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Thermal stability and its improvement of the alumina membrane top-layers prepared by sol–gel methods

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The thermal stability of unsupported alumina membrane top-layers was studied by determining the pore structure (mainly pore size) change of alumina gels, prepared by sol–gel methods, after sintering at different temperatures ranging from 450 to 1200 °C. The average pore size of the pure alumina membranes and PVA-added membranes increased sharply after sintering at temperatures higher than 1000 °C. Addition of 3% lanthanum, either by mixing lanthanum nitrate in the alumina sol or impregnating lanthanum nitrate into calcined alumina gel, followed by a second heat treatment, can considerably stabilize the pore structure of the alumina membrane top-layers. The pore diameter for the lanthanum-doped membranes was stabilized within 25 nm after sintering at 1200 °C for 30 h, about one-sixth of that for the pure alumina membranes after sintering at 1200 °C for 30 h. The substantial increase in the pore size for the pure alumina membranes at the sintering temperature of 1000 to 1200 °C was accompanied by the phase transformation from γ-to α-alumina. The addition of lanthanum can raise this phase transformation temperature by about 200 °C.

1. Introduction

The potential applications of ceramic membranes in separation, filtration as well as catalytic reactions have stimulated increasing research on synthesis, characterization and property improvement of these inorganic membranes [1]. There are several processes for making ceramic membranes, e.g. chemical leaching, solid-state sintering and sol–gel processing. The sol–gel methods [2, 3] are considered to be most practical for ceramic membrane preparation because of the advantages of being able to make micro-scale thin membrane top-layers with nanoscale pore diameter and narrow pore-size distribution. In the sol–gel methods, a stabilized sol made from metal alkoxide is prepared and coated on a coarse ceramic support to form the membrane top-layer. Ceramic membrane top-layers of alumina, ceria, titania and zirconia, and combinations of these materials have been made by the sol–gel methods [4–6]

For the ceramic membrane top-layers prepared by the sol–gel methods, the smallest possible pore size is determined by the primary particle size in the sol (colloid suspension) [4]. In most cases the pore size of a membrane top-layer, starting from the smallest pore size when the gel is formed by drying and calcination at a relatively low temperature, increases with sintering temperature. This kind of temperature dependency of the membrane (pore size) has been confirmed in the top-layers of γ-Al_2O_3, TiO_2 and ZrO_2 [3, 6, 7]. For sintering temperatures higher than 1000 °C, no ceramic membrane top-layer with a pore diameter smaller than 50 nm has been reported. Recently, there has been growing interest in the application of ceramic membranes at elevated temperatures. Examples include the potential high-temperature application of ceramic membrane for gas purification [8] and chemical vapour deposition (CVD) modification of the membranes prepared by the sol–gel method [9]. Thus, a systematic investigation of the thermal stability of the ceramic membrane top-layers is of importance from both theoretical and practical points of view.

In the current literature, very limited studies have been reported on the thermal stability of ceramic membranes. Burggraaf and co-workers [2, 4, 7, 10] determined the pore size of some ceramic membrane top-layers at different sintering temperatures, and reported that the pore size of γ-alumina top-layers increases significantly at temperatures between 900 and 1000 °C. Without indicating sintering time, pore size–sintering temperature (500 to 1000 °C) data for a γ-alumina top-layer have been reported by Cot and co-workers in several publications [3, 11, 12]. These papers, however, have mainly dealt with the synthesis of the ceramic membranes and their characterization, rather than the thermal stability study. In this paper, a more systematic investigation is presented of the thermal stability of the alumina membrane top-layers, made by sol-gel method, and the improvement of the microstructure thermal stability of these membrane top-layers.

2. Experimental procedure

The thermal stability of the unsupported alumina

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membrane top-layers was investigated by determining the pore-size distribution, average pore size, and surface area as a function of sintering temperature, or sintering time. The unsupported top-layers studied were based on the following four gels:

(A) gel formed from pure boehmite (γ-AlOOH) sol;

(B) gel formed from boehmite sol mixed with 3% lanthanum [$La(NO_3)_3$ (mol)/γ-AlOOH(mol) = 0.033 in the sol)];

(C) gel formed from boehmite sol mixed with polyvinyl alcohol (PVA);

(D) gel first formed from pure boehmite sol and then impregnated with $La(NO_3)_3$ solution (about 3% lanthanum).

The pure boehmite sol (1 M boehmite) was prepared by adding alumina secondary butoxide to water and peptized with nitric acid (HNO_3 (mol)/alkoxide (mol) = 0.07) in the procedure as presented in [7]. A correct amount of lanthanum nitrate solution (pH = 1) was added to the pure boehmite sol to form the 3% lanthanum boehmite sol. The lanthanum-added sol was shaken thoroughly to give a homogeneous mixture. The solution of PVA (with M_w = 72 000) was prepared by adding 7 g PVA to 200 ml 0.05 M HNO_3 solution. The boehmite sol with PVA was made by mixing the PVA solution with pure boehmite sol (ratio 2:3).

Gels A, B and C were prepared by drying about 40 ml pure boehmite sol, lanthanum added sol, and PVA-added sol, respectively, in petri dishes (diameter = 10 cm) in air at room temperature for a few days. The gels were then calcined at 450 °C for 4 h to form thin (about 75 nm thick) unsupported membrane top-layers. Gel D was prepared by immersing a correct amount of the calcined pure alumina gel (gel A) into a given amount of the lanthanum nitrate solution [$La(NO_3)_3$(mol)/γ-AlOOH(mol) = 0.033], and drying the mixture of the gel and nitrate solution in air at room temperature. This dried gel was again calcined at 450 °C for 4 h to form the corresponding membrane top-layer.

The four types of membrane top-layers were fired at different temperatures (450 to 1200 °C) in temperature-calibrated furnaces. In all sintering experiments, the furnaces were heated up at a rate of $90\,^{\circ}C\,h^{-1}$ to reach the given sintering temperature. For investigating the temperature effects on the thermal stability of the membrane, the sintering time was 30 ± 2 h for all samples. To study the sintering kinetics, the sintering time was varied but the sintering temperature was kept at 800 °C. After the membranes had been sintered for a period of time at a given temperature, the pore-size distribution, average pore size, pore volume and surface area (BET) for most membrane samples were determined by nitrogen adsorption and desorption porosimetry (liquid-nitrogen temperature) (Micromeritics, Asap 2400). For the membrane samples with an average pore diameter larger than 20 nm, a mercury porosimetry (Carlo-Erba, Series 200) was used to determine the pore structure. The phase structure of some sintered membrane samples was examined by X-ray diffractometry (Philips, PW1710, Cu$K\alpha$).

3. Results and discussion

The drying times required for gels A, B, and C were found to be 3, 5 and 7 d, respectively. The cracking extent followed the order: gel A (considerable cracking), gel B (slight cracking), and gel C (no cracking). The longer the dry time required and the lower extent of cracking for gels B and C are due to the fact that the sols become more viscous on the addition of lanthanum nitrate solution and PVA. The increase in the sol viscosity on adding the lanthanum nitrate solution is probably a result of a decrease in the pH value because of the acidity of the lanthanum nitrate solution (pH = 1). The increase in the sol viscosity on adding PVA has led to its application as an additive for making crack-free supported-membrane top-layers [4].

After calcining at 450 °C and sintering at a temperature lower than 900 °C, all three gels became transparent because of the presence of small pores which hardly scatter visible light. However, some gels sintered at temperatures higher than 900 °C, became opaque as a result of an increase in pore size. The lanthanum-impregnated gel (gel D) after drying in air at room temperature, appeared opaque, probably due to the presence of $La(NO_3)_3$ inside the gel pores. The impregnated gel became transparent after heating at 150 °C for 5 h as a result of decomposition of the residual $La(NO_3)_3$.

The four types of membrane were sintered at 600, 800, 900, 1000, 1100 and 1200 °C for about 30 h. Fig. 1 shows the pore-size distribution calculated from desorption isotherms of the four types of membrane sintered at 1000 °C. The pore-size distributions for the four membranes are generally rather narrow, with a broader distribution and smaller average pore size for the membranes doped with lanthanum (gels B and D). The pure alumina membrane had the narrowest pore-size distribution, but the average pore size was larger than those for gels B and D. It is interesting to note that the PVA-added membrane (gel C) sintered at 1000 ° C had a two-peak pore-size distribution, indicating growth of a second group of pores with an average pore size of about 30 nm. The PVA-added membranes sintered at temperatures lower than

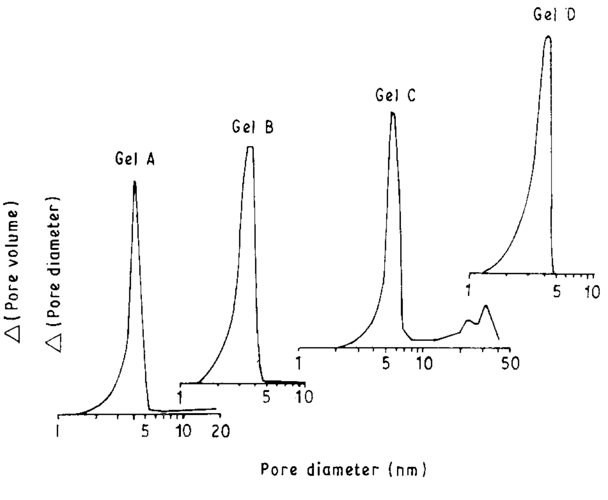

Figure 1 Determined pore-size distributions for the four types of membrane sintered at 1000 °C for 30 h.

TABLE I Average pore diameter, *d*, and BET surface area, *S*, for the four types of membrane sintered at different temperatures for 30 h

Temp.	Membrane A		Membrane B		Membrane C		Membrane D	
(°C)	*d* (nm)	*S* ($m^2 g^{-1}$)	*d* (nm)	*S* ($m^2 g^{-1}$)	*d* (nm)	*S* ($m^2 g^{-1}$)	*d* (nm)	*S* ($m^2 g^{-1}$)
450	3.24	366	3.14	280	3.08	349	3.13	324
600	4.04	257	—	—	3.68	258	—	—
800	5.10	187	4.21	180	5.17	178	—	—
900	6.27	116	5.86	103	7.78	95.5	5.56	135
1000	8.34	56.6	5.94	89.0	12.6	43.3	6.30	100
1100	90.6	9.3	10.9	31.9	—	—	9.78	54.9
1200	120	4.5	23.8	16.5	—	—	—	—

1000 °C, however, did not show the two-peak pore-size distribution.

The average pore diameter calculated from the desorption isotherms and BET surface area for the four types of membrane sintered at different temperatures are listed in Table I. The pore size for the four types of membrane increases less significantly at sintering temperatures lower than 1000 °C, but more significantly at sintering temperatures higher than 1000 °C. For membranes A and C (without addition of lanthanum), pore structure became rather unstable at higher sintering temperatures. For a similar pure alumina membrane, a pore diameter of 4.8 and 5.4 nm was reported after sintering at 800 and 900 °C for 33 h [4, 7, 10]. Larbot *et al.* [3, 11, 12] also reported an increase in pore diameter from about 5 to 10 nm as the sintering temperature increased from 500 to 1000 °C for an unsupported alumina membrane top-layer (sintering time was not given). The results presented in Table I are consistent with the previous studies. The surface area for the four types of membrane, as shown in Fig. 2, was found to decrease with sintering temperature (sintering time of about 30 h). The specific pore volume of the four types of membrane sintered at different temperatures is also presented in Fig. 3. It was found that the pore volume, in general, decreased with increasing sintering temperature. Both the pure alumina membrane and the lanthanum-doped membrane are not completely densified at 1200 °C (V_p is about 0.1 ml g^{-1}), as shown in Fig. 3. The smaller pore volume of the lanthanum-doped membranes at temperatures lower than 900 °C is probably due to the occupation of the doped lanthanum oxide inside the gel pores. The surface-area shrinkage and the pore-volume densification with increasing sintering temperature are the common sintering phenomena for alumina [13, 14, 15, 16].

The average pore diameters for membranes A and B (from sol mixed with 3% lanthanum) are plotted against sintering temperature in Fig. 4. The pore size for both types of membrane increased slightly as sintering temperature increased from 450 to 1000 °C. A substantial increase in the pore size for membrane A was found, in contrast to only a small increase for membrane B, when the sintering temperature was higher than 1000 °C. It was found that the substantial pore growth for the pure alumina membranes occurs

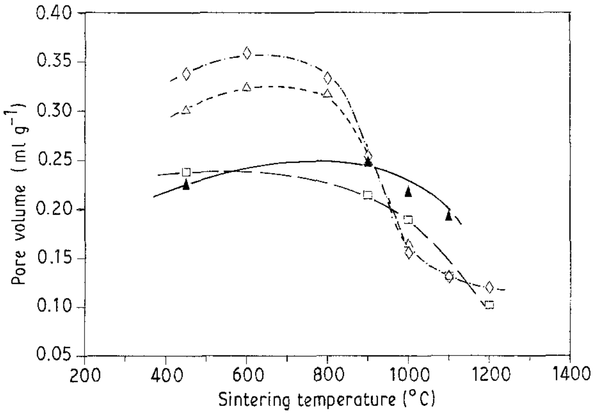

Figure 3 Effects of sintering temperature on pore volume of the four types of membrane. For key, see Fig. 1.

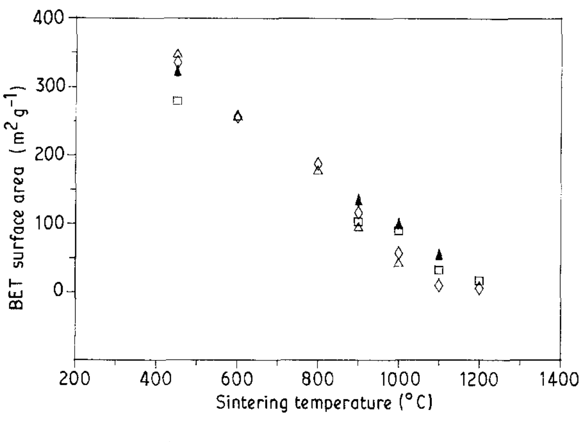

Figure 2 Effects of sintering temperature on BET surface area of the four types of membrane: (◇) A, (□) B, (△) C, (▲) D.

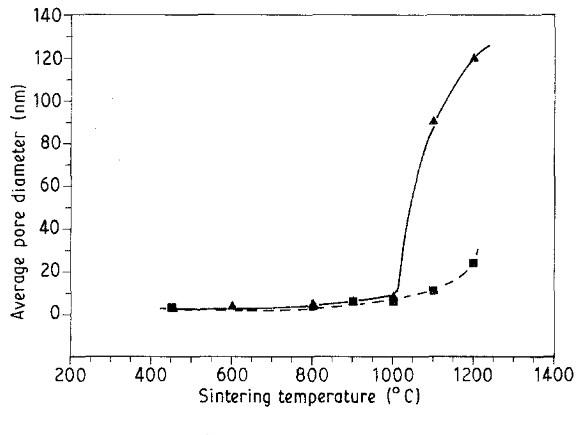

Figure 4 Comparison of pore size and sintering temperature for the (▲) pure alumina membrane and (■) lanthanum-doped membrane.

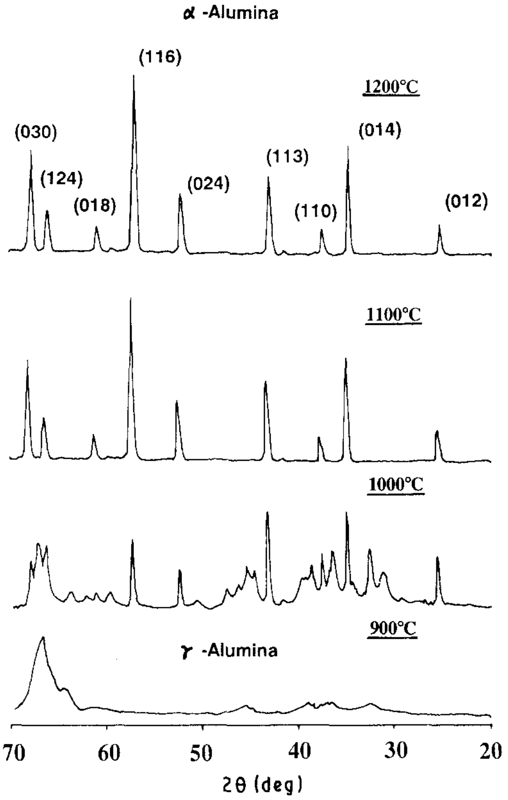

Figure 5 X-ray diffraction patterns for the pure alumina membrane sintered at different temperatures.

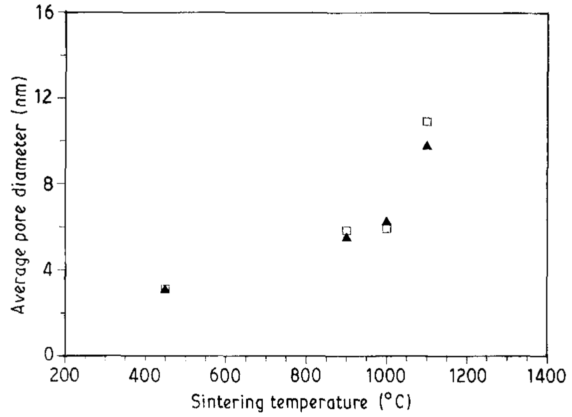

Figure 6 Comparison of pore size against sintering temperature for the lanthanum-doped membranes prepared by different doping methods. (□) Membrane B, (▲) membrane D.

in the temperature range around the phase transformation temperature of γ-alumina to α-alumina [17]. The addition of 3% $La(NO_3)_3$ to the alumina sol can stabilize the membranes with a pore diameter smaller than 25 nm even at a temperature as high as 1200 °C.

The slow pore growth for these two types of membrane at sintering temperatures lower than 1000 °C is caused by the normal sintering process, e.g. the forming of necks between crystallites by surface and volume diffusion. The substantial increase in the pore size for membrane A at sintering temperatures higher than 900 °C is believed to be a result of the phase transformation from γ-Al_2O_3 (through δ-Al_2O_3 and θ-Al_2O_3) to α-Al_2O_3 [17]. The XRD patterns for the four samples of membrane A sintered at 900, 1000, 1100, 1200 °C, as shown in Fig. 5, confirm the phase transformation of the pure alumina membranes in the higher temperature range.

It was earlier reported [16] that the addition of some metal oxide dopes could reduce the surface area loss of γ-alumina catalyst support during sintering. The addition of lanthanum was shown to stabilize rather effectively the surface area of γ-alumina because of the large ionic radius of lanthanum [18]. In the present study, the retardation of the pore growth by addition of lanthanum (gel B) was probably caused by the presence of lanthanum oxide in the surface of the pure alumina crystallite particles. To examine this, the pore size data for membrane B (from 3% lanthanum sol) and membrane D (3% lanthanum impregnated gel) at different sintering temperature are compared in Fig. 6. Considering the experimental errors and the fact that the content of $La(NO_3)_3$ introduced by the two different methods is not exactly the same, the data presented in Fig. 6 show almost identical results for the lanthanum-doped membranes prepared by the two different doping methods. The molecules of $La(NO_3)_3$ impregnated into the calcined pure alumina gel are most likely present on the surface of the primary γ-alumina crystallite particles. Thus, the results presented in Fig. 6 may suggest that the lanthanum doped by mixing $La(NO_3)_3$ with the pure alumina sol was also present on the surface of the γ-AlOOH crystallite particles and remained on the particle surface after the γ-AlOOH particles transform to γ-Al_2O_3 by calcination at 450 °C. It was reported that the lanthanum doped in alumina catalyst support by wet impregnation was present on the γ-alumina crystallite surface in the form of a two-dimensional lanthana overlayer [18, 19], which lowered the driving force for sintering and thus reduced the sintering rate and extent. This could also explain the retardation of the pore growth for the lanthanum-doped membranes in this study.

The presence of the lanthanum on the γ-alumina crystallite particle surface may also raise the phase transformation temperature. The XRD patterns presented in Fig. 7 show that for the lanthanum-doped membranes (membranes B) only a very small portion of the γ-alumina has become α-alumina at the sintering temperature of 1200 °C, about 200 °C higher than the transformation temperature for the pure alumina gel (see Fig. 5). It is known that the phase transformation from γ-alumina to α-alumina proceeds via a nucleation and growth mechanism with one nucleus being formed per crystallite [20]. The presence of the lanthanum oxide on the γ-alumina crystallite surface may reduce the possibility of the nucleation of α-alumina, thus raising the phase transformation temperature.

For a brief study on the sintering kinetics, the two types of membrane (A and B) were also sintered at 800 °C for different periods of time. The BET surface area and pore diameter for membranes A and B at different sintering times are shown in Fig. 8. It was found that the pore size for the pure alumina membranes was larger than that for the lanthanum doped ones, for the sintering time of 30 h, and the difference in the pore size between these two types of membrane

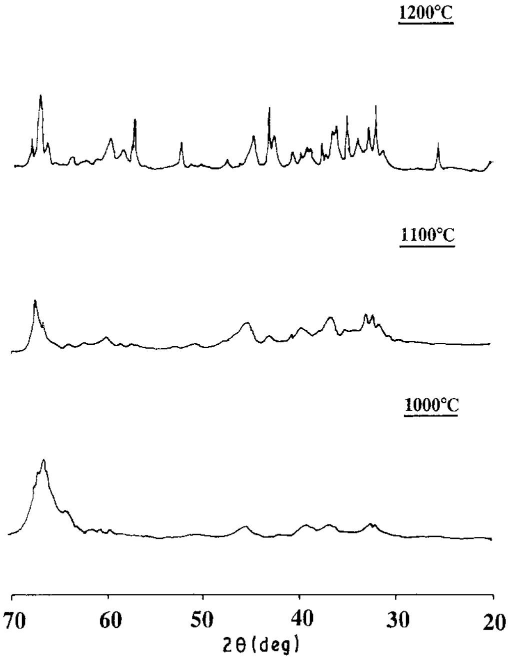

Figure 7 X-ray diffraction patterns for the lanthanum-doped membrane sintered at different temperatures.

increased with sintering time. For the lanthanum-doped membranes, the surface area and pore size reached stable values at a sintering time of 90 h, indicating that the presence of lanthanum on the crystallite surface not only reduced the surface diffusion rate but also shifted the final state. For the pure alumina membranes, however, the pore structure still changed in the sintering time ranging from 90 to 120 h.

As PVA is often used as an additive in the alumina sol in order to render the supported membrane top-layer crack-free, it is interesting to examine the thermal stability of the membranes made from the sol with the addition of PVA. In Fig. 9 the pore size data at different sintering temperatures for PVA-added membranes (from gel C) are compared with those for pure alumina membranes (from gel A). It was found that the pore size of the PVA-added membranes was slightly smaller than that of the pure alumina membranes at sintering temperatures lower than 800 °C. However, at a sintering temperature higher than 800 °C, the pore size of the PVA-added membranes became much larger than that of pure alumina membranes.

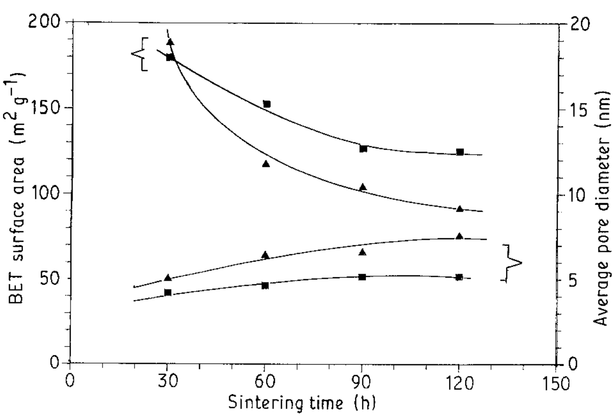

Figure 8 Effects of sintering time at 800 °C on pore structure of the (▲) pure alumina membrane, A, and (■) lanthanum-doped membrane, B.

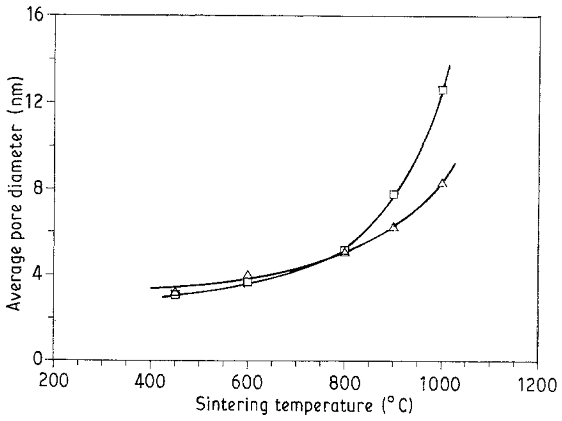

Figure 9 Comparison of the pore size and sintering temperature for the (△) pure alumina membrane, A, and (□) PVA-added membrane, C.

The microstructure of the pure alumina gel, formed when sol is dried, is built up of penny-shaped primary particles of size 25 to 50 nm [7, 9]. The addition of the large molecular weight PVA to the alumina sol may result in a locally different microstructure, where PVA molecules are present, for the PVA-added gel. After calcination at 450 °C, the PVA molecules are burnt out, leaving some micro-cavities in the gel. The volume of those cavities may also increase during the sintering process. The smaller peak with a larger average pore size in the pore-size distribution curve for membrane C, as shown in Fig. 1, possibly indicates the growth of these cavities. The larger average pore size of the PVA-added membranes at higher sintering temperature may be a result of the growth of the cavities created by the PVA molecules.

4. Conclusions

For the four types of alumina membrane top-layers studied, the average pore size increased gradually with sintering temperature when sintering temperatures were lower than 1000 °C. For the pure alumina membranes and PVA-added membranes, the pore size increased substantially at sintering temperatures higher than 1000 °C, due to the phase transformation from γ-alumina to α-alumina. Compared to the pure alumina membranes, the PVA-added membranes had a smaller pore size at sintering temperatures lower than 800 °C and a larger pore size at sintering temperatures higher than 800 °C. Addition of 3% lanthanum in the pure alumina sol considerably stabilized the pore size of the membranes. For the lanthanum doped membranes, the pore diameter was stabilized at around 25 nm after sintering at 1200 °C for 30 h. The addition of lanthanum by mixing La$(NO_3)_3$ in the pure alumina sol or impregnating La$(NO_3)_3$ in the calcined alumina gel, stabilized the membranes to the same extent. For the lanthanum-doped membranes, the sintering process reached equilibrium faster than that for the pure alumina membranes.

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