열적 안정성이 향상된 나노구조 티타니아막의 제조

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Synthesis of Nanostructured Titania Membranes with Improved Thermal Stability

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1. Introduction

Nanostructured titania membranes have received significant attention in recent years because of their unique characteristics such as high water flux, semi-conductance, 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 for liquid and gas separations and catalytic/photocatalytic membrane reactor systems[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.

2. Experimental

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 the 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℃ for 12h. For hydrothermal treatment, the peptized sol was transferred into Teflon beaker in the metal jacket(autoclave) and the autoclave was aged under hydrothermal conditions. Unsupported titania membranes were prepared by pouring peptized sol and hydrothermally treated sol in the petridishes. The phase composition and pore structures of titania membranes were characterized by XRD and N_2 porosimetry.

3. Results and Discussion

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 phase before calcination, as the amorphous hydrous gels gradually developed into crystalline titania with further hydrolysis/condensation reactions during peptization or structural rearrangement under hydrothermal conditions. After calcination at 450℃, both membranes maintained anatase phase. However, the titania membranes from peptization started to exhibit rutile phase after calcination at 600℃, whereas those from hydrothermal process maintained the anatase phase. This result indicates that hydrothermal process retarded the anatase-to-rutile phase transformation.

For a comparison of the pore structures of the titania membranes, their nitrogen adsorption/desorption isotherms were studied and presented in Fig. 2. According to BDDT classification, all isotherms shown in Fig. 2(a) 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. After calcination at 450℃, the membranes from peptization have a narrow pore size distribution (PSD) with 3-5 nm pore diameters, while those from hydrothermal process have a wider PSD in the range of 3-12 nm. This is attributed to the difference of primary particle sizes. When the titania membranes were calcined at 600℃, 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 sintering (crystallite growth). This result shows that the membranes from hydrothermal process have better thermal stability compared to the membranes from peptization.

4. Acknowledgements

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5. References

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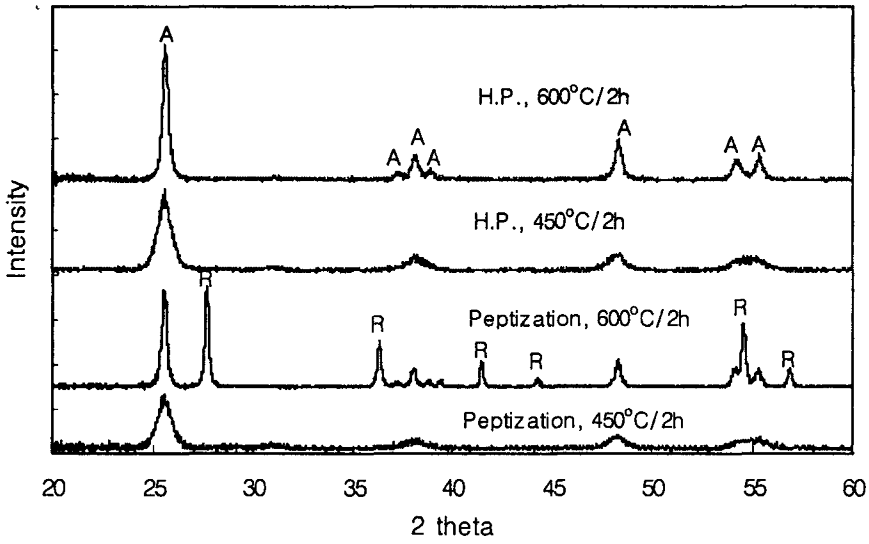

Fig. 1. XRD patterns of the unsupported titania membranes from peptization and hydrothermal process after calcination.
(A: Anatase, R: Rutile)

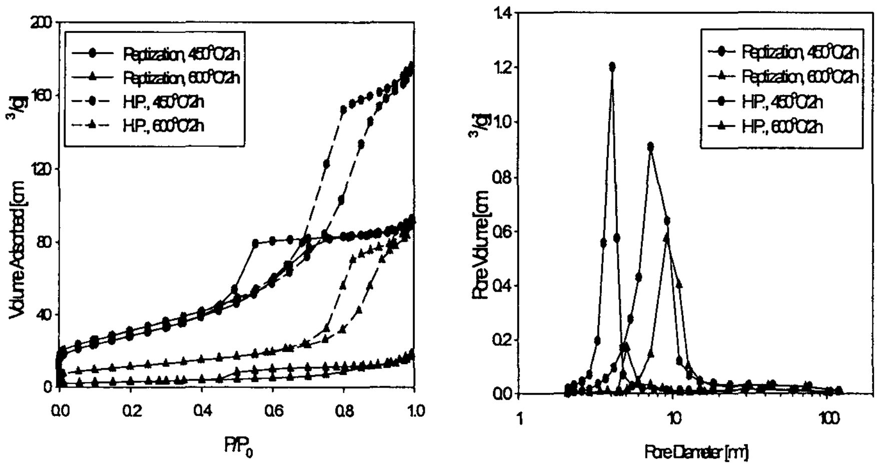

Fig. 2. Isotherms(a) and PSDs(b) of the unsupported titania membrane from peptization and hydrothermal process after calcination.