Nanostructured titania membranes with improved thermal stability

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Nanostructured titania membranes have received significant attention in recent years because of their unique characteristics such as high water flux, semiconductance, photocatalysis, and chemical resistance over other membrane materials including γ-alumina, silica and zirconia [1, 2]. The potential applications of titania membranes include ultrafiltration processes and catalytic/photocatalytic membrane reactor systems for liquid and gas separations [3, 4]. However, their practical applications are limited due to the reduction of porosity and surface area at the elevated temperatures.

Hydrothermal process is a low temperature crystallization method, which can produce thermally stable crystalline titania particles [5]. Although hydrothermal process has been used as an independent process to produce ultrafine crystalline oxide particles, this process can be also combined with sol-gel process to promote crystallization of sol-gel products under mild conditions. In this work, hydrothermal process was combined with sol-gel process to improve the thermal stability of titania membranes.

Titania sol was prepared by hydrolysis and condensation of titanium isopropoxide (TTIP, $Ti(OC_3H_7)_4$, 97%), followed by peptization [6]. The TTIP was first dissolved in anhydrous ethyl alcohol at a C_2H_5OH/TTIP molar ratio of 5. Hydrolysis and condensation were conducted at room temperature, by adding the mixed solution slowly into distilled water up to an H_2O/TTIP molar ratio of 200. The white precipitates were centrifuged and washed with distilled water. After redispersing the precipitates in the certain amount of water, a 1 M HNO_3 solution was added to the white precipitates to attain a $[H^+]/[Ti]$ molar ratio of 0.3–0.5. Then, the solution was refluxed at 80 °C for 12 hr. For hydrothermal treatment, the peptized sol was transferred into Teflon beaker in the metal jacket (autoclave) and the autoclave was aged at 135 °C for 12 hr. Unsupported titania membranes were prepared by pouring peptized sol and hydrothermally treated sol into petri dishes, followed by drying under the controlled atmosphere. The dried membranes were further heat treated at 450 °C for 2 hr and 600 °C for 2 hr.

The specific surface area(SSA), pore volume, and pore size distribution (PSD) of the titania membranes were obtained by nitrogen-gas adsorption/desorption at 77 K (ASAP 2020, Micromeritics). The SSA was determined by the multipoint Brunauer–Emmett–Teller (BET) method, using the adsorption data in the relative pressure (P/P_0) range 0.05–0.25. The PSD was calculated from the desorption isotherms. The Barrett–Joyner–Halender (BJH) method, with cylindrical pore size calculated from the Kelvin equation, was used in data processing. X-ray diffractometry (XRD; D5000, Siemens) was used to identify crystallinity, with Ni-filtered CuKα radiation, over the 2θ range from 20 ° to 60 °.

The phase composition of unsupported titania membranes from peptization and hydrothermal process were studied as a function of calcination temperature (Fig. 1). Both membranes already exhibited anatase peaks before calcination, because the amorphous hydrous gels gradually developed into crystalline titania with further hydrolysis/condensation reactions during peptization or structural rearrangement under hydrothermal conditions [7]. After calcination at 450 °C for 2 hr, both membranes maintained anatase phase. However, the titania membranes from peptization started to exhibit a rutile phase after calcination at 600 °C, whereas those from hydrothermal process maintained the anatase phase. This result indicates that hydrothermal process retarded the anatase-to-rutile phase transformation of the membranes.

For a comparison of the pore structures of the titania membranes, their nitrogen adsorption isotherms were studied and presented in Fig. 2. According to BDDT classification [8], all isotherms are of type IV with a hysteresis loop, indicating the presence of mesopores. Also, the shape of hysteresis loop is the same as type H3. The hysteresis loop shifts to the right as the calcination temperature increases, indicating pore growth. Fig. 3 shows the PSD of the titania membranes, calculated

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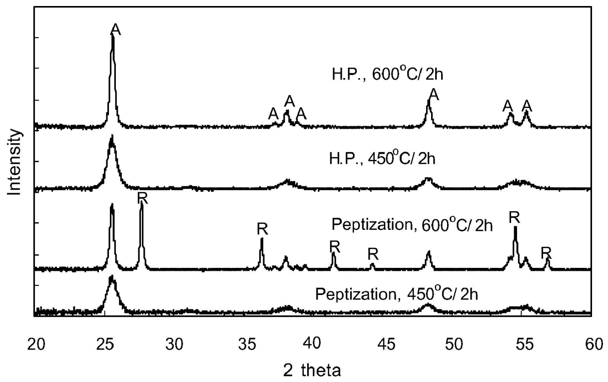

Figure 1 XRD patterns of titania membranes from peptization and hydrothermal process after calcination at 450 °C for 2 hr and 600 °C for 2 hr. (A: anatase, R: rutile)

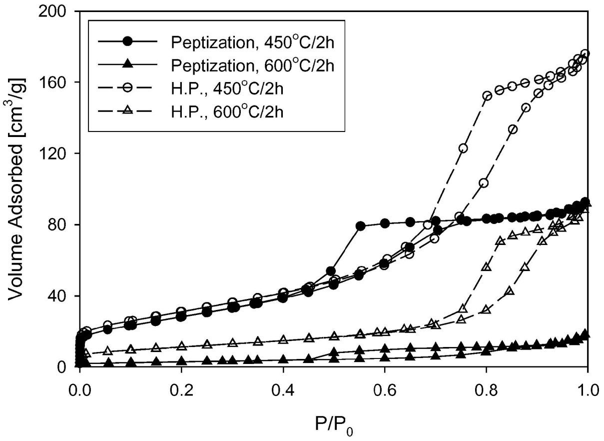

Figure 2 Isotherms of titania membranes from peptization and hydrothermal process after calcination at 450 °C for 2 hr and 600 °C for 2 hr.

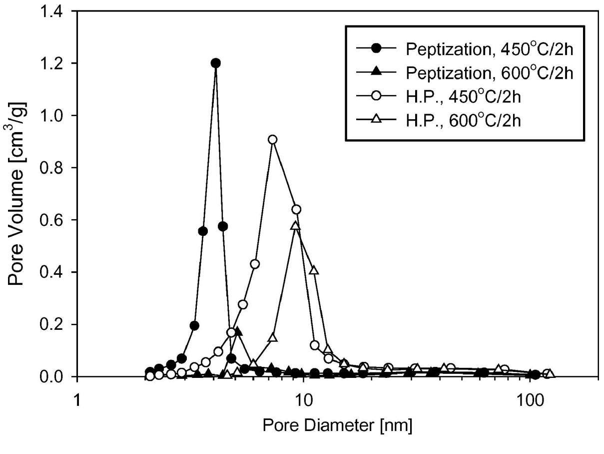

Figure 3 Pore size distributions of titania membranes from peptization and hydrothermal process after calcination at 450 °C for 2 hr and 600 °C for 2 hr.

TABLE I Comparison of pore structure data of titania membranes from peptization and hydrothermal process after calcinations at 450 °C for 2 hr and 600 °C for 2 hr

	SSA (m^2/g)	Pore volume (cm^3/g)	Porosity (%)
Membranes from peptization			
After calcination at 450 °C/2 hr	103.3	0.136	34.3
After calcination at 600 °C/2 hr	10.4	0.022	8.2
Membranes from hydrothermal process			
After calcination at 450 °C/2 hr	112.9	0.257	46.2
After calcination at 600 °C/2 hr	40.8	0.127	30.8

from the desorption branch of the isotherms presented in Fig. 2. After calcination at 450 °C for 2 hr, the membranes from peptization have a narrow PSD with 3–5 nm pore diameters, while those from hydrothermal process have a wider PSD in the range from 3–12 nm. This is attributed to the difference of primary particle sizes. When the titania membranes were calcined at 600 °C for 2 hr, they showed different behavior. The membranes from peptization lost most of their porosity, mainly due to the grain growth from the phase transformation of anatase to rutile. On the contrary, the membranes from hydrothermal process maintained pore structures, shifting to larger pore sizes, indicating pore growth by crystallite growth.

The pore structure data of the titania membranes from peptization and hydrothermal process were presented in Table I. After calcination at 450 °C for 2 hr, the BET surface areas of both membranes were similar in the range of 103–113 m^2/g. However, after calcination at 600 °C for 2 hr, the titania membranes from peptization showed a big decrease in SSA that is attributed to the phase transformation from anatase to rutile, resulting in the collapse of pore structures. For the titania membranes from hydrothermal process, the SSA decreased relatively slowly, maintaining the anatase phase. This decrease is attributed to the crystallite growth only.

The pore volume and porosity of the titania membranes showed different behavior upon calcination. The pore volume of the membranes from peptization decreased rapidly from 0.136 cm^3/g after calcination at 450 °C to 0.022 cm^3/g after calcination at 600 °C, resulting in porosity decrease from 34.3 to 8.2%. In contrast, the pore volume of those from hydrothermal process was slowly reduced from 0.257 to 0.127 cm^3/g. This result shows that the membranes from hydrothermal process have better thermal stability compared to the membranes from peptization.

In summary, unsupported titania membranes were prepared from peptized sol and hydrothermally processed sol. After calcination at 450 °C for 2 hr, the membranes from peptization have a narrow PSD with 3–5 nm pore diameters, while those from hydrothermal process have a wider PSD in the range from 3–12 nm. Upon calcination at 600 °C for 2 hr, however, the membranes from peptization lost most of pore structures attributed to the phase transformation from anatase to rutile. For the membranes from hydrothermal process, the PSD shifts to larger pore sizes with increasing calcination temperature from 450 to 600 °C. This is attributed to the crystallite growth, maintaining anatase phase. Hydrothermal process was shown to be an effective means to prepare thermally stable titania membranes.

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