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W. P. Yang[a]; Shu-Ling Huang[a]
[a] Department of Chemical Engineering, National United University, Taiwan, Republic of China

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Synthesis and Characterization of Titania Membrane

W. P. Yang* and Shu-Ling Huang

Department of Chemical Engineering, National United University, Taiwan, Republic of China

ABSTRACT

Unsupported titania membrane without pinholes or cracks was prepared by sol–gel techniques from alkoxide starting materials. The influence of the amount of PVA additives in the gel preparation process was studied by thermal analysis, function group analysis, and x-ray diffraction analysis. The prepared membranes were characterized by different methods. The results show that the exothermic reactions between PVA and titania gel occurred at lower calcination temperatures, strengthening the gel network during the process. The PVA as well as calcination temperature can be used to control the microstructure properties of the

*Correspondence: W. P. Yang, Department of Chemical Engineering, National United University, Miao-Li 360, Taiwan, Republic of China; Fax: 886-37-332397; E-mail: wpy@mail.nuu.edu.tw.

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titania membrane top layer. The results after calcination at 400°C for 4 hours show that the sharp degree of pore size distribution increases with the PVA/TiO_2 ratio rising, ending at a 18.7 wt% ratio.

Key Words: Sol–gel process; Microstructure; PVA; Titania membrane.

INTRODUCTION

Recently, ceramic membranes with pores in the nanometer (nm) range have been rapidly developed because of their excellent advantages: higher chemical, thermal, and mechanical stability and good catalytic properties.[1,2] Several processes for making ceramic membranes, e.g., chemical leaching, sol–gel, and solid-state calcining have been investigated, but the sol–gel method could be the most practical. One of the major advantages of the sol–gel method is that the properties of the derived materials can be controlled by means of the conditions of the process, such as additives, calcination treatment, and dispersion media selection. The membranes prepared by sol–gel have a narrow pore size distribution, no pinholes, and are crack free.[3–6]

A series of studies[2,7–12] used the sol–gel method for preparing porous ceramic membranes, such as alumina, titania, and silica. These studies explored the characteristics of ceramic membranes extensively. In the sol–gel process for the production of metal oxides, the colloidal sols can be prepared by a number of different routes, such as polycondensation of metal salts to form oxides or hydrolysis and polycondensation of metal alkoxides. Yoldas[13] suggests basic preparation conditions for clear colloidal sol prepared from titanium alkoxide by means of the sol–gel method and the titania monoliths prepared from this sol. However, Yoldas's procedure was rather restricted and the prepared titania film cracks easily. A number of recent studies attempted to improve the procedure and influence the microstructure of the titania membrane by using a variety of additives, such as lanthanum, PVA, cellulose compounds, $NaNO_3$, and diethanolamine[2,7,12,14,15]. Various theories concerning the role of organic additives were studied by Zarzycki.[16] But the exact mechanism by which organic additives work is still unknown. A possible mechanism might be that the neck growth strengthens the gel network.

In the present work, unsupported titania membrane without defects was made by means of the modified sol–gel method. The PVA effect on the physical characteristics of membranes during the different thermal

treatments was studied. Several methods, like IR spectroscopy and thermal measurement analysis, were used to investigate the sol–gel process.

EXPERIMENTAL SECTION

Sample Preparation

Pure sols of titania were prepared using the procedure described by Yoldas et al.[8,11,13] Titanium tetra-isopropoxide (TTIP) was hydrolyzed by the large excess of water (hydrolysis molar ratio H_2O/alkoxide = 300) with vigorous stirring at 80°C. The solution was kept at 80°C for 2 hours. Nitric acid was used as catalyst as well as a peptizer with a HNO_3/alkoxide ratio of 0.5. The sol was maintained at boiling point in an open container for a few hours to remove the isopropanol produced by the reaction. Then, it was cooled down to room temperature. Water was added to adjust the concentration.

Polyvinyl alcohol (PVA) (grade BF-24, Mn = 105,000) was obtained from the Chang Chun Petrochemical Co. (Taiwan, R.O.C.). Various amounts of PVA (1 g, 2 g, etc.) were separately added to the flasks containing 100-ml boiled H_2O and stirred at a high speed for the different solutions. Each PVA solution, after refluxing for 4 hours, was mixed with pure titania sol (ratio: 1:12.5), to obtain the casting solutions. The gel films with different PVA/titania ratios were formed in polystyrene Petri dishes under filtered air and at room temperature for 3 weeks. The five gel films of about 50-μm thickness were prepared by the above-mentioned method to give the following weight ratio of PVA/TiO_2: (a) 0, (b) 9.36, (c) 18.7, (d) 28.1, and (e) 56.2 percent. The gel films were then calcined to form a thin unsupported membrane top layer.

Characterization

Differential scanning calorimetry (DSC) measurements were performed with a DSC TA-2000 (DuPont Co.) for samples of approximately 10 mg each at a heating rate of 10°C/min. Thermal gravimetric and differential thermal analysis (TG/DTA, Seiko instrument) was executed at a temperature rising rate of 15°C /min and ended at 1200°C.

The transmission IR spectra of individual films in the spectral region, 4000 to 400 cm^{-1}, were acquired using a Bio-Rad FTS-7 spectrometer with 4-cm^{-1} resolution. A Shimadzu XD-5 diffractometer with a Ni-filtered Cu Kα radiation was used for obtaining the diffraction patterns. The voltage and current of the x-ray source were 30 kv and 20 mA, respectively. The average pore size, surface area, and pore size distribution were also

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determined by nitrogen adsorption and desorption porosimetry (PMI BET-202A Model) (liquid–nitrogen temperature). To study the morphology of some calcined membranes, a Hitachi S-2300 scanning electron microscope (SEM) was used.

RESULTS AND DISCUSSION

Structural Investigation of the Gels

The influence of the PVA additive on the structure properties of the gels during calcination was studied by thermal analysis (DSC and DTG and DTA) and transmission IR spectroscopy. Typical DSC curves for the pure PVA, pure gel, and composite gel are given in Figure 1. Two major endothermic peaks were found at around 223°C and 328°C for the pure

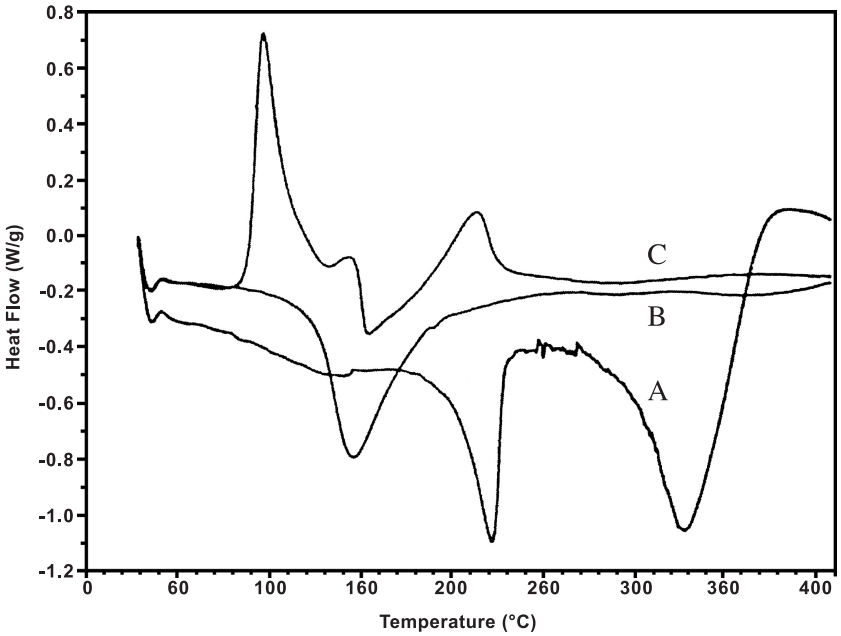

Figure 1. DSC curves of (A) pure PVA, (B) pure titania gel, and (C) a composite gel film with a PVA/TiO_2 ratio of 18.7 wt% at a heating rate of 10°C/min in N_2 atmosphere.

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PVA (curve A) after drying. The 223°C peak represents the melting temperature of the semicrystalline PVA polymer[17] and 328°C is the point of the PVA decomposition. The pure titania gel (curve B) also exhibits a sharp endothermic peak around 146°C. The results show that the condensed water in the pores and the adsorbed water on the surface of the pores evaporated even though the gel films were dried at a humidity lower than 35%. The DSC results of the composite gel film with a 18.7% of PVA/TiO_2 ratio are shown in curve C, which is quite different from curves A and B. Three exothermic peaks (107, 142, and 213°C) appear only in this curve. The area (J/g) variety of the peaks, both 107 and 142°C, changed with the different PVA/Titania ratios, as indicated in Figure 2. It is clear that a chemical exothermic reaction happened between the titania gel and the PVA. The IR spectroscopic investigations provide information about the existence of specific O—H and C—O groups during the different calcinations steps of the gel. The composite gel films at various lower

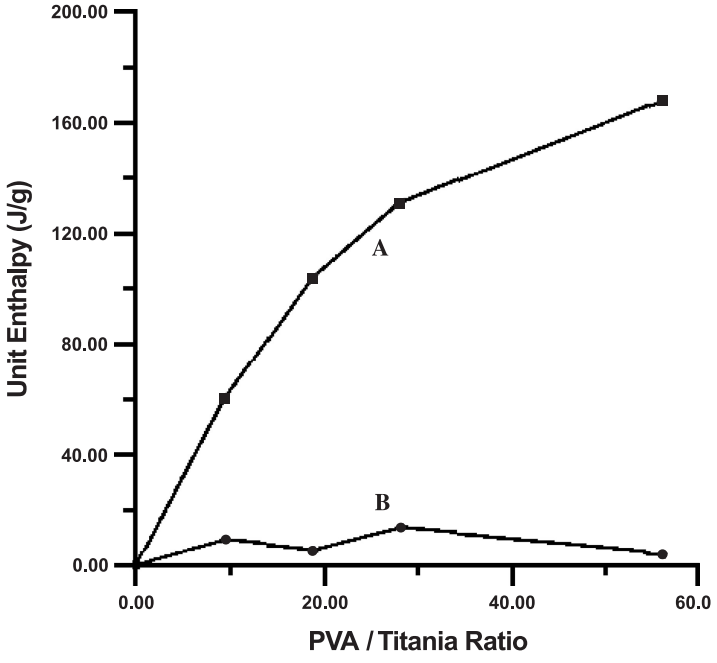


Figure 2. PVA/titania ratio for the various composite gel films vs. the unit enthalpy of the exothermic peak at (A) 107°C and (B) 142°C.

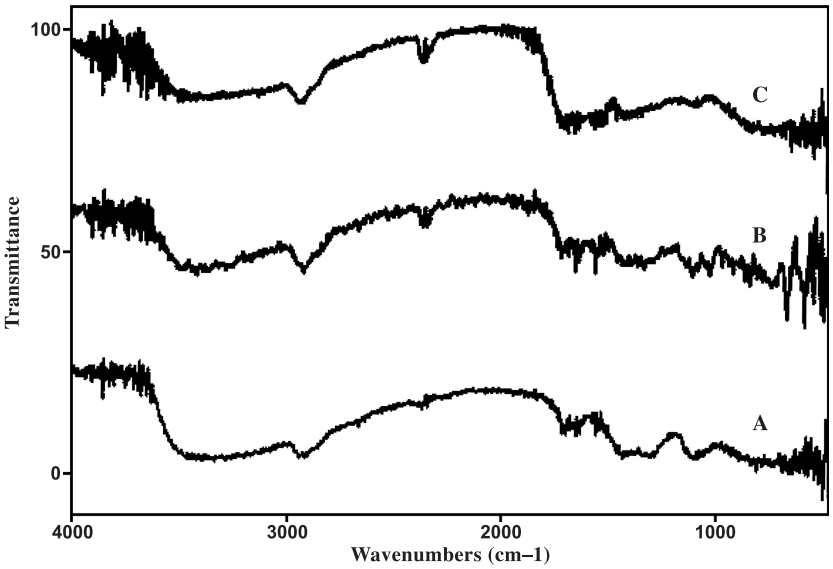


Figure 3. Infrared spectra of the composite gel film with a PVA/TiO_2 ratio of 56.2 wt % after calcination at various temperatures for 1.5 h: (A) 80°C, (B) 150°C, and (C) 220°C.

calcination temperatures are shown in Figure 3. The band at about 3350 cm^{-1} is assigned to the O—H stretching. As can be seen from curves A (80°C) and B (150°C), the O—H group absorption decreased significantly. However, the absorption intensity of C—O vibrations (1090 cm^{-1}) hardly changed. These results indicate that the C—O—H group of the PVA was transformed into C—O—X (X being either C or Ti) due to the reaction. Comparing that with curve C of Figure 1, confirms that the dehydration reaction between the hydroxyl group of the PVA and the titania gel occurred below 150°C; the X atom in C—O—X is Ti. As shown in curve C (220°C), the sharp band at 1090 cm^{-1} decreases significantly and the C—H band at 2920 cm^{-1} decreases slightly. In comparison with the FTIR curve of the pure PVA,[18] the sharp band at 1090 cm^{-1} is almost unchanged. Therefore, the disappearance of the C—O bond may have been caused by the decomposition of the reacted PVA. This is in agreement with the calorific loss at 213°C in curve C of Figure 1. The decomposition temperature (213°C) of the reacted PVA is smaller than the decomposition temperature (328°C) of the pure PVA. Furthermore, it is changed from an endothermic to an exothermic reaction.

Yoldas[13] reported that, ''These pure titania gels initially contained 70 to 82% equivalent oxide. The volume shrinkage occurs as a result of the formation of bridging oxygens by the reaction of dangling bonds with each other.'' Therefore, the pure gel film will crack because of internal stress during the drying and calcination process. The PVA can be used as both a surfactant and a binder,[16] since it reduces the surface tension of the gel in the drying and heating processes. The PVA, which possesses the higher molecular weight, is a linear organic polymer. As the reaction between the titania gel and the PVA took place, they formed a composite gel film with a new network type structure. The addition of PVA will reduce the tendency to crack. Zaspalis et al.[14] also reported that ''PVA was added to the sols to strengthen the gel network during the drying and calcination process.''

The DTG and DTA diagrams of the gel films are given in Figures 4 and 5. The maximum rate of the crystallization phase changes the pure

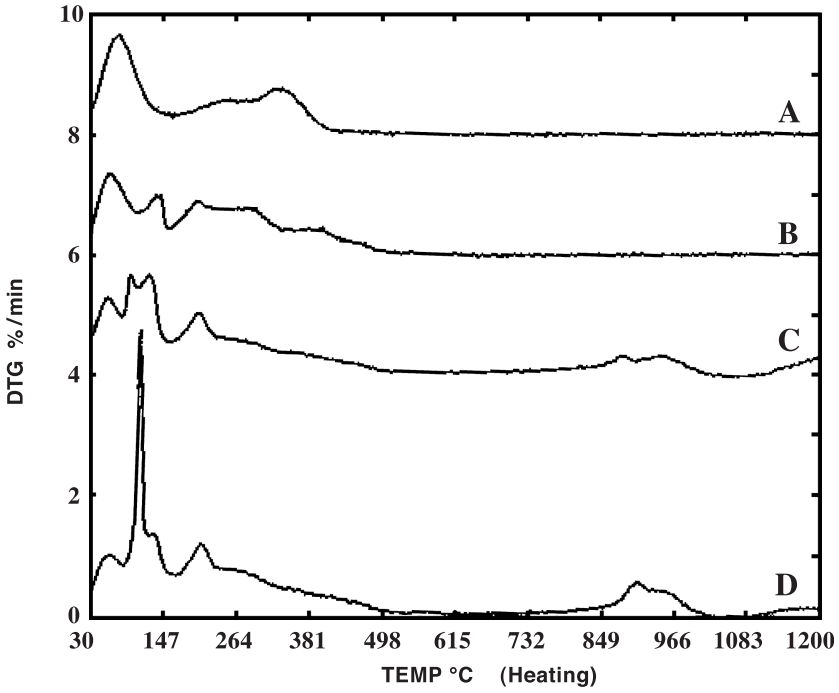


Figure 4. DTG curves of (A) pure titania gel and composite gel films with the following PVA/ TiO_2 ratio: (B) 9.36 wt%, (C) 18.7 wt%, and (D) 28.1 wt% at a heating rate of 15°C/min in N_2 atmosphere.

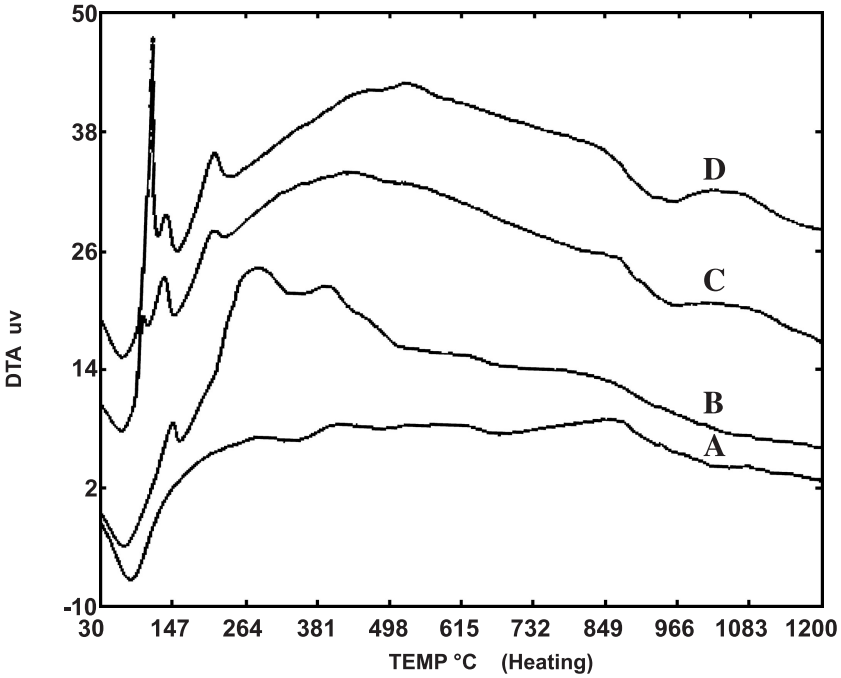


Figure 5. DTA curves of (A) pure titania gel and composite gel films with the following PVA/TiO_2 ratio: (B) 9.36 wt%, (C) 18.7 wt%, and (D) 28.1 wt% at a heating rate of 15°C/min in N_2 atmosphere.

titania gel transition to anatase TiO_2 at around 338°C. The 338°C peak presents a broad range, from 155 to 420°C. This is in agreement with published research.[14] Larbot and Anderson et al.[8,15] reported that the lowest temperature permitting a good sintering is 400°C for titania membrane. The weight loss in this temperature range (about 142°C) is also apparent in the DTG curve in Figure 4. As can be seen from curve B, the small content of PVA in the gel films may cause a significant change to the thermal behavior. It was also found that the peak caused by the phase change of the reacting titania gel and by the main degradation peak of the reacted PVA, apparently superimposed, formed a plateau from 155 to 420°C. The peak of the maximum phase transformation rate of the anatase was around 400°C. When the PVA/TiO_2 ratio was over 9.36 wt%, there was no sharp transformation to the anatase crystalline phase. For the pure titania gel film, the final weight loss was 16.7 wt%. This result agrees with published research.[19] The total mass of calcination loss was about

4 $\sim$ 5 wt% PVA-titanium composite gel (not shown) as the content of PVA in the film increased with 9.36 wt% PVA/TiO_2. As can be seen from Figure 5, the other transition peak for the higher PVA content of gels occured at 626 and 872°C. In comparison with the DTG curve, the endothermic peak was higher than 872°C, indicating a limited loss of weight in some composite films. The endothermic phenomenon might be attributed to the evaporation of residual organic carbon in the films.

Figure 6 shows the x-ray diffractograms for the pure and composite gel films both at room temperature and at 400°C. Characteristically, diffraction peaks at $2\theta = 25.2$ (101), 37.8 (004), 47.8 (200), and 54.7 (211) correspond to the anatase. The major peak is the (101) plane of the anatase, as shown in Figure 6. It is clear that the uncalcined composite gel films had some titania crystalline phase in it. Although the PVA content was increased, the intensity of the diffraction peak resulted in the titania hardly changing at room temperature. The small peak at $2\theta = 30.8$ can be attributed to the (121) reflection of the brookite TiO_2 phase at 400°C. Unfortunately, the main brookite peak, the (120) reflection, was at $2\theta = 25.3$ and could not be resolved from the main anatase peak at $2\theta = 25.2$.

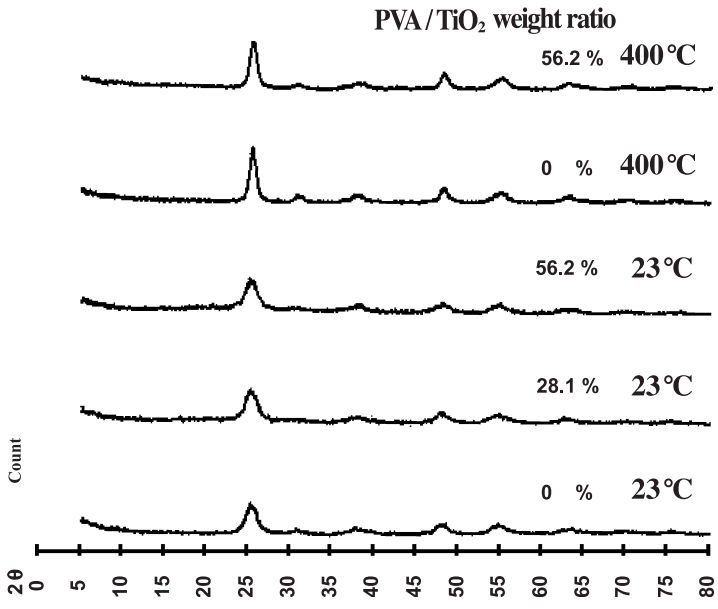


Figure 6. X-ray diffraction intensity curves of the composite gel films at room temperature and 400°C.

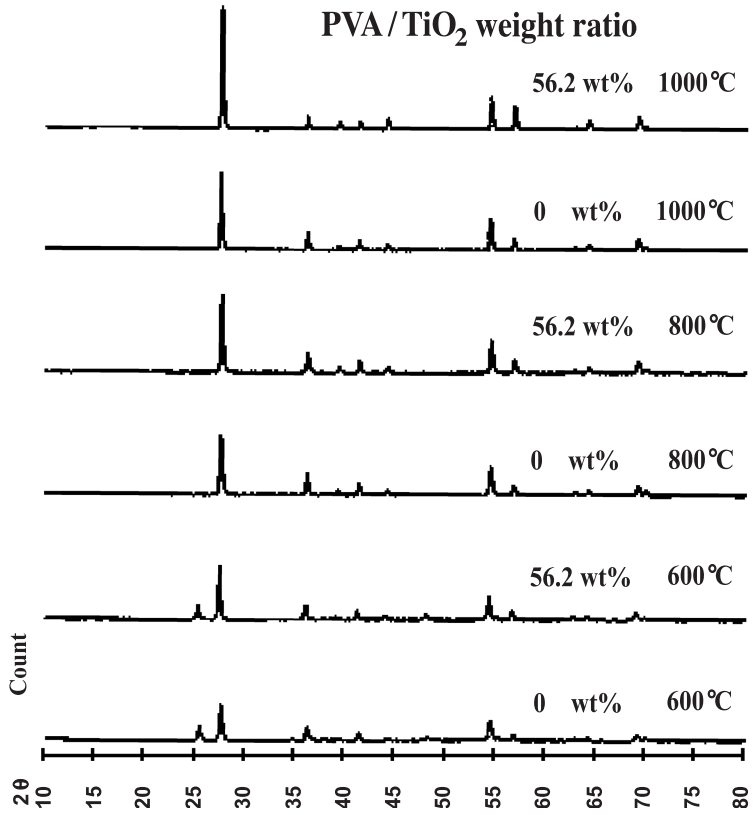


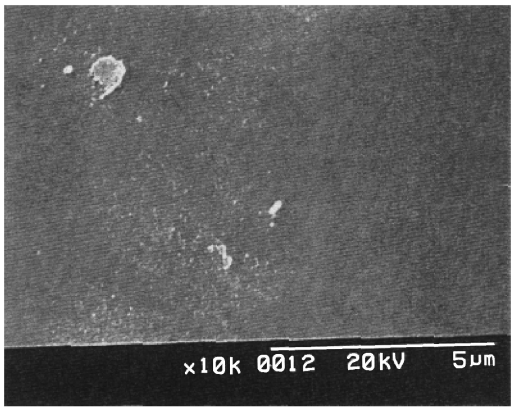
Figure 7. X-ray diffraction intensity curves of the pure titania membrane and the titania membrane with a PVA/TiO_2 ratio of 56.2 wt% at higher calcination temperature (600°C, 800°C, and 1000°C).

The XRD patterns of the pure titania gel film, as well as the composite film (56.2 wt%) after calcination treatment at higher temperature, are given in Figure 7. The titania phase did not completely convert the anatase to rutile and the gels with PVA accelerated the phase transition to rutile at 600°C. It was found that the rutile crystallite size for the PVA gels was larger than that for the pure gels at a calcining temperature higher than 600°C.

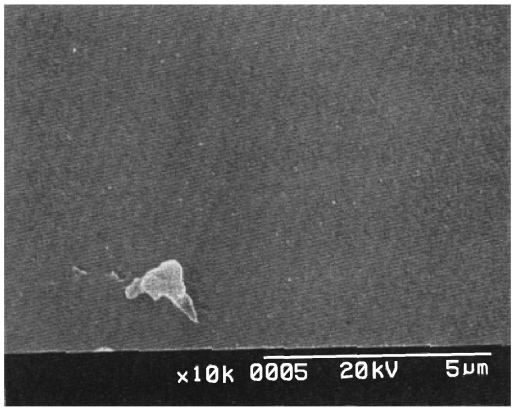
Microstructure Analysis

Experimental observation after calcining shows that these films, except for pure titania gel, are able to form unsupported membranes of a crack-free

layer. Figure 8 (A) (B) show the SEM of an unsupported membrane with $PVA/TiO_2 = 18.7$ wt% after calcining at 400°C for 4 hours. In Figure 8 (A), the surface morphology shows no pinholes or craze. In Figure 8 (B), the fracture cross-section morphology has a uniform structure in general. As can be seen from the thermal analysis, the burn-out of the PVA additives was almost complete at temperatures below 400°C. It is known that the



A



B

Figure 8. SEM photographs of the surface (A) and fractured cross-section (B) of an unsupported membrane with $PVA/TiO_2 = 18.7$ wt% after calcining at 400°C for 4 hours.

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slow pore growth for these anatase titania membranes at a calcining temperature higher than 400°C is caused by the normal sintering process, e.g., the forming of necks between crystallites because of surface and volume diffusion. The microstructure of the inorganic membranes was studied by using different quantities of PVA for 4 hours at 400°C. The average pore diameter (4V/S) by using the BJH adsorption method was 50.9, 50.4, 48.9, 58.0, and 76.0 Å for the PVA/TiO_2 composition 0.0, 9.36, 18.7, 28.1, and 56.2 wt%, respectively. Generally, the pore size increased with the organic concentration rising after the film calcined. In the present measurements, a small decrease in the pore diameter was exhibited when a small quantity of PVA was added. The pore size distribution can be calculated from the isotherm desorption by applying the Kelvin equation and using the BJH method. The various pore size distribution curves for the films with different PVA additions are shown in Figure 9. The results show

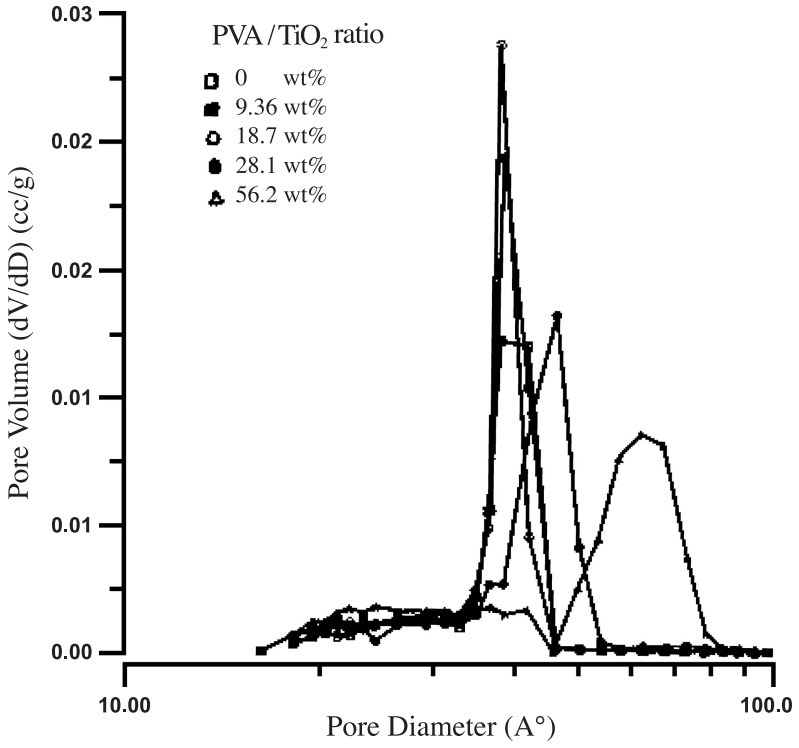

Figure 9. Pore size distribution curves for the membrane with various PVA additions after calcining at 400°C for 4 hours.

that the pore size distribution peaks become sharper and more symmetrical with the PVA/TiO_2 ratio increasing up to 18.7 wt% and pore diameters less than 50 Å. Two reasons for this result should be considered: 1) PVA is linearly molecular with a good flexibility of its main chain; and 2) the pores that are formed from the titania gel are strong. Thus, the smaller quantity of PVA should fill the formed pores, leading to a sharper distribution of the pore sizes, and so they have a similar pore diameter upper limit. As can be seen from Figure 9, the structure greatly changed due to the disrupted pores of the titania gel formed when the PVA content increased significantly. The specific surface area by using BET method was 76.15, 84.75, 84.68, 82.63, and 99.19 m^2/g for the PVA/TiO_2 composition 0.0, 9.36, 18.7, 28.1, and 56.2 wt%, respectively.

CONCLUSIONS

The preparation and property of the unsupported titania membrane were studied. The following results were drawn. 1) The exothermic reactions of the composite gel film occurred when the calcination temperature was lower than 150°C. It is likely that the titania gel and the PVA underwent a dehydration reaction. 2) The anatase phase transition to rutile can be accelerated at a higher PVA/TiO_2 ratio. 3) Treated at 400°C, a small quantity of PVA is effective in reducing the pore size of the films until the PVA/TiO_2 ratio reaches 18.7 wt%.

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