

Fabrication of TiO₂-CeO₂ Composite Membranes with Thermal Stability

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Ceramic membranes of the supported TiO₂-CeO₂ were prepared by dip-coating method on an α -Al₂O₃ porous substrate. The mean pore diameter of an alumina support was 0.125 μ m. The mean particle diameter of TiO₂-CeO₂ top layer varied with firing temperature and ranged from 20 to 85 nm. The thermal stability of the composite membranes was studied from their surface microstructure after calcination at 600-900°C. The supported TiO₂-CeO₂ composite membranes exhibited much higher heat resistance than the TiO₂ membrane.

Key words : Composite membrane, TiO₂-CeO₂, Dip-coating, Thermal stability

I. Introduction

Inorganic membranes made from inorganic polymers and ceramics have been proposed for liquid and gas separation applications. The interest in utilizing such membranes in separations has increased because inorganic membranes exhibit unique physical and chemical properties that are only partially or not shown by organic membranes. These properties have made these membranes desirable for industrial applications in food, pharmaceutical and electronic industries currently utilizing polymeric, organic and metal membranes¹.

Inorganic membranes are known to be much more thermally stable than polymeric membranes. A ceramic membrane 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 negligibly change at that temperature for a period of time comparable to the practical application time².

A systematic study on the thermal stabilities of the ceramic membranes is needed in order to improve the understanding of the mechanism of pore structure change of these ceramic membranes at elevated temperatures. Thermally, chemically, and mechanically stable materials with controlled porosities are required in such technology areas as gas separation, catalysis, membrane reactors³. Often such applications require rather exquisite control of pore size and pore size distribution combined with processability, e.g., the ability to prepare ultrathin supported films within tubular support⁴.

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. Since particle size and pore size are

directly related, the slip used as the membrane precursor needs to contain well dispersed particles of uniform size. Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by sol-gel method, etc⁵. In the sol-gel techniques, ultrafine particles of a few nm in diameter can be prepared by polycondensation or redox reactions of titanium salts or hydrolysis and condensation of titanium alkoxides. After treatment with a peptizing agent such as an acid and optionally with a viscosity modifier, the slip is deposited on the porous support by the dipping or slip casting procedure⁶.

In this study, we have developed heat resistant microporous ceramic membranes of TiO₂-CeO₂ by destabilization of colloidal solution process. The thermal stability of the membranes was evaluated by measuring the change of the mean particle diameter and microstructure of membranes after sintering at different temperatures from 600°C to 900°C.

II. Experimental

Supported TiO₂-CeO₂ composite membrane was prepared by the sol-gel technique. Fig. 1. shows the preparative procedures. These sols were prepared via hydrolysis and condensation of mixed-alkoxide precursors. Titanium alkoxide solution containing Ce was prepared by dissolving 3.72 g of CeCl₃ · 7H₂O in 100 ml of H₂O and adding titanium alkoxide to the solution (CeO₂ mol%=2.7, 3.8, 5.5, 7.7). The titanium alkoxide used was Ti[OCH(CH₃)₂]₄. Titania sol was prepared by dissolving 2.92 ml of titanium tetra-isopropoxide in 100 ml water. The product was then peptized by adding HCl at 50°C under refluxing conditions. This sol contains mixed-oxide particles which are less than 30 nm in diameter. A PVA solution,

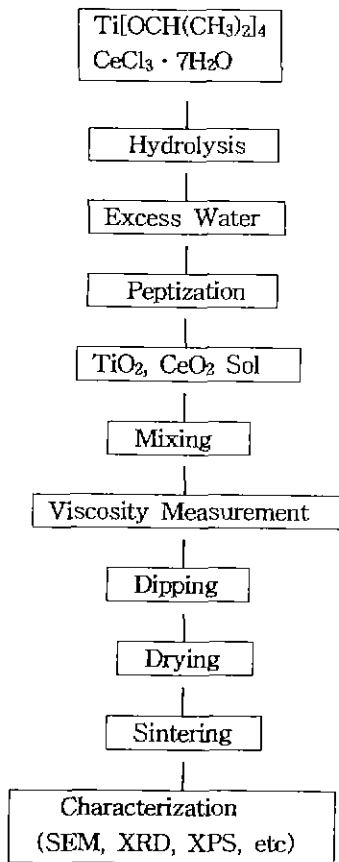


Fig. 1. Preparative procedure of supported $\text{TiO}_2\text{-CeO}_2$ composite membranes by destabilization colloidal solution process.

prepared by dissolving 5 g of PVA (Aldrich, MW=72000) in 95 ml water, was used as a DCCA for making supported ceramic membranes. Tube-shape large pore supports were prepared from α -alumina with a mean particle size $\sim 40 \mu\text{m}$. Each support tube was made by extrusion of the alumina powder in a specially designed mold using an extruder, followed by a controlled heat treatment program. After extrusion, the support have been prepared by the slip casting. The Al_2O_3 powders used were Sumitomo AES-11, which had an average particle size of $0.4 \mu\text{m}$. The final support tubes were 35 mm in outer diameter and 5 mm in thickness with an average pore diameter $\sim 0.125 \mu\text{m}$ and a porosity of $\sim 35\%$. The support was immersed in mixed sol for 5 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 substrate. After drying at 45°C in dry oven for 24 hour, the samples were heated at $600\text{-}900^\circ\text{C}$ temperature and then they were furnace cooled. The sol particle size was determined in situ using dynamic light scattering method (Nicomp 370). The surface morphology and thickness of membranes after heat treatment at 600°C to 900°C were observed with a scanning electron microscope (SEM, Hitachi S-4200). The linear intercept

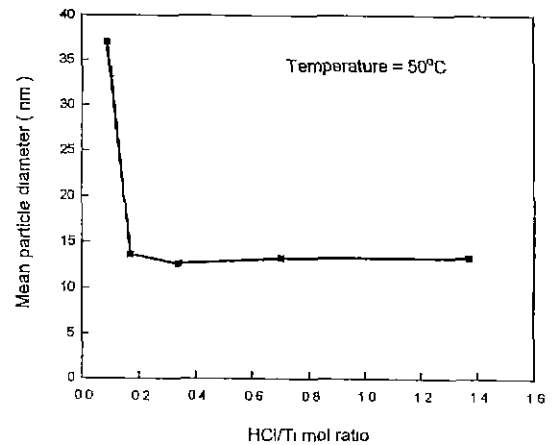


Fig. 2. Mean particle diameter (nm) vs. HCl/Ti mol ratio.

method was used to determine the mean particle diameter. The structure changes were analyzed by X-ray diffraction (Phillips, PW 1825/00) with $\text{CuK}\alpha$ radiation: voltage, 30 kV; and current, 30 mA.

III. Results and Discussion

According to Leenaars and Burggraaf¹⁰, 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. The most important conditions for preparing stable sols include: (1) the dilution degree of the metal alkoxide; (2) the amount of water used for hydrolysis of alkoxide and (3) the peptization conditions.

In this study, the influences of the amount of acid used to peptize the sol on the particle size in the sol were studied. Fig. 2. shows the change of the particle diameter in the sols containing 0.16-1.37 mol HCl per mol Ti with 7 days aging. In these solutions the aggregation of particulates is avoided by introducing at least 0.17 mol of HCl acid. The acid addition alone does not cause the peptization of the slurry. The slurry must be heated above 50°C and held until a clear sol is formed. Particle size was determined in situ using dynamic light scattering analysis. The sol of 0.34 HCl/Ti mole ratio was most transparent and had the smallest mean particle diameter of about 12.6 nm. However, if more than 0.34 mol of acid are used per mole of alkoxide, the stability of the solution is reduced and it turns cloudy after several days to several months, depending on the acid concentration. In the pH range of 1.23 to 1.32, the particle size of TiO_2 sols (0.16 mol/l) increased gradually up to $\sim 25 \text{ nm}$. 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.

The sol-gel coating is very sensitive to support characteristics and frequently yields defect films. The pore size distribution of the $\alpha\text{-Al}_2\text{O}_3$ support can be obtained by

such methods as capillary flow analysis. Fig. 3 and Fig. 4 show the pore size distribution and microstructure of the $\alpha\text{-Al}_2\text{O}_3$ support after firing at 1300°C for 1 hour in air respectively. The average pore diameter of the support was $0.125\ \mu\text{m}$ and the shape of the particles seem to spherical. Polyvinylalcohol (molecular weight $72000\ \text{g/mol}$) is added to the mixed-oxide precursor to improve this sol-gel coatings. This addition results in a less critical and better controllable drying and calcining procedure. The addition of PVA is necessary to make $\text{TiO}_2\text{-CeO}_2$ membranes on supports with pore diameters of $0.125\ \mu\text{m}$ on multi-layer supports. If PVA is no additive, the gel layer could not formation because the sol went through the supports. The lower slip casting rate obtained with dipping solutions containing PVA can be explained by the combined effect of PVA on the viscosity and surface tension of the dipping solution. The viscosity

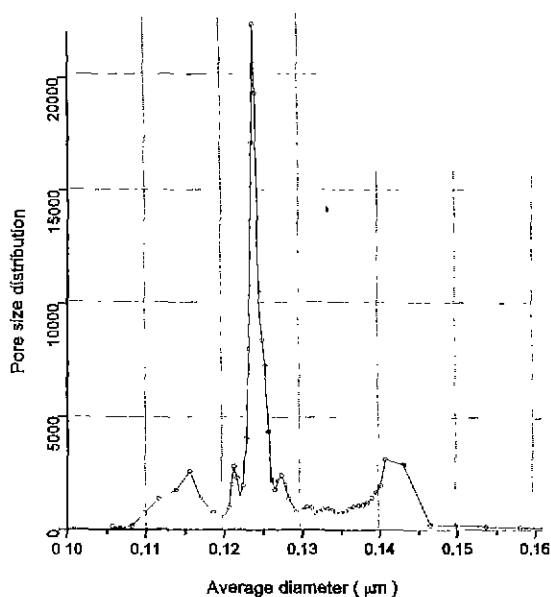


Fig. 3. Pore size distribution of the $\alpha\text{-Al}_2\text{O}_3$.

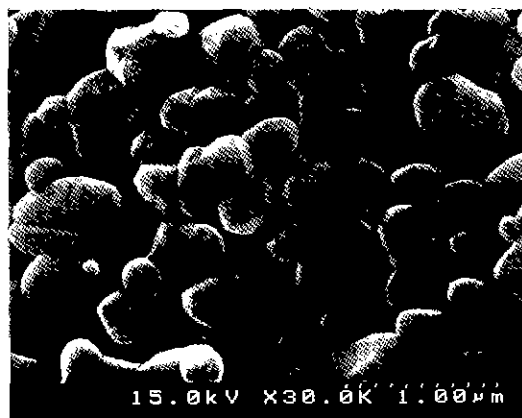


Fig. 4. SEM of the $\alpha\text{-Al}_2\text{O}_3$ support sintered at 1300°C for 1 hour in air.

of the dipping solution increases by the addition of PVA, leading to a lower slip casting rate. However, this would lead to a thicker adherent layer. The observations that the membrane thickness increases linearly with the square root of the dipping time and that the casting rate increases if the sol concentration increases, the pore size of the support decreases or the gelling concentration decreases, are all in accordance with this slip casting model⁹. The thickness of calcined membrane layers increased linearly from ~ 1.4 to $\sim 2\ \mu\text{m}$ with the square root of the dipping time (5-60 sec). With addition of PVA, crack-free supported $\text{TiO}_2\text{-CeO}_2$ mixed-oxide gels were obtained by drying at 45°C for 24 h. The pore morphology of the $\text{TiO}_2\text{-CeO}_2$ composite membrane prepared in this study is also very similar to literature data reported by Cot and coworkers⁹, despite conditions for preparing the titania sols were slightly different. The consistency on the pore morphology of titania membranes prepared by different investigators indicates the high reproducibility of the sol-gel processing for synthesis of the particulate sols. Thin layers of $\text{TiO}_2\text{-CeO}_2$ of $0.2\text{-}2\ \mu\text{m}$ in thickness could be coated on the porous $\alpha\text{-Al}_2\text{O}_3$ support tubes by the dip-coating method.

The pore morphology data for the $\text{TiO}_2\text{-CeO}_2$ composite membranes after heat treatment at different temperatures for 1 hour under air atmospheres are graphically presented in Fig. 5. The shape and size of the particles was studied by SEM. The intercept method was used to determine the mean particle diameter. The average mean particle diameter increased and the mean particle diameter distribution became broader with increasing calcination temperature. The mean particle diameter of the $\text{TiO}_2\text{-CeO}_2$ membrane was increased from 20 to 85 nm with increased calcination temperature from 600 to 900°C . Fig. 6. shows the microstructure of the $\text{TiO}_2\text{-CeO}_2$ membranes after calcination at 600 to 900°C in air. The surface of as-deposited membranes is smooth and flat, i.e., neither cleavages nor cracks are observed. Particles seem to be spherical in shape. The morphology

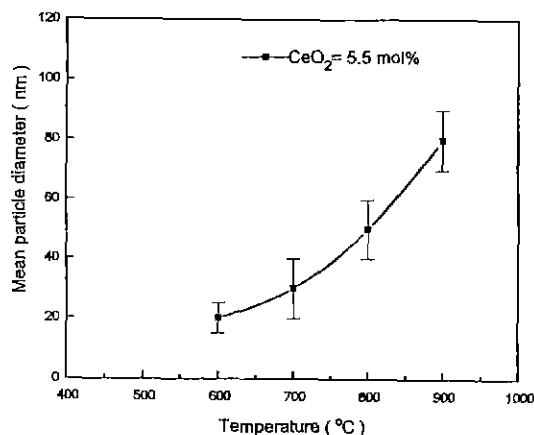


Fig. 5. Mean particle diameter (nm) vs. heat treatment temperature.

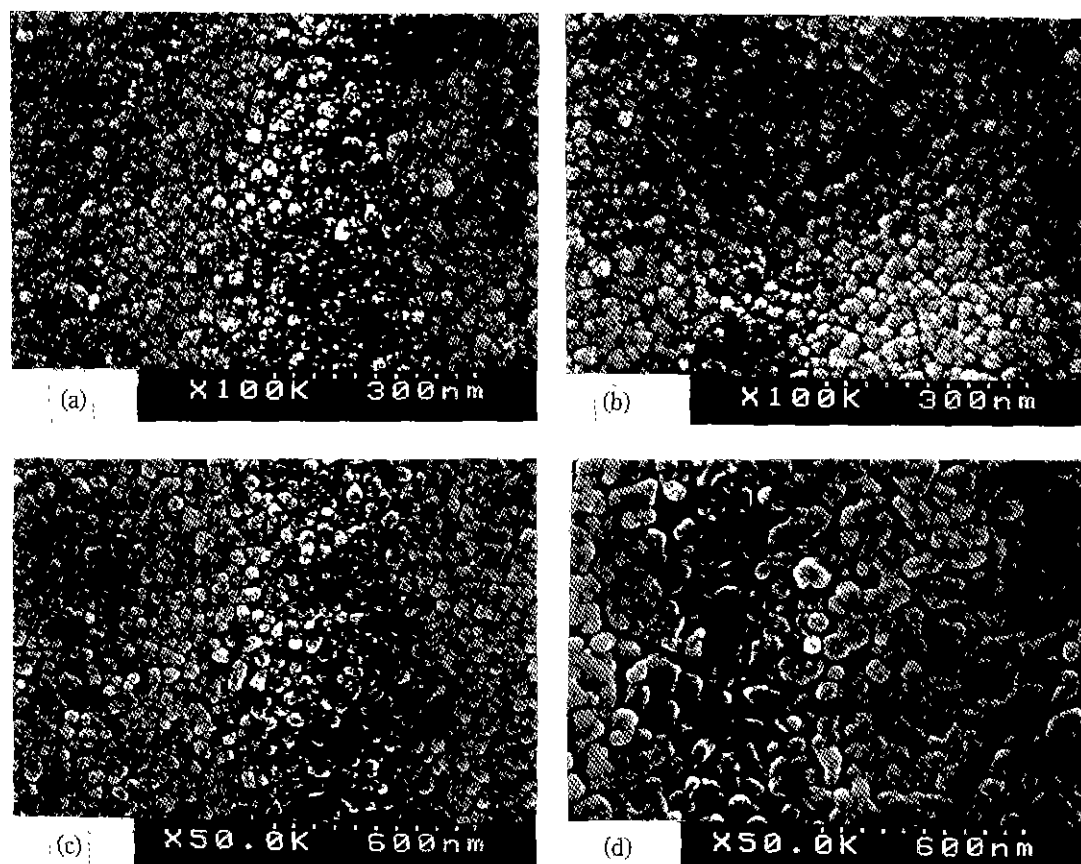


Fig. 6. Microstructure of 5.5 mol% $\text{TiO}_2\text{-CeO}_2$ composite membrane sintered at a) 600°C, b) 700°C, c) 800°C, d) 900°C.

formed are extremely uniform in particle diameter. $\text{TiO}_2\text{-CeO}_2$ membrane maintained the initial microstructure up to 700°C. In order to understand the causes of this uniformity, the membrane forming mechanism has been studied in more detail.

As mentioned above, the major phenomena occurring during heat treatment of the ceramic membranes are sintering and phase transformation. At temperature lower than the starting temperature of phase transformation, sintering is primarily responsible for the change of the pore structure. Sintering is a process of densification that is driven by the need for reducing the interfacial energy. The type of processes that predominates depends on the properties of the material, conditions of the heat treatments and the stage of sintering. After firing at different temperatures under an air atmosphere, the pore size of the titania membrane increases several times. Similarly, the surface area of the $\text{TiO}_2\text{-CeO}_2$ composite membrane is reduced after firing under an air atmosphere at high temperatures.

The phase transformation is responsible for the change of the pore structure of the $\text{TiO}_2\text{-CeO}_2$ composite membranes at the temperature range investigated. Fig. 7. shows X-ray diffraction patterns of $\text{TiO}_2\text{-CeO}_2$ composite membranes, after calcination at 800°C for 1 hour in air. The pattern of the $\text{TiO}_2\text{-CeO}_2$ membrane indicated that

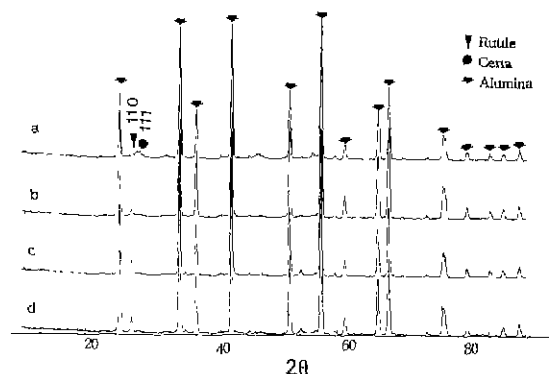


Fig. 7. X-ray diffraction patterns of $\text{TiO}_2\text{-CeO}_2$ membrane sintered at 800°C for 1 hour a) 7.7 mol% CeO_2 , b) 5.5 mol% CeO_2 , c) 3.8 mol% CeO_2 , d) 2.7 mol% CeO_2 .

the phase of TiO_2 was rutile, the phase of CeO_2 was ceria at 800°C.

Recently, Kumar *et al.*¹⁰ studied the phase-transformation behavior of unsupported and supported titania membranes. For the sintering time of 8 hour, titania membranes undergo anatase to rutile phase transformation in the temperature range of 550-600°C¹¹. In contrast, only a small portion of the $\text{TiO}_2\text{-CeO}_2$ sample exhibited the phase transformation from anatase to rutile even after calcination at 600°C. This effect of the additive was confirmed for CeO_2

doped TiO₂ membrane. It is well known that the phase transformation from anatase to rutile proceeds via a nucleation and growth mechanism. These rutile phases have been reported to be resistant to sintering at high temperatures; and hence effective in suppressing pore growth and crack formation of TiO₂-based membranes. Supported TiO₂-CeO₂ composite membranes showed a higher transformation temperature compared to the unsupported ones. It is noted that TiO₂-CeO₂ membranes retain a small pore size. The pore size of these doped TiO₂ membranes is generally smaller than that of the undoped TiO₂ membranes^{12,13}. It is interesting to note that CeO₂ doped TiO₂ membranes have higher heat resistance than the TiO₂ membrane. The average pore diameter of the pure membrane increased significantly with temperature, but the pore growth of the CeO₂ doped TiO₂ membranes was slow. Compared to a pure TiO₂ membrane, the addition of CeO₂ into the membrane improves the thermal stability of microporous in the membrane. Supported membranes showed a higher transformation temperature, about ~100°C higher, (slow rate of transformation) compared to the unsupported ones¹⁴.

IV. Summary

TiO₂-CeO₂ layers of 0.2 to 2 μm in thickness were successfully coated on a porous α-Al₂O₃ support tubes by dip-coating method. The membrane consists of an alumina support with a mean pore diameter of ~0.125 μm and TiO₂-CeO₂ top layer with particle diameters from 20 to 85 nm. The sols prepared by destabilization of colloidal solutions, were the nanoparticle sols with the average particle size less than 15 nm. The forming mechanism of supported TiO₂-CeO₂ composite membranes can be described by the slip casting model. With addition of PVA, mixed-oxide gels were dried and calcined to form a TiO₂-CeO₂ composite membrane. The mean particle diameter of TiO₂-CeO₂ composite membranes increases during heat treatment which is consistent with the typical phenomenon observed for a sintering process. After calcination at 800°C, the resulted phases of TiO₂-CeO₂ composite membranes were rutile and ceria. The TiO₂-CeO₂ membranes prepared by a sol-gel method higher heat resistance than pure TiO₂ membranes. The TiO₂-CeO₂ composite membranes retained a crack-free microstructure and narrow particle diameter distribution even after calcination up to 700°C.

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