average Pressure for Ceramic Support.

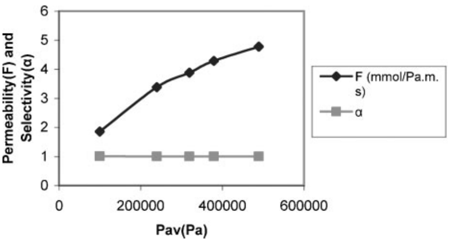

Figure 4.
Variation of Permeability and Selectivity with Average Pressure for Treated Membrane.

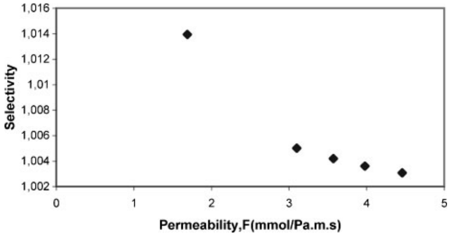

Figure 5.
Variation of Permeability with Selectivity for Ceramic Support.

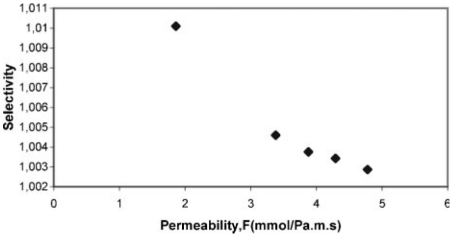

Figure 6.
Variation of Permeability with Selectivity for Treated Membrane.

Although, there are some fluctuations especially in Figure 9, in general, it is seen that the permeability increases with the average pressure, which is indicative of a viscous flow mechanism. Since, determination of the viscous flow permeability from gas permeation data is not always straightforward due to the appearance of slip-flow and compressibility effects as observed from Figure 9.

The Knudsen mechanism of transport is the dominant one at low Pav-values, a lower limit of the Knudsen permeability can be extracted from the intersection with the permeability axis.[20,21,22]

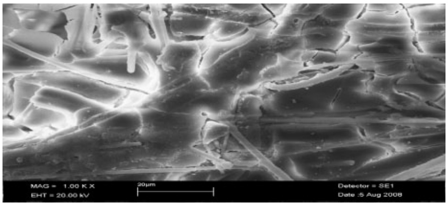

Figure 7.
Surface modification of membrane after the application of silica-sol dip coating method.

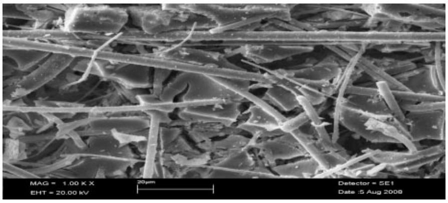

Figure 8.
Surface modification of membrane after the application of silica-sol processing.

Even though selectivity seemed to decrease with an increase in pressure difference, the results obtained from Figures 11 and 12 showed that selectivity was independent of ΔP in both silica-sol dip coating and silica-sol processing methods. This result can be explained in terms of predominant Knudsen flow.

It was also determined that silica sol-gel process could effectively make the pore size small enough for Knudsen flow to be a dominant transport mechanism and generated an additional surface diffusive flow.

Conclusion

In the first step of this study, porosity, pore surface area, mean pore size and Knudsen diffusion coefficient of membrane increased and total surface area decreased with the application of sol-gel process into ceramic support, gas permeance increased

Table 2.
Comparison of the structural properties for ceramic support and membrane after the application of silica-sol dip coating method.

	Ceramic Support	Membrane
Porosity (ε)	0.218	0.069
Pore diameter (μm)	20	7.64
Total surface area (m^2/g)	0.37	2.05
Knudsen diffusion coefficient (m^2/s)	0.00252	9.64E-04
Surface diffusion coefficient (cm^2/s)	0.035	5.67E-03

Table 3.
Comparison of the structural properties for ceramic support and membrane after the application of silica-sol processing.

	Ceramic Support	Membrane
Porosity (ε)	0.218	0.082
Pore diameter (μm)	20	5.35
Total surface area (m^2/g)	0.37	6.48
Knudsen diffusion coefficient (m^2/s)	0.00252	6.75E-04
Surface diffusion coefficient (cm^2/s)	0.035	0.0129

and selectivity decreased continuously with increasing the gas flow rate in both ceramic support and membrane.

In the second step, silica-sol dip coating and silica-sol processing methods were applied to ceramic support separately. As a result of this, porosity, mean pore size, Knudsen diffusion coefficient decreased and total surface area increased in both methods. However, surface diffusion coefficient gained an importance due to the small pore diameter. The lower pore diameter and higher surface diffusion coefficient were obtained in silica-sol processing method. In gas permeability test, viscous flow and Knudsen flow permeability were determined. Therefore, it was found that Knudsen flow to be a dominant transport mechanism besides having surface diffusive flow owing to the small pore diameter in both methods.

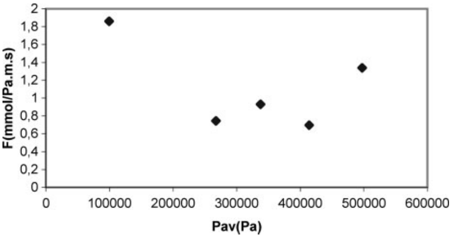

Figure 9.
Permeability of CO_2 with average pressure in silica-sol dip coating method.

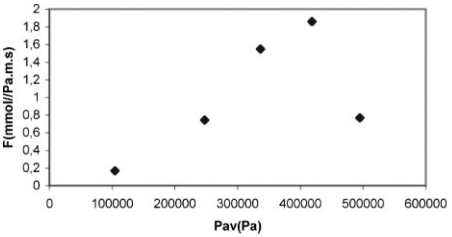

Figure 10.
Permeability of CO_2 with average pressure in silica-sol processing method.

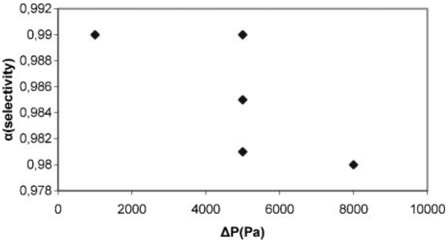

Figure 11.
Variation of selectivity with pressure difference in silica-sol dip coating method.

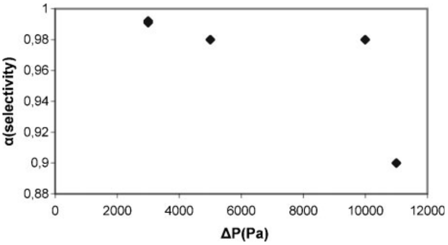

Figure 12.
Variation of selectivity with pressure difference in silica-sol processing method.

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