

## Preparation and Characterization of the Pt doped TiO<sub>2</sub> Membranes

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The Pt doped TiO<sub>2</sub> composite membranes were prepared by the sol-gel process. The Pt doped titania sol was peptized with hydrochloric acid in the pH range of 1.23 to 1.32 at 50°C. The average particle size of the Pt doped titania sol was shown to be below 15 nm and well dispersed in the solution. XPS show the Pt elements continuous and homogeneous dispersed in the TiO<sub>2</sub> membrane. The mean particle size of the Pt doped TiO<sub>2</sub> composite membrane has smaller than that of the undoped TiO<sub>2</sub> composite membrane. The average pore size of the Pt doped TiO<sub>2</sub> composite membrane was increased from 58 to 193 Å with firing temperature changed from 550 to 850°C. It was observed that the Pt doped TiO<sub>2</sub> composite membranes showed crack-free and homogeneous microstructure as well as narrow particle size distribution up to above 750°C.

**Key words :** Pt doped TiO<sub>2</sub>, composite membrane, Sol-Gel process, Thermal stability

### I. Introduction

Ceramic membranes, owing to their novel properties, are important materials widely used in separation, filtration, and catalytic reactions.<sup>1)</sup> Ceramic membranes have several advantages over polymeric membranes such as better chemical and thermal stabilities, longer life, and better defouling properties. These properties have made ceramic membranes desirable for use in food, pharmaceutical and electronic industries.<sup>2)</sup>

Among several methods, the sol-gel approach is considered to be most practical one for the preparation of ceramic membranes because the smallest possible pore size is determined by the primary particle size in the colloid suspension.<sup>3)</sup> Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by the sol-gel method, etc.<sup>4)</sup> The sol-gel process is consisted of a series of steps which are i) hydrolysis of an organometallic compound, ii) peptization, iii) dipping, iv) drying and v) sintering. This technique allows rapid synthesis of ultrafine membranes.

Titania membranes often show excellent chemical resistance as well as interesting photochemical and photocatalytic properties.<sup>5)</sup> Titania membranes, however, can not be applied at high temperature ( $\geq 500^\circ\text{C}$ ) because of poor thermal stability.

In the limited studies related to the thermal stability of ceramic membranes, Burgfraaf *et al.*<sup>6,7)</sup> have determined the pore size of some ceramic membrane top layers at different sintering temperatures.

This high thermal stability of the ceramic membrane allow it to use in gas separation at high temperatures, especially in combination with a chemical reaction where

the membrane is used as catalyst as well as a selective barrier to remove one of the components which has been formed.<sup>8-11)</sup>

In order to improve the thermal and physical properties of titania membranes, the Pt doped TiO<sub>2</sub> composite membranes were prepared by the sol-gel process. The effects of the Pt on the grain growth, pore size and mean particle diameter of the Pt doped TiO<sub>2</sub> composite membranes are discussed in this paper.

### II. Experimental Procedures

Titanium isopropoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ) and Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ) were used as the starting materials. The titania sol was prepared by dissolving titanium tetra-isopropoxide in isopropanol, followed by hydrolysis with excess water. Peptization requires the amount of hydrochloric acid and the amount of acid added was derived from the solution pH. Reaction temperature of the slurry was kept at about 50°C. The Pt solution was prepared by dissolving precursor in water. The Pt solution was mixed with the titania sol to form the mixed solution. The mixed solution was stirred thoroughly to give a homogeneous mixture. The PVA solution was then mixed with the mixed solution to form a PVA+mixed solution.

The tubular support was prepared by extrusion process, followed by the slip casting. The alumina powders, which have average particle sizes of 0.3-4.0  $\mu\text{m}$  were used. The multi-layer support was about 12 mm in outer diameter and about 2 mm in thickness. The multi-layer support was immersed in mixed sol for 5 to 60 sec. The support with gel layer was dried for 48 h at 45°C in the

oven. The support with thin film was calcined at 550 to 1000°C for 1 h. The supported membranes were calcined at slow heating rate of 1°C/min up to objective temperature and holding for 1 h, followed by cooling down to room temperature at a rate of 2°C/min. The particle size and shape as well as the thickness of the membrane was investigated by a scanning electron microscope (SEM, Hitachi S-4200). Transmission electron microscope (JEOL-200 CX, Philips CM30) was performed to investigate the dispersion of the particles in solution. The chemical composition of the top layer was analyzed by X-ray photoelectron spectroscopy (SS1, 2803-S). The analysis of the pore size, the surface area and pore size distribution of the membranes was performed by gas adsorption-desorption (Micromeritics, ASAP 2000) studies using N<sub>2</sub> at 77 K. The particle size of the mixed sols was determined by using dynamic light scattering method (Ar laser, Nicomp 370). The viscosity of the sol was measured by using viscometry (Brookfield, Mode DV-II).

### III. Result and Discussion

#### 1. Mixed sol

Formation of a good gel layer depends greatly on the sol conditions used.<sup>12)</sup> It is expected that the membranes having smaller pore diameter and narrower pore size distribution can be prepared from the sol whose particle size is smaller.

A general feature of this technique is peptization, in which hydrolysis occurs without addition of any acid. Figure 1 shows the titania particles obtained via hydrolysis of Ti(OH)<sub>4</sub> without adding hydrochloric acid. The particles aggregation was formed under these conditions. The particles aggregation can then be dispersed by adding an acid to increase the surface charge on the solid particles. Figure 2 shows the dispersion of the Pt particles in TiO<sub>2</sub> sol was continuous and homogeneous. Then,



Fig. 1. TEM micrograph of a titania sol obtained via hydrolysis of Ti(OiP)<sub>4</sub> without HCl.

diffraction pattern indicates that the phase of the mixed sol is anatase.

The nature of this peptization can be explained by electrostatic interactions (Derjaquin *et al.* theory).<sup>13)</sup> The repulsion forces that prevent particle aggregation in the sol is result of the electrical double layer caused by the amphoteric behavior of the oxide surface. In this conditions, the primary particles of the sols were well dispersed in the solution and the average particle size was observed to be below 15 nm. The viscosity of the mixed sol was in the range of 12 to 35 cps at about 25°C.

#### 2. Ceramic supports

The tubular support has particles typically of 20~40 μm and a porosity around 30~45%. The particle diameter diminishes with each successive layer, typically to 2~10 μm in the second layer and 0.3~2.0 μm in the third layer. The surface microstructure and the pore size distribution of the α-Al<sub>2</sub>O<sub>3</sub> support which was sintered at 1300°C for 1 h in air atmosphere, was reported.<sup>14)</sup> The shape of the particles is found to be spherical and the average pore diameter of the final support was about 0.125 μm.

#### 3. Microstructure of the the Pt doped TiO<sub>2</sub> membranes

The separation efficiency of inorganic membranes depends, to a large extent, on the microstructural features of

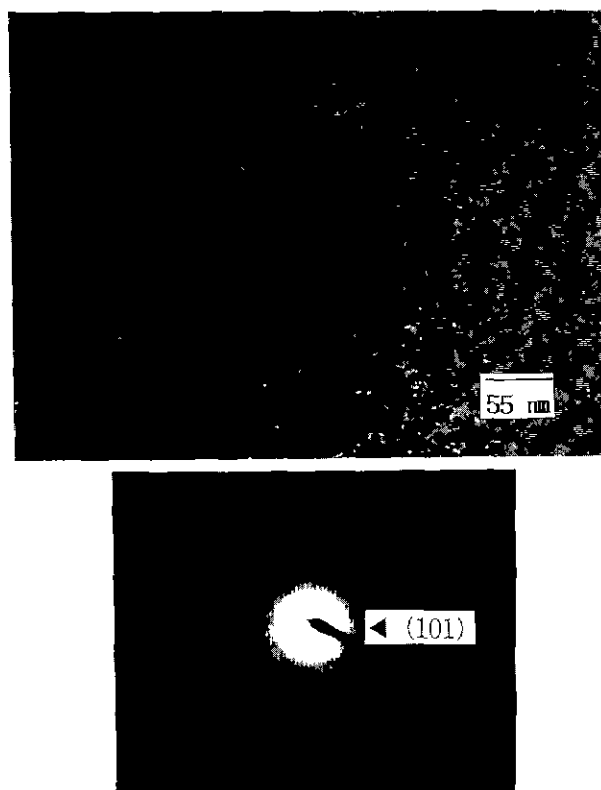


Fig. 2. TEM micrograph and diffraction pattern of the Pt doped TiO<sub>2</sub> sol obtained via hydrolysis of Ti(OiP)<sub>4</sub> with HCl.

the membrane/support composites such as pore size and its distribution, pore shape, porosity and tortuosity.<sup>15,16)</sup> For efficient separation, porous inorganic membranes need to be crack-free and uniform in pore size.

The effect of the Pt on microstructural change in TiO<sub>2</sub> gels with increasing temperature have been investigated. It should be noted that addition of the Pt into the TiO<sub>2</sub> gel were conducted at the first stage of mixing two alkoxides, so that, after the sol-gel transformation, Pt should be distributed uniformly throughout the TiO<sub>2</sub> network. No different local concentration of the Pt in the TiO<sub>2</sub> gel have been assumed.

Figure 3 shows the XPS spectrum of the Pt doped TiO<sub>2</sub> top layers which was obtained by sintering at 650°C for 1 h. This figure demonstrate the presence of Pt and TiO<sub>2</sub>. It can be concluded that the Pt doped TiO<sub>2</sub> composite membranes can be made through a sol-gel process.

Figure 4 shows that the surface microstructure of the Pt doped TiO<sub>2</sub> membranes after calcination at 550 to 850°C for 1 h in air atmosphere. In all cases, the surface of deposited membranes are smooth, neither cleavages nor cracks are observed. Particle shape seem to be spherical and necks was formed between the particles. The morphology of the grain are nearly uniform. This grain growth at low temperatures may still be caused by surface energy reduction. The average mean particle diameter increased and the mean particle diameter dis-

tribution became broader with increasing calcination temperature.

In order to improve thermal stability of the TiO<sub>2</sub> composite membranes, the Pt elements were introduced into the TiO<sub>2</sub> sols. Thermal stabilities of the Pt doped TiO<sub>2</sub> composite membranes were determined using the mean particle size and membrane morphology after heat treatments at 550 to 850°C for 1 h in air atmosphere.

Figure 5 illustrates that the particle size of the Pt doped TiO<sub>2</sub> composite membranes were increased with firing temperature. The mean particle size was determined by counting the number of particle size in a given area of the membrane.

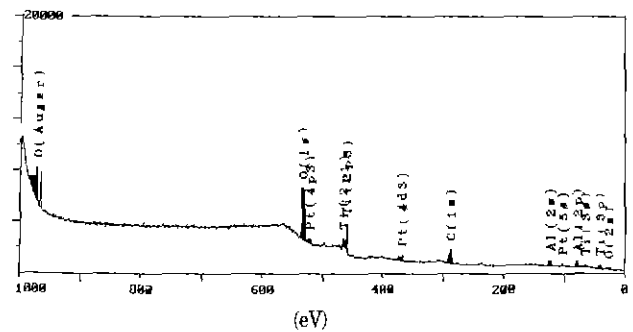


Fig. 3. XPS spectrum of the Pt doped TiO<sub>2</sub> composite membranes sintered at 650°C for 1 h.

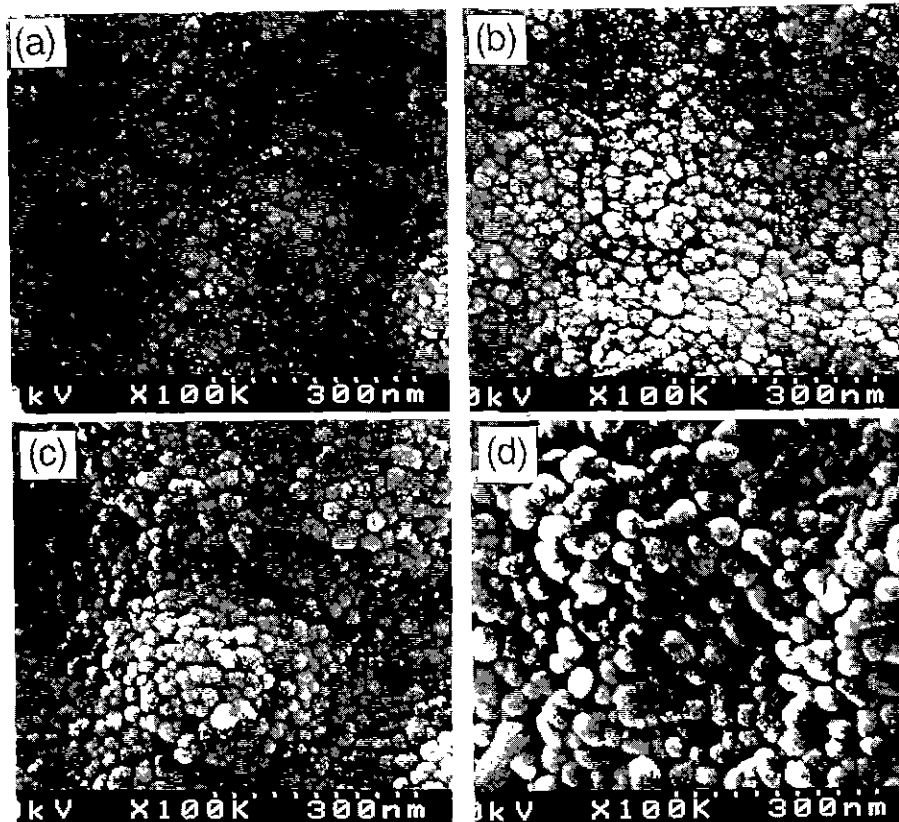


Fig. 4. Microstructure of the Pt doped TiO<sub>2</sub> composite membranes sintered at a) 550°C, b) 650°C, c) 750°C and d) 850°C for 1 h.

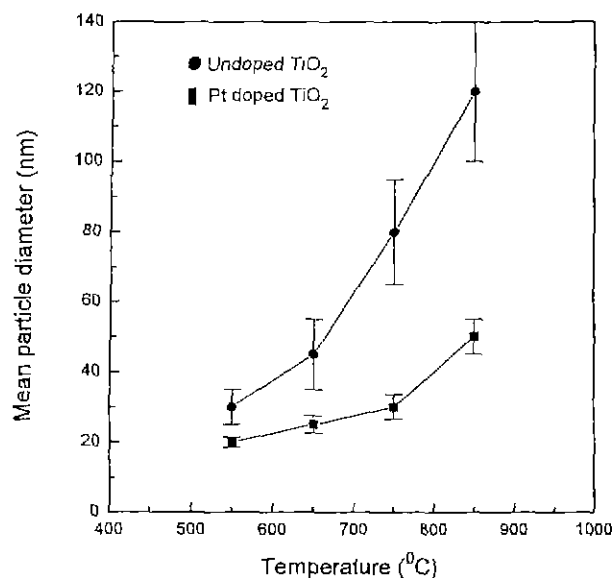


Fig. 5. Mean particle diameter (nm) vs. heat treatment temperatures.

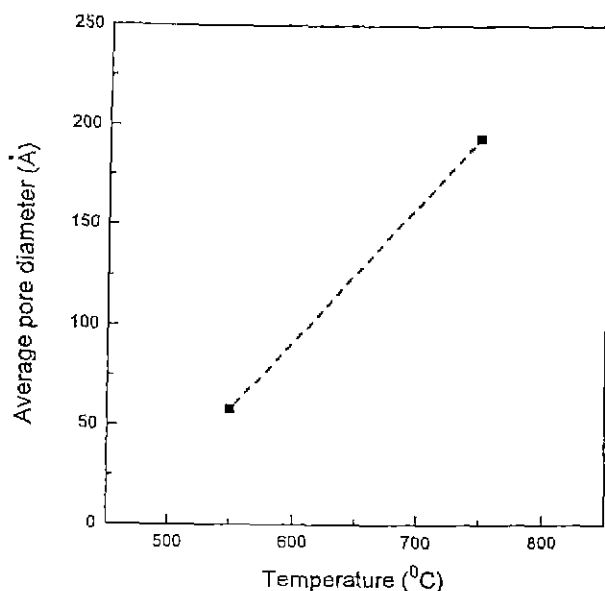


Fig. 6. The average pore diameter (Å) vs. heat treatment temperature.

Whether it is sintering-caused or crystallization-induced, grain growth has been retarded by introducing the Pt into the TiO<sub>2</sub> membrane. The mean particle diameter of the Pt doped TiO<sub>2</sub> membrane was increased from 20 to 50 nm as firing temperature was changed from 550 to 850°C. Under the similar conditions, the mean particle size of the TiO<sub>2</sub> composite membrane was increased from 30 to above 100 nm.

The average pore size was determined by nitrogen adsorption/desorption. Figure 6 illustrates the average pore size increase with increasing temperature in Pt doped TiO<sub>2</sub> composite membrane. After calcined at 550 to 850°C for 1 h, the measured pore size were 58 Å, 193 Å,

respectively. It was observed that the average pore size of the doped TiO<sub>2</sub> composite membranes was increased with firing temperature.

The mean pore diameter of the Pt doped TiO<sub>2</sub> membranes increases beyond the mesoporous region at temperature higher than 600°C for the pure TiO<sub>2</sub>. This can be increased to above 750°C for the Pt doped TiO<sub>2</sub> membranes. This increase in critical temperature is very important in the application of mesoporous ceramic membranes in high temperature applications.

#### IV. Conclusions

The Pt doped TiO<sub>2</sub> composite membrane was prepared by the sol-gel process. The titania sol was prepared by destabilization of colloidal solution process. The average particle size of the Pt doped titania sol was below 15 nm in the pH range of 1.23 to 1.32. The crack-free microstructure of the gel layer was obtained by drying at 45°C for 48 h. Thickness of the top layers was 0.1 to 0.5 μm. The average pore size of the alumina support was about 0.125 μm.

Whether it is sintering-caused or crystallization-induced, grain growth has been retarded by introducing the Pt into the TiO<sub>2</sub> membrane. XPS show the Pt elements continuous and homogeneous dispersed in the TiO<sub>2</sub> membrane. The mean particle size of the Pt doped TiO<sub>2</sub> composite membrane has smaller than that of the undoped TiO<sub>2</sub> composite membrane. The average pore size of the Pt doped TiO<sub>2</sub> composite membrane was increased from 58 to 193 Å with firing temperature changed from 550 to 850°C. It was observed that the Pt doped TiO<sub>2</sub> composite membranes showed crack-free and homogeneous microstructure as well as narrow particle size distribution up to above 750°C.

In view of their thermal stabilities, the Pt doped TiO<sub>2</sub> composite membrane is a good candidate for use in ultrafiltration.

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