Pore Modification Using the Supercritical Solution Infiltration Method

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When a supercritical (SC) solution infiltrates through micropores, its pressure will fall off considerably along the flow direction, and significant solute supersaturation can be obtained inside the pores. Thus the solid solute can deposit onto the pore surface due to nucleation. The supercritical solution infiltration (SCSI) method was applied to modify porous ceramic membranes. A mathematical model was used for the membrane pore-size change during the SCSI process. Numerical solution of this model showed that for a membrane with initial pore-size distribution (PSD), its average pore size could be increased or decreased due to dissimilar kinetics of the solute precipitation under different conditions. α-Al_2O_3 microfiltration membranes were modified by the SCSI method using SC solution of the aluminum isopropoxide/propane system under different conditions. The PSD change was determined for the modified membranes after hydrolysis and sintering. With the reduction in permeability, the average pore size was reduced when the process conditions were more favorable for homogeneous nucleation and increased under the opposite conditions. Experimental results qualitatively coincided with those by the proposed model.

Introduction

Supercritical fluids (SCF) exhibit a number of characteristics that are of great potential utility in the processing of ceramic materials. They possess high solvent power for many normally insoluble substances, with strong dependence on the system pressure, moderate temperature processing capability, low viscosity and high diffusivity, and the absence of surface tension. Recent applications of SCF technology in ceramic-material technology include the formation of powders and thin films (Matson et al., 1987), densification of ceramic materials (Berneburg and Krukonis, 1985), and production of metallic-oxide-coated carbon fibers (Berneburg and Krukonis, 1989). These applications are implemented by a general mechanism of solute deposition from SC solution due to the supersaturation caused by the reduction of SCF density or system depressurization in practice (Debenedetti et al., 1993). Moreover, the low viscosity and the absence of surface tension improve the penetration of the SCF solution into submicron pores, and make it practicable for the SCF to carry ceramic precursors or target materials into the pores of ceramic hosts.

In this work, a method of supercritical solution infiltration (SCSI) is developed to modify the pore-size distribution (PSD) for ceramic membranes. Modification of PSD or pore surface for ceramic membranes is currently an active research area due to the requirements of new developments of ceramic membrane technology. Up to now, several techniques have been successfully used to change the PSD of ceramic membranes. The slip-casting method, which has been widely used in membrane preparation, can change the pore size of a ceramic membrane by coating an active layer with the desirable pore size onto the original top layer. But this method is not suitable when the material of the coated layer is much different in thermal dilation from the support membrane. In the vapor-phase and liquid-phase approaches, precursors are introduced into the pores of a ceramic membrane and, in most cases, a solid is formed and deposited on the internal pore surface of the membrane after a chemical reaction process. Therefore materials other than the support with different thermal properties can be used to modify the porous struc-

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ture or internal surface property of the matrix membrane. Nevertheless, these approaches need long operation times and rigorous control of operational parameters, and consequently are difficult to get scaling-up.

The basic mechanism of the SCSI approach presented in this work is the deposition of ceramic precursor from the SC solution (with homogeneous and/or heterogeneous nucleation) due to the supersaturation caused by the pressure drop inside the membrane pores. A mathematical model is established to explain the mechanism of the SCSI method and to semiquantitatively represent the evolution of the membrane PSD during the SCSI process. Subsequently, SCSI experiments are performed for the modification of ceramic MF membranes as proofs of the new method and the proposed model.

Modeling and Solution

Modeling and analysis

In the SCSI process, the saturated SC solution infiltrates through the membrane layer. During the infiltration, pressure of the SC solution drops along the flow direction, and the SC solution becomes supersaturated inside the pores. Deposition of the precursor from the SC solution occurs in the membrane pores in forms of homogeneous and/or heterogeneous nucleation, and thus the membrane pores are narrowed.

In order to establish a simple and application model, the usual assumption of cylindrical pores with certain PSD (Lin, 1993) is adopted for the membrane in this study. As illustrated in Figure 1, pore-size change can be attributed to the solid deposition in the pores along the flow direction and radial direction. In Figure 1, H is the length of the modified zone, and r^o and r are radii of the original pore and the modified zone, respectively. Figure 1 is similar to the one used earlier by Lin (1993), for illustrating the chemical vapor deposition (CVD) process, because the principle of pore narrowing in the SCSI process is, except for the mechanism of solid formation, analogous to that in the CVD process. The solid precipitation is attributed to a physical mechanism in the SCSI process and is of a chemical mechanism in the CVD process.

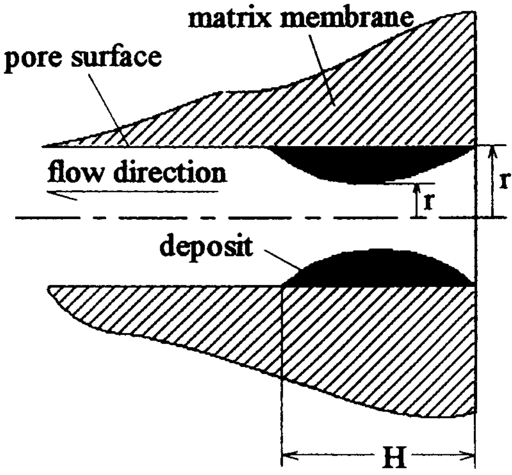

Figure 1. Pore modification by the SCSI method.

Following the work of Lin (1993), the PSD change of the membrane during the SCSI modification process can be described as

$$\frac{\partial n}{\partial t} + G\frac{\partial n}{\partial R} = -n\frac{dG}{dR}, \tag{1}$$

where n is the number pore-size distribution function based on a unit surface area of the membrane surface being modified, $n = n(R)$; t is the time of SCSI; R is the pore radius; and G is the pore-size change rate:

$$G = \partial R/\partial t, \tag{2}$$

which is a function of pore size

$$G = g(R). \tag{3}$$

The initial number of PSD of the membrane, $n^o(R)$, can be used as the integral boundary:

$$n(R,t)|_{t=0} = n^o(R). \tag{4}$$

It can be seen that integral result of Eq. 1 turns on the functions of $g(R)$ and $n(R)$. In the CVD process, $g(R)$ is determined by the kinetics of the chemical reaction, while in the SCSI process, $g(R)$ is based on nucleation mechanism of the solute. $g(R)$ can be obtained by using the equation of mass balance on the deposited solute during the SCSI process:

$$-2H\pi R(dR/dt) = I_{\text{hom}} + I_{\text{heter}}, \tag{5}$$

where I_{hom} and I_{heter} are the precipitation rates of the solid in homogeneous nucleation and heterogeneous nucleation in the pores, respectively. Nucleation kinetics in a supercritical solution is currently not clear, especially for heterogeneous nucleation. In the present study, we follow the classic nucleation theory (Hirth and Pound, 1963). The homogeneous nucleation rate in per unit volume can be described as

$$J_{\text{hom}} = \left[\frac{4}{3}\pi(r^*)^3\right]\frac{a_c P}{\sqrt{2\pi m k T}}\cdot n_i \cdot \exp\left\{-\frac{1}{kT}\cdot\frac{16\pi\sigma^3}{3}\cdot\left[\frac{kT}{\nu_m}\ln S\right]^{-2}\right\}, \tag{6}$$

where k is the Boltzmann constant; σ and ν_m are the interfacial tension and the molecular volume of the solid solute, respectively; n_i is the solute concentration in per unit volume; a_c is the condensation coefficient; $n_i P(2\pi m k T)^{-1/2}$ is the thermal flux of solute molecules; and r^* is the critical size of the crystal nucleus, which can be estimated by the following equation

$$r^* = 2\left(\frac{\sigma\nu_m}{kT}\right)\frac{1}{\ln S}. \tag{7}$$

When the physical and chemical constants are determined, J_{hom} is found to be a function of the supersaturation ratio of the solute:

$$J_{\text{hom}} = k_1(S). \tag{8}$$

The supersaturation ratio S, $S = y_2/y_2^e$, can be represented by thermodynamic models such as the Chrastil equation (1982):

$$\ln y_2 = k_s \ln \rho + a/T + b, \tag{9}$$

where k_s, a, b are coefficients obtained from experimental data; ρ is the SC solvent density that may be estimated by the corresponding state method (Pitzer et al., 1955). When the temperature is maintained constant in the SCSI process, S depends only on the pressure drop between two sides of the membrane (ΔP):

$$\ln S = \ln\left(\frac{y_2}{y_2^e}\right) = k_s \ln\left(\frac{\rho_1}{\rho_2}\right), \tag{10}$$

where ρ_1 and ρ_2 are the SCF densities above and under the membrane layer with system pressures at P and $P - \Delta P$, respectively. Therefore the homogeneous nucleation rate in a modified pore is proportional to the pore volume:

$$I_{\text{hom}} = H\pi R^2 J_{\text{hom}} = H\pi R^2 \cdot k_1(S). \tag{11}$$

In the SCSI process, heterogeneous nucleation occurs on the pore surface. For a unit area of the pore surface with q lattice points, the heterogeneous nucleation rate can be expressed as (Jackson and Hirth, 1976):

$$J_{\text{heter}} = \left[\frac{4}{3}\pi(r^*)^3\right] \cdot \frac{-\nu_m a_c (\sin\varphi) q \rho d \Delta G_\nu}{2kT[2\pi m\ \sigma f(\varphi)]^{1/2}} \cdot \exp\left[\frac{\Delta E_{\text{des}} - \Delta G_{\text{heter}} - \Delta E_d}{kT}\right], \tag{12}$$

where ΔE_{des} and ΔE_d are the activation energies of desorption and surface diffusion, respectively; and φ is the contact angle between the pore surface and the solute; ΔG_ν, ΔG_{heter}, and $f(\varphi)$ are given by the following:

$$\Delta G_\nu = \frac{kT}{\nu_m} \ln S \tag{13}$$

$$f(\varphi) = \frac{(2 + \cos\varphi)(1 - \cos\varphi)^2}{4} \tag{14}$$

$$\Delta G_{\text{heter}} = \frac{16\pi\sigma^3 f(\varphi)}{3\Delta G_\nu^2}. \tag{15}$$

Thus the heterogeneous nucleation rate is a function of S and φ and can be written as

$$J_{\text{heter}} = k_2(S, \varphi). \tag{16}$$

It can be known from Eqs. 12–15 that the heterogeneous nucleation rate increases with a decrease of the contact angle φ. At $\varphi = 0$, ΔG_{heter} is zero and the heterogeneous nucleation rate reaches the maximum value; at $\varphi = \pi$, the heterogeneous nucleation cannot take place, and J_{heter} is zero. Consequently, the contact angle of the solute on the pore surface can greatly affect the nucleation kinetics, and thereby affect the trend of the PSD evolution during the modification.

The heterogeneous nucleation rate in a modified pore is proportional to the pore surface area:

$$I_{\text{heter}} = 2H\pi R \cdot J_{\text{heter}} = 2H\pi R \cdot k_2(S, \varphi). \tag{17}$$

Therefore, Eq. 5 becomes

$$-2H\pi R(dR/dt) = H\pi R^2 \cdot k_1(S) + 2H\pi R \cdot k_2(S, \varphi). \tag{18}$$

Equation 18 can be rewritten as

$$G = \frac{dR}{dt} = -k_1(S) \cdot R - k_2(S, \varphi). \tag{19}$$

The solution of Eq. 1 with Eq. 4 is then obtained as

$$n(R,t) = n^o \left[\frac{e^{k_1(S)t}[k_1(s)R + k_2(S,\varphi)] - k_2(S,\varphi)}{k_1(S)}\right] e^{k_1(S)t}. \tag{20}$$

Using the preceding equations, the membrane PSD change during the SCSI process could be calculated if the necessary data are available. Unfortunately, many of the necessary properties of the solid compounds are unavailable in the literature at present. In order to analyze the effects of the process conditions on the results of SCSI modification, the numerical solution of the proposed model will be performed based on some assumed values of physical properties. Such an analysis of the model is highly valuable for choosing conditions of the SCSI process.

Solution and discussion

As an example, the SCSI modification process of α-Al_2O_3 microfiltration (MF) membrane using the SC solution of the propane/aluminum isopropoxide system is simulated. The solubilities of aluminum isopropoxide in the SC propane were previously determined in our laboratory and will be reported elsewhere (the experimental value of k_s is 20.826). Other necessary properties are assumed as given in Table 1. The initial area PSD, $P^o(R)$, of the matrix membrane is shown in Figure 2. The number PSD and area PSD can be mutually converted by the following expressions:

$$n^o(R) = A^o P^o(R)/R^2 \tag{21}$$

$$P(R,t) = \frac{R^2 n(R,t)}{\int_0^\infty R^2 n(R,t)\,dR}, \tag{22}$$

where A^o is a constant proportional to the total area of open pores and is eliminated during the expression transformation.

Table 1. Properties and Constants

Property or Constant	Value
a_c	1.0
$\Delta E_{\mathrm{des}} - \Delta E_d$	0.0
q	2×10^{15}
d	2×10^{-7}
m	3.39×10^{-22}
k	1.38×10^{-23}
σ	0.0045
υ_m	4×10^{-28}

To quantitatively study the effects of φ and ΔP on the two kinds of modification mechanism (homogeneous and heterogeneous), the ratio of $k_2(S,\varphi)$ and $k_1(S)$ is calculated for different values of φ and ΔP. The results of the calculations are presented by Figure 3. In Figure 3, both the increases in φ and ΔP are advantageous in enhancing the proportion of homogeneous nucleation. In the investigated range of ΔP, for small values of φ ($\varphi \leq 54°$), $k_2(S,\varphi)/k_1(S)$ decreases with the increase in ΔP, but is always greater than 1; for moderate values of φ ($72° \leq \varphi \leq 108°$), $k_2(S,\varphi)/k_1(S)$ is greater than 1 at small ΔP and is less than 1 at large ΔP; for large values of φ ($126° \leq \varphi$), $k_2(S,\varphi)/k_1(S)$ is always smaller than 1. Therefore, two kinds of hypothetical pore surface with very different contact angle, φ, values for the aluminum isopropoxide are used in the simulation. Both the concepts of mean pore size and average pore size are used in this work. The former refers to the pore size with which the PSD function reaches the maximum value, and the latter is defined as (Lin, 1993)

$$R_{k\nu} = \frac{\int_0^\infty R^2 P(R)\,dR}{\int_0^\infty R P(R)\,dR}, \tag{23}$$

where $P(R)$ is the area pore-size distribution function. For uniform pore membranes, $R_{k\nu} = R$.

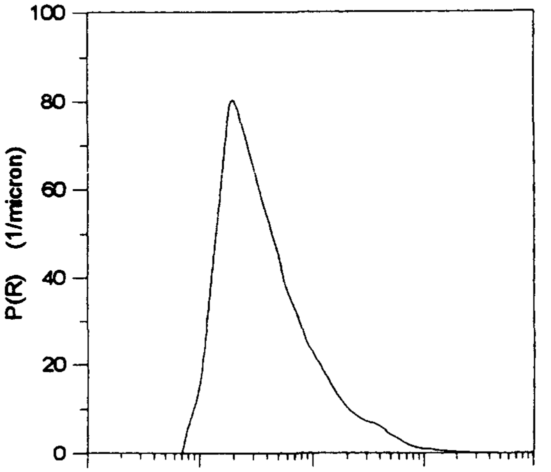

Figure 2. Initial area PSD of the ceramic membrane used in the simulations.

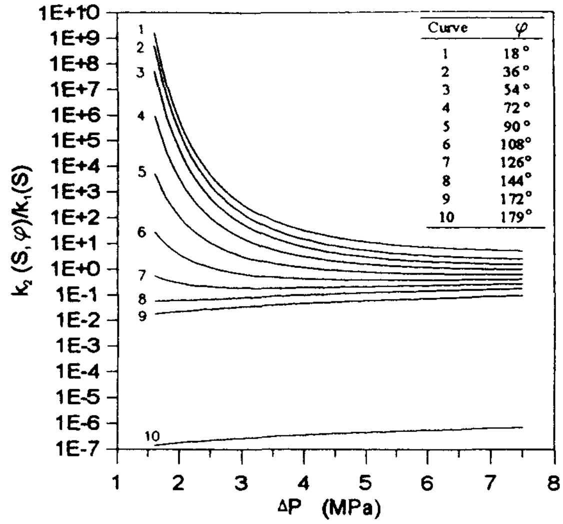

Figure 3. Relationships between the ratio of $k_2(S,\varphi)/k_1(S)$ and the ΔP for different φ.

Under the given pressure drop of 2.5 MPa and the contact angle of 36°, $k_1(S)$ and $k_2(S,\varphi)$ are found to be 4.38×10^{-6} and 7.79×10^{-3}, respectively; $k_2(S,\varphi)$ is much larger than $k_1(S)$, and the modification process will be dominated by heterogeneous nucleation that should cause an increase in the mean pore radius of the membrane after being modified. The PSD change in the membrane during the SCSI modification process is simulated by Eq. 20, and the results of the simulation are shown in Figure 4. It can be seen from Figure 4 that the peak of the membrane PSD shifts to the right, which implies that the mean pore size increases with the increase of SCSI time.

When $\varphi = 180°$, $k_1(S)$ and $k_2(S,\varphi)$ are 4.38×10^{-6} and 0.0, respectively, and only homogeneity would occur inside the pores if growth of the nucleus is not considered. As we know, an increase in the ΔP is also advantageous for homogeneous nucleation. Thus, the PSD change is simulated under different values of pressure drop after the same modification time of 1 h. The results of the simulations are shown in Figure 5.

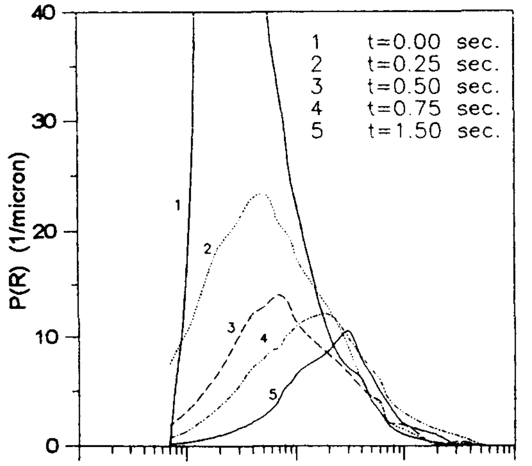

Figure 4. Evolution of the membrane PSD during the SCSI modification process.

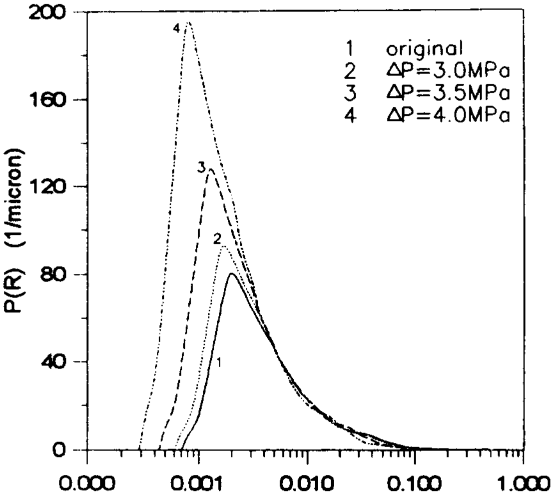

Figure 5. PSD change under different values of ΔP after being modified for 1 h.

In Figure 5, the PSD peak shifts to the left which indicates that the mean pore size decreases with the increase in ΔP.

The preceding results of the simulation suggest that distinct conditions should be controlled for different applications of the SCSI method. For pore narrowing and PSD modification, large values of pressure drop and a large contact angle must be provided to avoid a serious reduction in pore number. On the other hand, a large value for pressure drop can augment the number of nucleolus from the homogeneous nucleation, and reduce the modification time. Thus the growth of nucleolus, which is bad for the PSD modification, can be effectively reduced.

Experimental

Apparatus and procedures

The experimental apparatus of SCSI is shown in Figure 6. It consists of two main units that are used for solute extraction (or dissolution) and infiltration of SC solution, respectively. The liquid propane is pumped to the desired pressure and heated to the set temperature by a coil to reach the supercritical state. After being stabilized by the buffer (with a volume of 500 mL), the SC propane flows through the saturation column to dissolve aluminum isopropoxide (conditions in the saturation column are 403 K, 30 MPa). The column is long enough for the SC solution to get saturated. The length and inner diameter of the saturation column are 450 mm and 6 mm, respectively. Aluminum isopropoxide was mixed with insoluble Al_2O_3 beads so that the SC propane can successfully make contact with the precursor. Both the inlet and outlet of the saturation column were plugged by asbestos mesh and glass wool to prevent the entrainment of fine aluminum isopropoxide powders. This part is placed in air bath 1, which provides temperature control to within about ±0.5 K. The temperature of air bath 1 was set at 403 K, and the pressure downstream of the saturation column was maintained at 30 MPa.

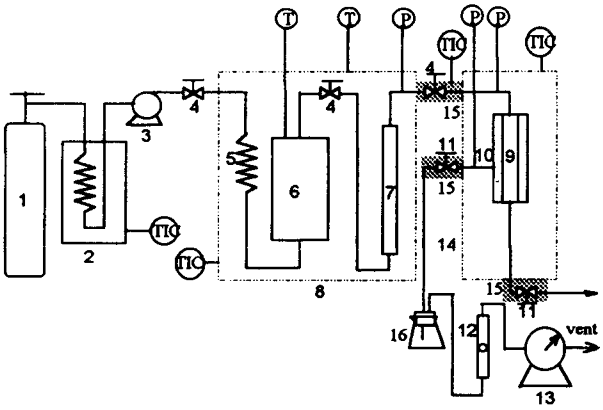

Figure 6, Apparatus of SCSI approach.

In the infiltration unit, SCSI was performed in a membrane permeater immersed in air bath 2, of which the temperature was also controlled at 403 K, within ±0.5 K, by a heater circulator. The SCSI process lasted for about 30 to 60 min. An α-Al_3O_3 MF membrane, which was used as the matrix membrane, was installed in the permeater. The membrane tube was covered with enamel, with an exposed part for modification, as shown in Figure 7. The pressure drop across the membrane layer is controlled by the micrometering valve located at the exit of the permeation side. The micrometering valves were heated to an adequate preexpansion temperature to prevent valve jam caused by phase changes during the expansion of the SC solution. The permeance rate and volume were measured by a rotameter and a wet test meter.

The system pressures were determined by precision pressure gauges that were calibrated by the dead-load method, and the temperatures were measured by thermocouples. The accuracy of the pressure and temperature measurements are estimated to be ±100 kPa and ±0.01 K, respectively.

The permeance rate was maintained at a constant value of about 150 mL (NS)/min by adjusting the micrometering valve at the permeation sides. Due to the deposition of the aluminum isopropoxide inside the membrane pores, the pressure difference between the two sides of the membrane increases as the SCSI process continues. In this study, SCSI is terminated when the pressure difference between the two sides of the membrane reaches a value of 2.7 MPa, because of the strength limits of membrane tubes.

After SCSI, the membranes were immersed in water vapor (363 K) for about 2 h to get complete hydrolysis of the aluminum isopropoxide. Then the membrane tubes were dried in a microwave oven and sintered at 723 K to obtain the final products.

Materials

The aluminum isopropoxide (chemical pure) was supplied

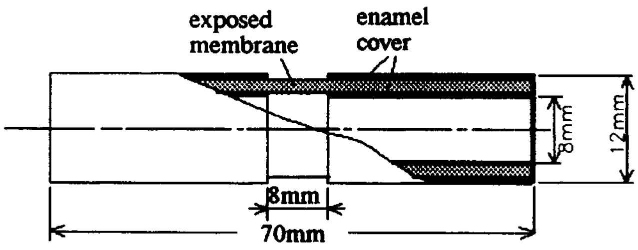

Figure 7. Matrix membrane tube.

by the Shanghai Chemical Reagent Co.; the propane (> 98.5 mol %) was supplied by the Nanjing Special Gas Co. Ltd.; and the methylcellulose (MC) (> 97.5 wt. %, MC450) was provided by the Guangzhou Chemical Reagent Factory.

Isopropanol adsorbed by the particles is the only soluble impurity in SC propane, and is removed by supercritical extraction using SC propane at a temperature and pressure of 388 K and 12.5 MPa, under which the solubility of aluminum isopropoxide is negligible.

The matrix membranes, α-Al_2O_3 MF membranes, were provided by our Center. Membranes with average pore diameters around 1.0 μm have only one layer on the inner surface of the support, and the membrane layers with average pore diameters around 0.15 μm are formed upon those layers with a pore size of 1.0 μm. Five sample membranes were used in this work. By the bubble-point method, Nos. 1 and 2 membranes have mean pore diameters around 0.1 μm, and Nos. 3, 4 and 5 membranes have mean pore diameters around 1.0 μm.

According to the kinetic model of the SCSI process, the result of the PSD change during the SCSI modification is determined by both the pressure drop of the SCF solution and the contact angle between the precursor and the pore surface. Nos. 2, 4, and 5 sample membranes were immersed in an MC aqueous solution (0.5 wt. % of MC) and dried to form a MC coating on the pore surface, while Nos. 1 and 3 samples were not pretreated.

The wetting equation proposed by Young can be written as

$$\cos\varphi = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}, \tag{24}$$

where σ_{SG}, σ_{SL}, and σ_{LG} are the interfacial free energy of vapor–solid, liquid–solid, and gas–liquid, respectively. Equation 24 implies that solids with higher surface energy can be more wettable than solids with lower surface energy. Generally, the surfaces of organic compounds and high polymer are regarded as lower energy surfaces, while the surfaces of metallic oxide are regarded as high-energy surfaces. Therefore, the Al_2O_3 surface should be more wettable by aluminum isopropoxide than the MC surface. In other words, the contact angle of aluminum isopropoxide on the Al_2O_3 should be much smaller than on the MC, but the specific values of these contact angles or pertinent data are currently unavailable.

Determination of membrane pore size

The PSD of the ceramic MF membranes were determined by the gas bubble point (GBP) method, of which many authors have developed the theory and data-processing model. Nitrogen flow through the dry (Q_d) and wet membranes (Q_w) were measured using rotameters at different pressures. Isobutanol was used as the soaking liquid. The largest pores of the membrane were determined by the lowest pressure needed for expelling the liquid from these pores, by which the earliest gas flow was registered. The procedure for measuring and data processing was compiled from those described in ASTM F316-86 (1986) and Coulter porosimetry (Roček and Uchytil, 1994). The area PSD of the membrane is presented by the following expression:

$$Fr(R) = \frac{d[Q(R)]}{dR}, \tag{25}$$

where $Q(R)$ is the dimensionless gas flow rate, $Q(R) = Q_w/Q_d$; Q_d and Q_w are the nitrogen flow rate through the dry and wet membrane at identical applied pressure; and R is the pore radius.

In order to provide a further demonstration of the membrane pore-size change after being modified by the SCSI method, a gas permeation (GP) method suggested by Lin and Burggraaf (1993) was also used. In the GP method, the nitrogen flow rate (Q) was measured under different applied pressures (ΔP) for the membrane before and after modification (after being sintered). ΔP was obtained at steady state by measuring the upstream pressure (P_h) and the downstream pressure (P_l) of the membrane using precision pressure gauges. The gas permeability is defined as

$$(F/L) = Q/S_{to}(P_h - P_l), \tag{26}$$

where L is the thickness of the membrane layer; and S_{to} is the total permeation area of the membrane. The permeability data were plotted as (F/L) vs. P_{av} and regressed with the following linear equation:

$$(F/L) = \alpha + \beta P_{av}, \tag{27}$$

where P_{av} is the average pressure, $P_{av} = (P_h + P_l)/2$, which was measured for the membrane before and after modification. Defining the porosity ϵ as, $\epsilon = S_{po}/S_{to}$, S_{po}, the total area of open pores of the membrane, α and β, can be correlated by the following equations:

$$\alpha = 1.06(1/L)(\epsilon/\tau)(R_g TM)^{-1/2}\int_0^\infty RP(R)\,dR \tag{28}$$

$$\beta = 0.125(1/L)(\epsilon/\tau)(\mu R_g T)^{-1}\int_0^\infty R^2\,P(R)\,dR, \tag{29}$$

where τ is the tortuosity that can be simply correlated with the porosity, $\tau = 1/\epsilon$. According to the conditions of this work, reductions of α and β can reflect the decreases in the porosity and the total area of the open pores.

Combining Eqs. 28 and 29 with Eq. 23, the expression of the average flow radius R_{kv} is derived as

$$R_{kv} = \left[8.47\mu(R_g T/M)^{1/2}\right](\beta/\alpha), \tag{30}$$

where μ and M are the viscosity and molecular weight of nitrogen gas, respectively; and R_g is the gas constant. The flow average pore size of the membrane can be calculated by using the coefficients α and β regressed from the experimental data. Therefore, experimental values of (α/β) for the membrane before and after modification can be used to examine the change of the flow average pore size.

Results and discussion

The gas permeation test and GBP measurements were performed for the membranes before and after the SCSI modification. Figures 8 and 9 show the relationship between the

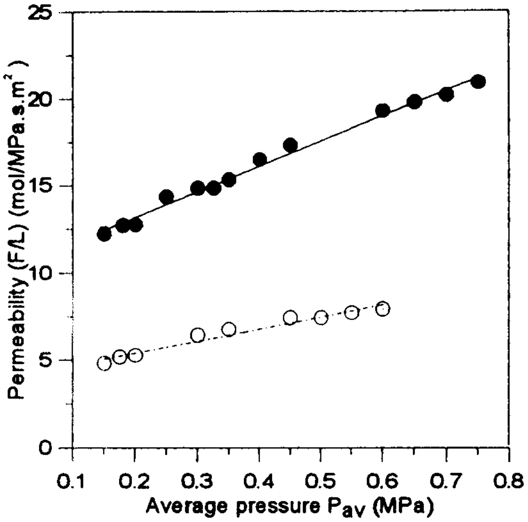

Figure 8. Permeability of nitrogen through sample 1 before (●) and after (○) modification; — and ···· are fitted lines.

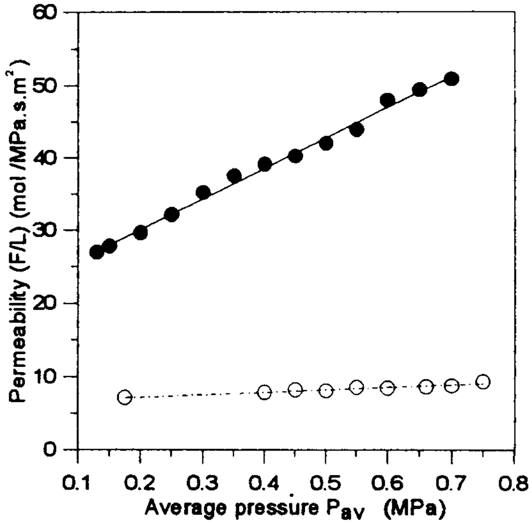

Figure 9. Permeability of nitrogen through sample 2 before (●) and after (○) modification; — and ···· are fitted lines.

nitrogen permeability and the average pressure for Nos. 1 and 2 membranes. From the experimental data, values of α, β, α/β, and R_{kv} were calculated and are given in Table 2. With a large reduction in permeability, α and β are found to be reduced for both numbers 1 and 2 samples after the modification. This indicates that the porosity and the total area of open pores of the membranes were decreased by solute deposition inside the pores. The R_{kv} of number 1 sample was increased from 0.2 μm to 0.24 μm, while R_{kv} of number 2 sample was reduce from 0.28 μm to 0.08 μm. In fact, the size of each pore always decreased when being treated by SCSI, and therefore the porosity of the membrane also always decreased under the mechanism of both heterogeneous and homogeneous nucleation. However, the process conditions that were more favorable for heterogeneous nucleation lead to the excessive pore-size decrease for smaller pores, since the deposited solid coated onto the pore surface equably. As a result, the percentage of pores with larger size was increased, and the average pore size also increased after modification. These observations can be explained by considering that the SCSI process was domintaed by heterogeneous nucleation for unpretreated membranes, and was dominated by homogeneous nucleation for pretreated ones.

Figures 10 and 11 show the area PSD of numbers 1 and 2 samples determined by the GBP method. Having been modified by the SCSI process, the mean pore diameter of the number 1 sample increased from 0.09 μm to 0.11 μm, while the mean pore diameter of the No. 2 sample decreased from 0.11 μm to 0.08 μm. Furthermore, the very large pores in the original membranes, which can be regarded as defects, are found to be gone after the modification. The maximum pore diameters of the number 1 and 2 original membranes were 1.8 μm and 0.9 μm, and were 0.23 μm and 0.15 μm after modification.

Similar results were obtained for the number 3, 4, and 5 samples. Figures 12–14 show the nitrogen permeability of the membranes before and after modification. The permeabilities of all three samples are found to be greatly reduced after being modified, and accordingly, coefficients α and β are much smaller than the values before the modification. R_{kv} of number 3 sample (without pretreatment) was increased, while those of Nos. 4 and 5 samples (pretreated by MC solution) were reduced after the modification. The PSD change of the number 5 sample membrane determined by the GBP method is shown in Figure 15. Results of the gas permeability analysis are given in Table 2.

The PSD of the modified membranes were determined after hydrolysis and sintering. Moreover, the real porous structure of the membrane is much different from the simplified structure used in the mathematical modeling. Consequently, quantitative comparisons between the experimental and simulated results are impossible in this work. Nevertheless, the experimental observations agree qualitatively with those presented by the proposed model.

Table 2. Results of the Measurements Using the Gas Permeation Method

Sample Number	α (mol/MPa·s·m^2)		β (mol/MPa^2·s·m^2)		β/α (MPa^{-1})		R_{kv} (μm)	
	Before	After	Before	After	Before	After	Before	After
1	10.26	4.02	14.54	6.88	1.42	1.71	0.202	0.244
2*	21.64	6.48	42.13	3.40	1.95	0.52	0.277	0.075
3	77.28	54.84	980.69	846.28	12.69	15.43	1.805	2.195
4*	124.43	71.19	1,761.57	845.04	14.16	11.87	2.013	1.688
5*	60.35	64.76	741.29	322.46	12.28	7.98	1.747	0.708

* Pretreated by methylcellulose solution.

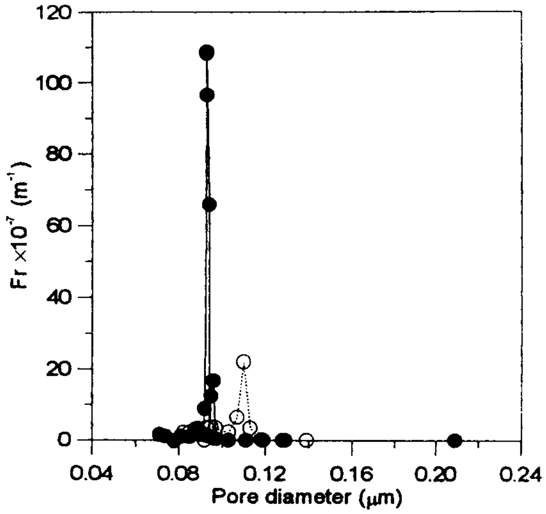

Figure 10. PSD of 1 sample measured by the GBP method; —●—: original membrane; ···○···: after modification.

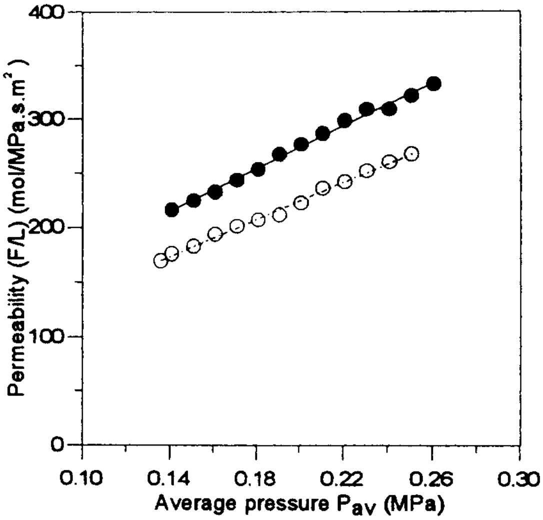

Figure 12. Nitrogen gas permeability through sample 3 before (●) and after (○) modification; — and ···· are fitted lines.

Conclusions

This article presents a novel approach to ceramic membrane modification using the SCSI process. A mathematical model was established for the SCSI process by combining the pore-narrowing kinetics, the classic nucleation theory, and the thermodynamic model of the SC solution. A computer simulation was performed by the proposed model, and the results show that two kinds of solute deposition mechanism—heterogeneous and homogeneous nucleation—could occur simultaneously or singly during the SCSI process, under different conditions.

In the case of heterogeneous nucleation, the pore-size change rate is independent of the original pore size, $(dR/dt) = -k_2(S, \varphi)$, and a large number of small pores can be eliminated, while changes in the size of the large pores is relatively slight. As a result, the mean (and average) membrane pore size will be enlarged with any significant reduction in porosity. Therefore heterogeneous nucleation is not promising for the modification of separation membranes. Since the deposited solid can be equably coated onto the pore surface, however, the SCSI method is probably very useful with heterogeneous nucleation for surface modification of porous ceramic materials.

With the mechanism of homogeneous nucleation, the pore-size change rate is proportional to the original pore size, $(dR/dt) = -k_1(S) \cdot R$. Thus the pore size will be reduced with the same relative rate for all pores. Although the porosity of the membrane will also be reduced during the SCSI process, this method is still valuable for the modification of separation membranes, because the loss of the separative pores would not be serious if the modification time is well controlled.

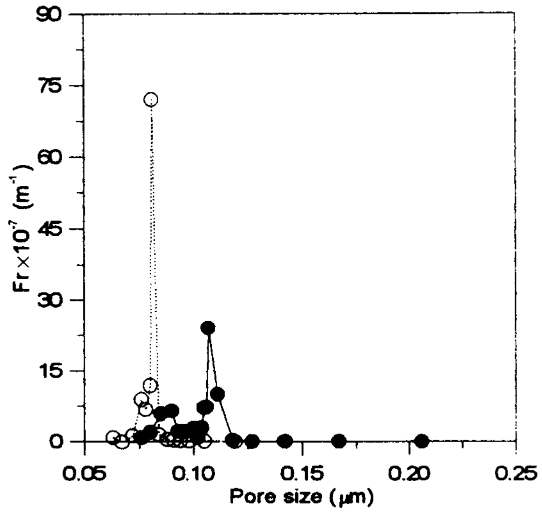

Figure 11. PSD of 2 sample measured by the GBP method; —●—: original membrane; ···○···: after modification.

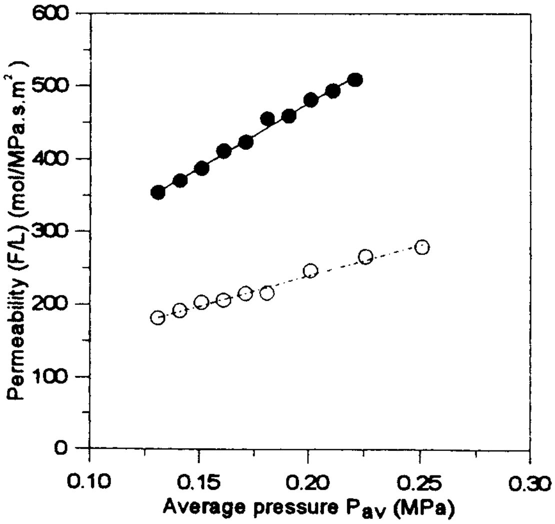

Figure 13. Nitrogen gas permeability through sample 4 before (●) and after (○) modification; — and ···· are fitted lines.

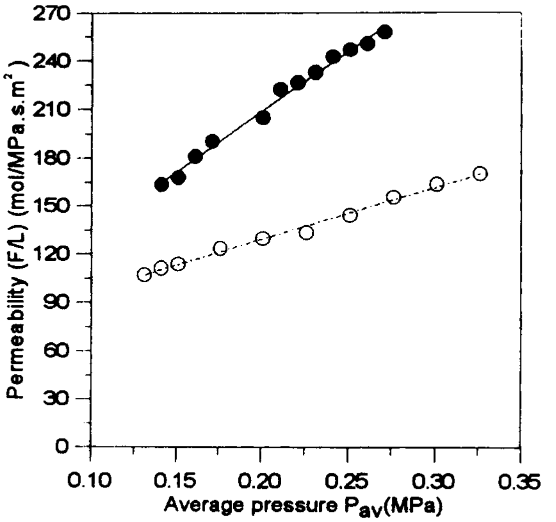

Figure 14. Nitrogen gas permeability through sample 5 before (●) and after (○) modification; — and ···· are fitted lines.

An increase in the solute supersaturation ratio will enhance both heterogeneous and homogeneous nucleation rates. But a higher supersaturation ratio is necessary for the occurrence of homogeneous nucleation than for heterogeneous nucleation, because the activation energy of the former is generally larger than that of latter. A large contact angle between the pore surface and the deposited solute is helpful for homogeneous nucleation and can be used in opposition to heterogeneous nucleation. Therefore homogeneous nucleation can be obtained by simultaneously increasing the pressure drop inside the pores and the contact angle using surface pretreatment.

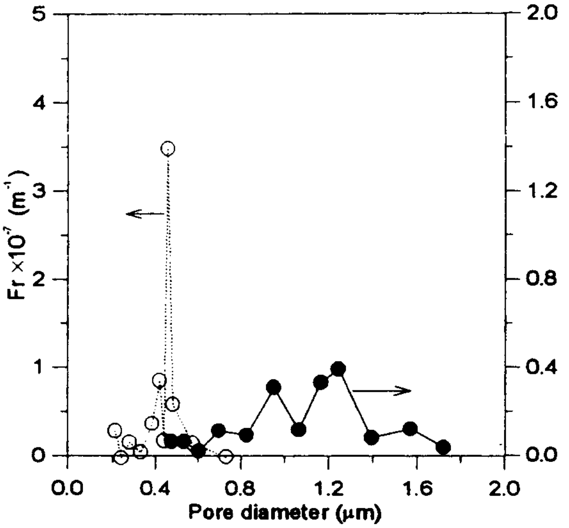

Figure 15. PSD of sample 5 obtained by the GBP method; —●—: original membrane; ··· ○ ···: modified membrane.

An experimental investigation of the modification of ceramic MF membranes using the SCSI method was performed. Both an increase and decrease of the mean pore size of the membranes were observed after SCSI modification under different conditions. The experimental results qualitatively conformed to the predictions of the proposed model.

Acknowledgments

The authors gratefully acknowledge the financial support of the National Nature Science Foundation of China (No. 29576244 and No. 29606005), the Nature Science Foundation of Jiangsu Province (BK95114408), and the Excellent Teacher Foundation of the National Educational Committee of China.

Notation

q = lattice points in per unit area
T = temperature (K)
y_2 = mole fraction of the solute in supercritical solution
α = permeation coefficient contributed by the Knudsen diffusion (mol/Pa·m²·s)
α_{av} = coefficient a for whole membrane sample (mol/Pa·m²·s)
β = permeation coefficient contributed by the viscous flow (mol/Pa·m²·s)
β_{av} = coefficient β for whole membrane sample (mol/Pa·m²·s)
θ = contact angle

Literature Cited

ASTM F316-86, *Standard Test Method for Pore Size Characteristics of Membrane Filters by Bubble Point and Mean Flow Pore Test,"* ASTM Committee on Standards, Philadelphia (1986).

Berneburg, P. L., and V. J. Krukonis, "Method for Densification of Ceramic Materials," U.S. Patent No. 4,552,786 (1985).

Berneburg, P. L., and V. J. Krukonis, "Improvement of Oxidation Resistance of Carbon-Carbon Composite," Japan Patent No. 01,308,873 (1989).

Chrastil, I., "Solubility of Solids and Liquids in Supercritical Gases," *J. Phys. Chem.*, **86**, 3016 (1982).

Debenedetti, P. G., J. W. Tom, X. Kwauk, and S.-D. Yeo, "Rapid Expansion of Supercritical Solution (RESS): Fundamentals and Applications," *Fluid Phase Equilibria*, **82**, 311 (1993).

Hirth, J. P., and G. M Pound, *Condensation and Evaporation*, Pregamon, London, p. 18 (1963).

Jackson, C. M., and J. P. Hirth, *Advances in Epitaxy and Endotaxy—Selected Chemical Problems*, H. G. Schneider, V. Ruth, and T. Kormany, eds., Elsevier, New York (1976).

Lin, Y. S., "A Theoretical Analysis on Pore Size Change of Porous Ceramic Membranes after Modification," *J. Memb. Sci.*, **79**, 55 (1993).

Lin, Y. S., and A. J. Burggraaf, "Experimental Studies on Pore Size Change of Porous Ceramic Membranes after Modification," *J. Memb. Sci.*, **79**, 65 (1993).

Matson, D. W., J. L. Fulton, R. C. Petersen, and R. D. Smith, "Rapid Expansion of Supercritical Fluid Solutions: Solute Formation of Powders, Thin Films, and Fibers," *Ind. Eng. Chem. Res.*, **26**, 2298 (1987).

Pitzer, K. S., D. Z. Lippmann, and R. F. Curl, Jr., "The Volumetric and Thermodynamic Properties of Fluids: II Compressibility Factor, Vapor Pressure and Entropy of Vaporization," *J. Amer. Chem. Soc.*, **77**, 3433 (1955).

Roček, J., and Uchytil, "Evaluation of Selected Methods for the Characterisation of Ceramic Membranes," *J. Memb. Sci.*, **89**, 119 (1994).

Manuscript received Feb. 7, 1997, and revision received May 12, 1997.