

## Fabrication and microstructure of the Fe doped TiO<sub>2</sub> composite membranes with ultrafine pores

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## 미세기공을 가지는 철이 첨가된 티타니아 복합여과막 제조 및 미세구조

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**Abstract** Ceramic membrane consisting of an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support and Fe doped TiO<sub>2</sub> top layer was prepared by the sol-gel method. The supported Fe doped TiO<sub>2</sub> top layer was made by dipcoating the support in a mixed sol. The microstructure of the composite membranes was studied by SEM after calcination at 550~850°C. After sintering at 650°C for 1 hr., the average particle diameter of the Fe doped TiO<sub>2</sub> top layer was ~40 nm. The supported Fe doped TiO<sub>2</sub> composite membranes exhibited much higher heat resistance than the TiO<sub>2</sub> membrane. The Fe doped TiO<sub>2</sub> composite membrane retained a crack-free microstructure and narrow particle size distribution even after calcination up to 650°C.

**요 약** 알파 알루미나와 철이 첨가된 티타니아 최종층으로 구성된 세라믹 여과막을 졸-겔 방법으로 제조하였다. 철이 첨가된 지지 티타니아 복합여과막은 지지체를 혼합졸에 침지하여 제조하였다. 복합여과막을 550°C에서 850°C까지 열처리온도에 따르는 미세구조 변화를 주사전자현미경으로 조사하였다. 650°C에서 1시간 소결한 경우, 철이 첨가된 티타니아 복합여과막의 평균입자 크기는 약 40 nm이었다. 철이 첨가된 티타니아 복합여과막은 티타니아 복합여과막보다 열적 저항성이 우수하였다. 철이 첨가된 티타니아 복합여과막은 650°C까지 균열이 없는 미

세구조와 좁은 입도분포를 유지하였다.

## 1. Introduction

Ceramic membranes are technically important in separation and filtration as well as in catalytic reactions, because of some unique characteristics in comparison with polymeric membranes. They have high thermal and chemical stability, long life and good defouling properties in their application, and they can have catalytic properties [1]. These properties have made these membranes desirable for industrial applications in food, pharmaceutical and electronic industries currently utilizing polymeric, organic and metal membranes [2].

The potential application of the ceramic membranes at elevated temperatures requires more study and further improvement in the ceramic membrane preparation. The sol-gel approach [3] is considered to be the most practical one for ceramic membranes synthesis.

A ceramic membranes being thermally stable at a certain temperature means that the properties (chemical composition, phase structure, mechanical strength and most importantly, the pore structure) of the membrane remain unchanged or change negligibly at that temperature for a period of the membrane remain unchanged or negligibly change at that temperature for a period of time comparable to the actual application time [4].

For the ceramic membrane top layers pre-

pared by the sol-gel approach, the smallest possible pore size is determined by the primary particle size in the colloid suspension [5].

Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by sol-gel method, etc [6]. In the sol-gel techniques, ultrafine particles of a few nm in diameter can be prepared by polycondensation or redox reactions of hydrolysis and condensation of metal alkoxides. After treatment with a peptizing agent such as acid and optionally with a viscosity modifier, the slip is deposited on the porous support by the dipping or slip casting procedure [7]. This smallest pore size is formed by drying and calcining the gel at a relatively low temperature. In most cases the pore size of a membrane top layer increases with the firing temperature. The pore growth with the temperature increase has been confirmed in top layers of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> [8,9]. Consequently, it is difficult to keep the pore diameter of a ceramic membrane top layer smaller than 50 nm at firing temperatures higher than 1000°C. In the limited studies related to the thermal stability of ceramic membranes, Burggraaf and Keizer and their coworkers [6,8] determined the pore size of some ceramic membrane top layers at different sintering temperatures. Kumar et al. [10] studies the phase transformation behavior of both unsupported and supported titania membranes. For the sinter-

ing time of 8 hrs. (in air), titania membranes underwent anatase to rutile phase transformation in the temperature range of 550~600°C.

The objective of the study is to report the fabrication and microstructure analysis of Fe doped TiO<sub>2</sub> composite membranes with ultrafine pores. We study microstructure changes of mixed-oxide membranes with firing. In particular, we investigate the effect of the second component on the thermal stability of mesoporous membranes. The thermal stability of the membranes was evaluated by measuring the change of the mean particle diameter of membranes after sintering at different temperatures from 550°C to 850°C.

## 2. Experimental

Supported Fe doped TiO<sub>2</sub> membranes were prepared using sol-gel method. Figure 1 shows the preparation procedures. These sols were prepared via hydrolysis and condensation of mixed-alkoxide precursors. Titanium alkoxide solution containing Fe was prepared by dissolving 3.23 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 50 ml of H<sub>2</sub>O and adding titanium alkoxide to the solution. Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> was used as starting material. Titania sol (0.16 mol) was prepared by adding titanium tetra-isopropoxide (Aldrich) to water and peptizing the solution with hydrogen chloride at ~50°C under refluxing conditions. This solution was stirred for 2 hrs. to ensure complete mixing. The percentages of Fe<sub>2</sub>O<sub>3</sub> in

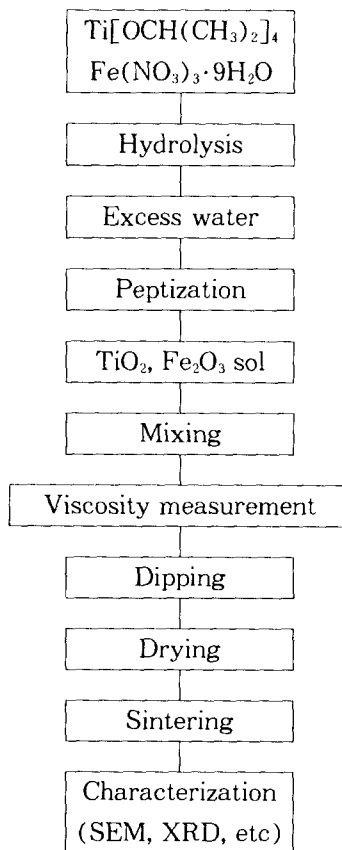


Fig. 1. Preparative procedure of Fe doped TiO<sub>2</sub> composite membranes by destabilization colloidal solution process.

total metals were varied from 5 mol% to 16.5 mol%. A PVA solution, prepared by dissolving 5 g of PVA (Aldrich, MW=7200) in 95 ml water, was used as a DCCA for making supported ceramic membranes. The support was immersed in mixed sol for 6 to 60 sec. The concentration of the sol increased as absorbing water and mixed gel were deposited in the pores near the surface of the support. After drying at 45°C in dry oven for 24 hrs., the samples were heated at

550~850°C temperature and then they were furnace cooled. The particle sizes were examined by the dynamic light scattering (Ar laser, Nicomp 370) method. The surface morphology of membranes after heat treatments at 550°C to 850°C were observed with a scanning electron microscope (SEM, Hitachi S-420). The linear intercept method was used to determine the mean particle diameter.

### 3. Results and discussion

The important parameters in the formation of gel layer are sol concentration, coating time, the pore size of the support and the type and amount of the acid used to peptize the sol [8]. Since particle size and pore size are directly related, the slip used as the membrane precursor needs to contain well dispersed particles of the uniform size.

The formation of clear solutions in titania requires the presence of HCl acids [11]. The stability of those clear solutions is a function of the acid/alkoxide ratio and there is a window for the most stable solution at 0.16~0.34 mol of acid per mole of alkoxides. The average mean particle size of mixed-sol was less than about 15 nm. There was no significant increase in the particle diameter after 7 day aging and the sols were transparent all the time, so the sol was stable. Transmission electron microscopy (TEM) measurement was performed to study the dispersion of particles in mixed-sol. Figure 2 shows the mixed sol particles are well dispersed in solu-

tion.

All characterization results are obtained from the multi-layer supported membrane. The sol-gel coating is very sensitive to the support characteristics and frequently yields defect film. In the slip casting method, a porous support is usually made by conventional ceramic processing technique to provide a rigid structure with relatively large pore size for slip deposition. Figure 3 shows the microstructure the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support after firing at 1200°C for 1 hr in the air. The shape of

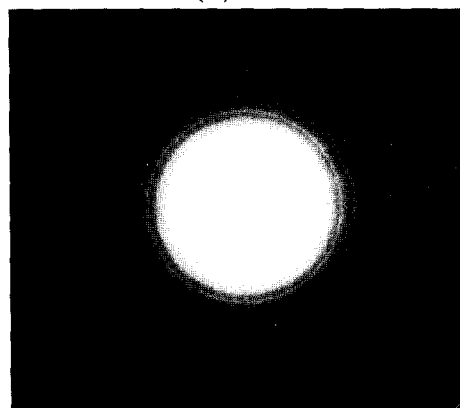
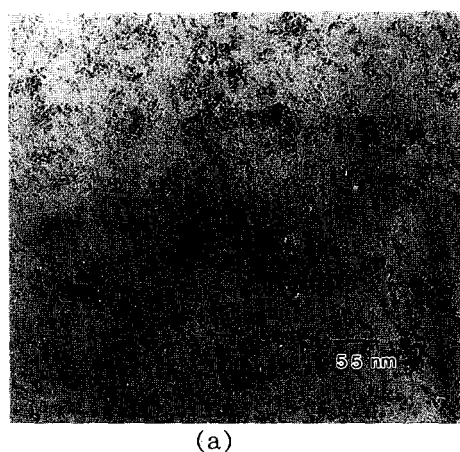


Fig. 2. TEM micrograph and diffraction pattern of the mixed sol with 10 mol% Fe<sub>2</sub>O<sub>3</sub>.

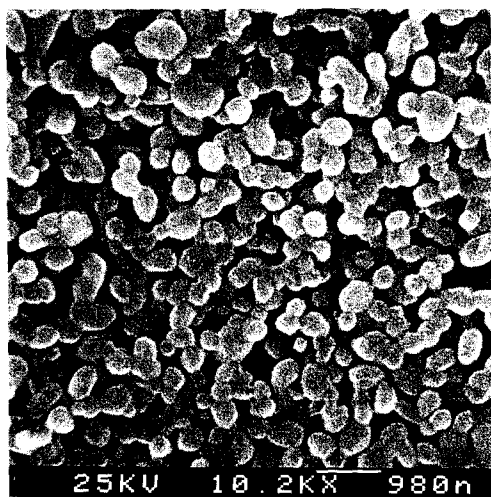


Fig. 3. SEM of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support sintered at 1200°C for 1 hr in the air.

the particles seems to be spherical and the particle size distribution was narrow. Polyvinylalcohol (molecular weight 7200 g/mol) is added to the mixed-oxide precursor to improve this sol-gel coatings.

For mixed sols the forming mechanism of supported thin films could be described by slip casting [12]. Due to the capillary forces, water is sucked into the pores of the support. The concentration of mixed sol at the entrance of the pores increases and gelation of the sol occurs. After a certain period (in the order of seconds), the support is taken out and the gel layer is dried and calcined. This mechanism is characterized by a linear increase of the layer thickness,  $L$ , as a function of the square root of dipping time,  $t$ , according to [12].

$$L = 2 \gamma \cos \beta / \eta K(t)^{1/2} \quad (1)$$

where  $\gamma$  is the surface tension (Nm<sup>-1</sup>),  $\beta$  is the contact angle between the liquid and the solid surface,  $K$  is a constant,  $\eta$  is the viscosity of the solution. The viscosity of the dipping solution increases by the addition of PVA, leading to a lower slip casting rate. Figure 4 shows the thickness of calcined composite membrane layer with 30 sec dipping was  $\sim 1 \mu\text{m}$ .

Figure 5 illustrates the particle size increase with temperature in Fe doped TiO<sub>2</sub> composite membrane. The effect of Fe<sub>2</sub>O<sub>3</sub> on microstructural change in TiO<sub>2</sub> gels with temperature during the presintering process has been investigated. It should be noted here that the addition of the Fe<sub>2</sub>O<sub>3</sub> into the TiO<sub>2</sub> gel was conducted at the first stage of mixing two alkoxides, so that, after the sol-gel transformation, Fe<sub>2</sub>O<sub>3</sub> should be distributed uniformly throughout the TiO<sub>2</sub> network. No other local concentration of the Fe<sub>2</sub>O<sub>3</sub> in

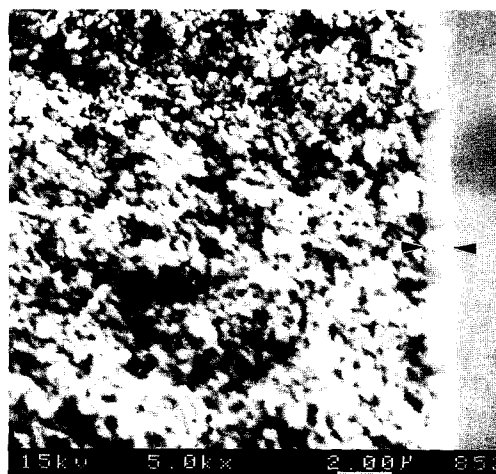


Fig. 4. SEM of the cross section of the Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composite membrane with 30 sec dipping.

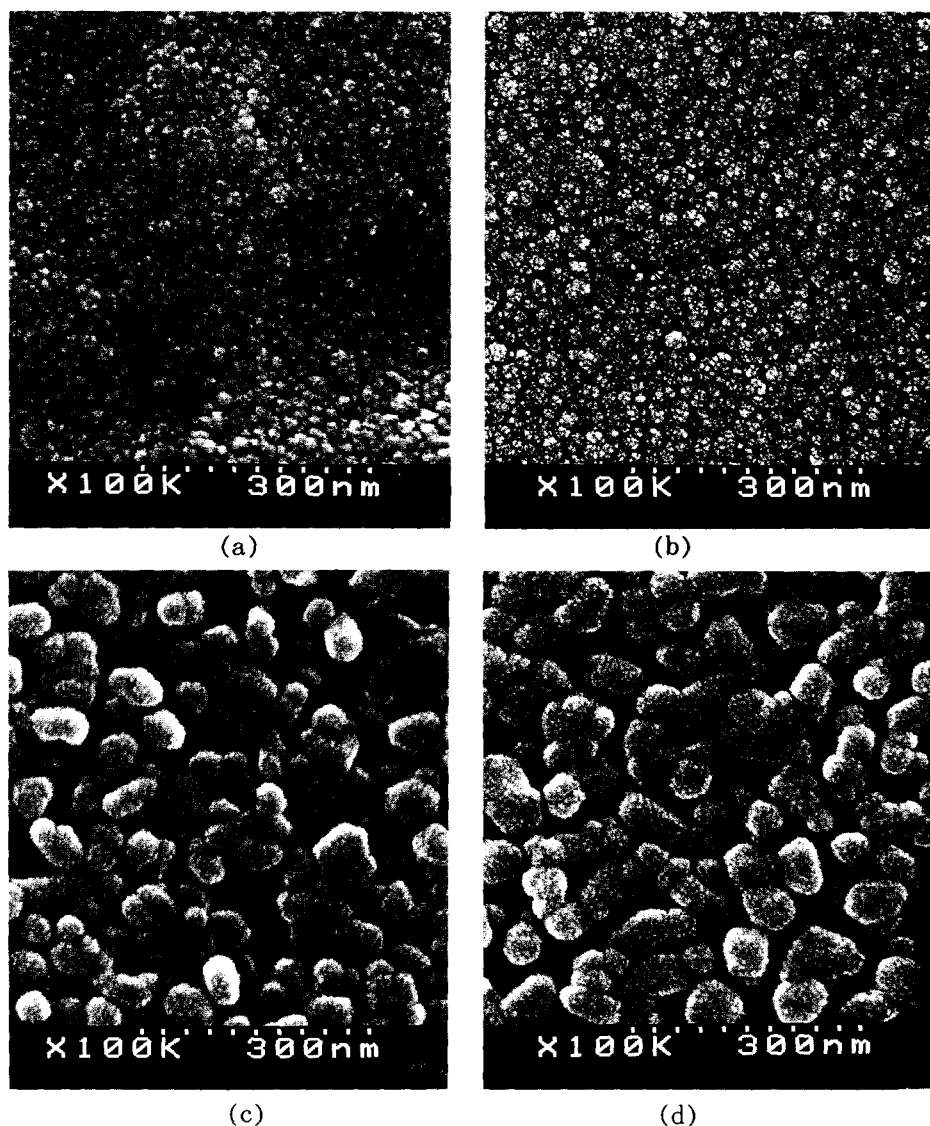


Fig. 5. Microstructure of the Fe doped TiO<sub>2</sub> composite membrane sintered at (a) 550°C, (b) 650°C, (c) 750°C and (d) 850°C.

the TiO<sub>2</sub> gel has been assumed. The shape and size of the particles were studied by SEM. The surface of as-deposited membranes is smooth and flat, i.e., neither cleavages nor cracks are observed. The mean particle size was determined by counting the

number of particles in a given distribution became broader with increasing calcination temperature. This grain growth at low temperatures may still be caused by the surface energy reduction due to the extremely small particle size ( $\leq 15$  nm) [13]. The mean

particle diameter of the TiO<sub>2</sub> membrane with 10 mol% Fe<sub>2</sub>O<sub>3</sub> was increased from ~20 to ~80 nm with increased calcination temperature from 550 to 850°C. After sintering at 550°C for 1 hr., the pores size of Fe doped TiO<sub>2</sub> composite membranes was less than 10 nm. The mean pore diameter of TiO<sub>2</sub> membranes increases beyond the mesoporous region at the temperature higher than 600°C for pure TiO<sub>2</sub>. This can be increased to 650°C for TiO<sub>2</sub> membranes doped with 5~16.5 mol% Fe<sub>2</sub>O<sub>3</sub>. This 50°C increase in the critical temperature is important in the application of mesoporous ceramic membranes in high temperature applications.

### 3. Summary

Thin layers of Fe doped TiO<sub>2</sub> of 0.2 to 1 μm in thickness could be coated on the porous α-Al<sub>2</sub>O<sub>3</sub> support tubes by the dip-coating method. The membrane consists of an alumina support and Fe doped TiO<sub>2</sub> top layers with mean particle diameter of 20 to 80 nm. The sols prepared by destabilization of colloidal solutions, in which the hydrolyzed precipitates of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> were the nanoparticle sols with the average particle size less than 15 nm. The forming mechanism of supported Fe doped TiO<sub>2</sub> composite membranes can be described by the slip casting mechanism. With addition of PVA, mixed-oxide gels can be dried and calcined to form a Fe doped TiO<sub>2</sub> composite membrane. The mean particle size of the Fe doped TiO<sub>2</sub> composite membranes increases

with firing temperature. The mean particle diameter increases during heat treatment which is consistent with the typical phenomenon observed for a sintering process. Whether it is sintering-caused or crystallization-induced, particle growth has been slightly retarded by mixing 5~16.5 mol% Fe<sub>2</sub>O<sub>3</sub> into the TiO<sub>2</sub> membrane. The critical temperature of TiO<sub>2</sub>, at which the mean pore size of the membrane shifts from the mesoporous region to macroporous region, increases by about 50°C as a result of introducing 5~16.5 mol% Fe<sub>2</sub>O<sub>3</sub>. The Fe doped TiO<sub>2</sub> composite membranes retained a crack-free microstructure and narrow particle diameter distribution even after calcination up to 650°C.

### References

- [ 1 ] Y.S. Lin and A.J. Burggraaf, *J. Am. Ceram. Soc.* 74(1) (1991) 219.
- [ 2 ] M. Cheryan, *Ultrafiltration Handbook*, (Technomic Publishing Company, Lancaster, PA, 1986).
- [ 3 ] A. Larbot, J.P. Fabre, C. Guizard and L. Cot, *J. Mem. Sic.* 39 (1988) 203.
- [ 4 ] W.D. Kingery, H.K. Bowen and D.R. Uhlmann, *Introduction to Ceramics*, Chap. 8, 10 (Wiley, New York, 1976).
- [ 5 ] R.J.R. Uhlhorn, M.H.B.J. Huis IN'T Veld, K. Keizer and A.J. Burggraaf, *J. Mat. Sci.* 27 (1992) 527.
- [ 6 ] Qunyin Xu and Marc A. Anderson, *J. Am. Ceram. Soc.* 76(8) (1994) 2093.
- [ 7 ] A. Makishima, M. Asami and K.

- Wada, J. *Non-Cry. Sol.* 121 (1990) 310.
- [ 8 ] A.F.M. Leenaars, K. Keizer and A.J. Burggraaf, *J. Mater. Sci.* 19 (1984) 1077.
- [ 9 ] A. Larbot, J.P. Fabre, C. Guizard and L. Cot. *J. Am. Ceram. Soc.* 72 (1989) 257.
- [10] K.M.P. Kumar, V.T. Zaspalis, F.F.M. DeMul, K. Keizer and A.J. Burggraaf, in M.J. Hampden-Smith, W.G. Klemperer and C.J. Brinker (Eds.) (*Better Ceramics Through Chemistry V. MRS, Pittsburgh, 1992*) pp. 499-504.
- [11] B.E. Yoldas, *Ceram. Bull.* 54(3) (1975) 289.
- [12] A.F.M. Leenaars, K. Keizer and A.J. Burggraaf, *J. Colloid Interface Sci.* 105 (1985) 27.
- [13] Waldron and Daniell, *Sintering*, (Heyden, London, U.K., 1978) p. 4.
- [14] K.N.P. Kumar, V.T. Zaspalis, F.F.M. De Mul, K. Keizer and A.J. Burggraaf, *Mat. Res. Soc. Symp. Proc.* (1992) 271.
- [15] C.J. Brinker, R. Sehgal, S.L. Hietala, R. Deshpande, D.M. Smith, D. Loy and C.S. Ashley, *J. Mem. Sci.* 94 (1994) 85.
- [16] C.H. Chang, R. Gopalan and Y.S. Lin, *J. Mem. Sci.* 91 (1994) 27.
- [17] M. Chai, M. Machida, K. Eguchi and H. Arai, *J. Mem. Sci.* 96 (1994) 205.
- [18] K.M.P. Kumar, V.T. Zaspalis, F.F.M. DeMul, K. Keizer and A.J. Burggraaf, *Thermal stability of supported titania membranes (Better Ceramics Through Chemistry V, MRS, Pittsburgh, 1992)* pp. 499-504.