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Synthesis and characterization of Pd/SiO_2 composite membranes by a reverse micelle and sol-gel process

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Pd-doped SiO_2 composite membranes were synthesized by a reverse micelle and sol-gel process. The average particle size of the mixed sol was below 30 nm and well dispersed in the solution. TEM results show the microstructure of the Pd-doped SiO_2 composite membranes was homogeneous. Average pore size of the support was about 0.125 μm and the pore size distribution was narrow. The average pore size of the Pd-doped SiO_2 composite membranes was smaller than that in the SiO_2 composite membranes. It was observed that the Pd-doped SiO_2 composite membranes showed a crack-free microstructure and a narrow particle size distribution even after heat treatment up to 1000 °C.

Key words : Pd/SiO_2, Nanocomposite membranes, Reverse micelle, Sol-gel process, Asymmetric membrane.

Introduction

Ceramic membranes, owing to their novel properties, are important materials widely used in separation, filtration, and catalytic reactions [1]. 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 the food, pharmaceutical and electronic industries, etc [2]. Among several methods, the sol-gel approach is considered to be the 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 [3]. Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by a sol-gel process [4]. Ceramic membranes often show excellent chemical resistance as well as interesting photochemical and photocatalytic properties [5]. In several studies related to the thermal stability of ceramic membranes, Burgfraaf *et al.* have determined the pore size of some ceramic membrane top layers at different sintering temperatures [6, 7]. Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by a reverse micelle and sol-gel process. Among the many catalysts that have been reported for soot oxidation, Pd exhibits a high level of catalytic activity. Also Pd is commonly said to be a good catalyst for hydrogenation of carbonyl and phenyl groups. Therefore, the Pd/SiO_2 nanocomposite system was selected for the nano-membrane in this study. The object of this study was to prepare SiO_2 membranes containing nanometer palladium particles by a combined reverse micelle and sol-gel technique. Pd/SiO_2 nano composite membranes were prepared on a porous Al_2O_3 support (asymmetric membrane structure) with a SiO_2 intermediate layer. The prepared nano-composite membranes were not densely packed nor had cracks due to the differences in the structure and thermal incompatibility between the nano-composite membrane material and the porous support.

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Experimental Procedures

Typically, micro-emulsions of total volume 150 ml were prepared at ambient temperature in a 300 ml beaker with rapid stirring, and they consisted of Igepal 520, cyclohexane and deionized water. After nanosized water droplets were formed while stirring, TEOS (Tetra-ethyl orthosilicate) was added into the stirred micro-emulsion. The micro-emulsion was mixed rapidly, $Pd(NO_3)_2 \cdot 6H_2O$ solution was added and after 5 minutes of equilibration, hydrazine hydrate (9 M $N_2H_4 \cdot xH_2O$, Aldrich Chemical Co.) was added as a reducing agent. The multi-layer Al_2O_3 tubes were used as an asymmetric support. The tubular support was prepared by extruding from α-alumina with a mean particle size of 20-40 μm, followed by slip casting from α-alumina with a mean size of 0.3-10 μm. 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 300 s. The support with a gel layer was dried for 24 h at 25 °C. The support with an

intermediate layer was calcined at 900 °C for 2 h. The Pd/SiO_2 nano-composite membrane was calcined at 1000 °C for 1 h. The supported membranes were calcined at a slow heating rate of 5 K/minute up to the objective temperature and held for 1-2 h, followed by cooling down to room temperature at a rate of 5 K/minute. The Pd/SiO_2 nano-composites were analyzed for phase composition using X-ray diffraction over the 2theta range from 10 degree to 80 degree. The morphology of the synthesized particles was observed using transmission electron microscopy (TEM, JEOL JEM-4010). The particle size and shape as well as the thickness of the membrane were observed with a scanning electron microscope (SEM, Hitachi S-4200).

Results and Discussion

Formation of a good gel layer depends greatly on the sol conditions used [8]. It is expected that the membranes having smaller pore diameters and narrower pore size distributions can be prepared from a sol whose particle size is smaller. The slip-casting process is a common technique used to fabricate ceramic membranes with complex shapes from particle suspensions, in which a ceramic powder suspension is poured into a porous plaster mold of the desired shape. Recently, this process has been extended to prepare ceramic asymmetric membranes, including porous ceramic filtration membranes and dense membranes. When a dry porous substrate is dipped into a ceramic suspension and subsequently withdrawn from it, a wet and more- or -less dense cake of well-defined thickness can be formed on the substrate surface. The thickness of the membrane must be carefully controlled for high quality. Therefore, it is necessary and important to analyze quantitatively the membrane formation process.

The separation efficiency of inorganic membranes depends, to a large extent, on the microstructural features of the membrane/support composites such as pore size and its distribution, pore shape, and porosity [9]. For efficient separations, porous inorganic membranes need to be crack-free and uniform in pore size. Spherical Pd/SiO_2 nanometre-sized particles were obtained in reverse micelles followed by in-situ hydrolysis and condensation in the micro-emulsion. The average size of the cluster was found to depend on the micelle size, the nature of the solvent, and the concentration of the reagent. The nano-composite particles are formed by a homogeneous nucleation and growth process. The nucleation and growth of Pd particles is likely to be a diffusion-controlled process through interaction between micelles, but it can be influenced by many other factors such as phase behavior and solubility, average occupancy of reacting species in the aqueous pool, and the dynamic behavior of the micro-emulsion [10, 11]. Figure 1 shows HRTEM (high-resolution transmission electron microscopy) images

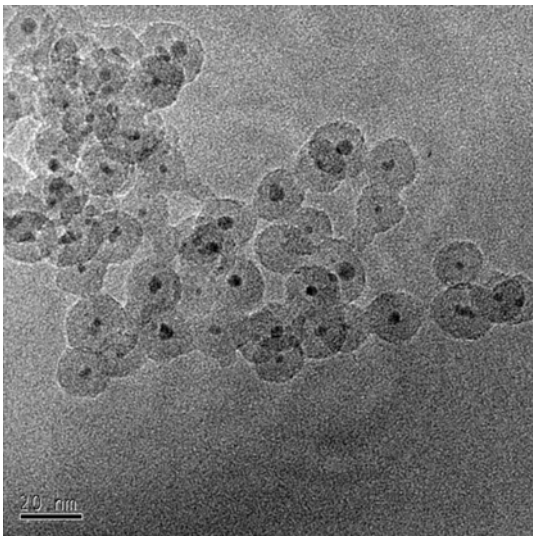

Fig. 1. HRTEM micrographs of Pd-doped SiO_2 nanosized powders by a reverse micelle and sol-gel process.

of Pd/SiO_2 nano-composite particles. The average size and size distribution of the synthesized SiO_2 particles were below 20 nm and uniform, respectively. The shape of the synthesized particles was nearly spherical. For most of the particles their lattice images of Pd were visible in the HRTEM micrographs. These results clearly mean that the synthesized particles of Pd were crystallized. The average size and size distribution of

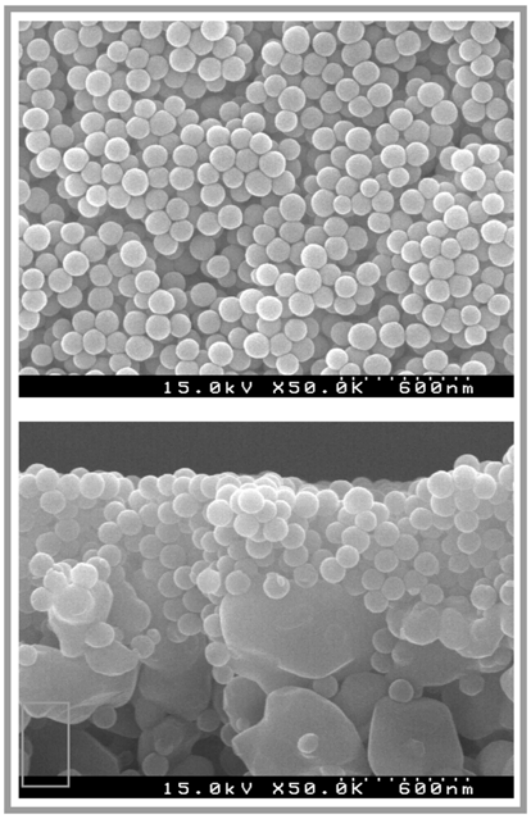

Fig. 2. Micostructure of the cross section and surface of the intermedate layers by dip-coating.

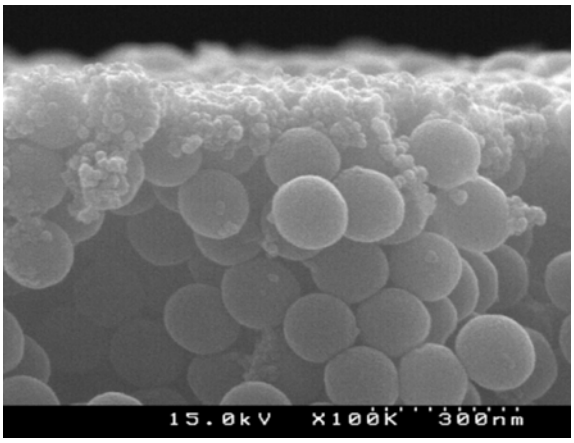

Fig. 3. Micostructure of the cross section of Pd-doped SiO_2 membranes by a reverse micelle and sol-gel process.

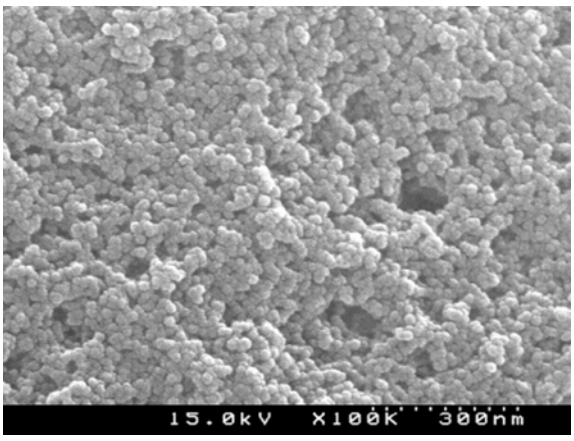

Fig. 4. Micostructure of the surface of Pd-doped SiO_2 membranes by a reverse micelle and sol-gel process.

the synthesized Pd particles were below 5 nm and narrow, respectively. The prepared nano-composite membranes were not densely packing or had cracks due to the differences in the structure and thermal incompatibility between the nano composite membrane material and the porous support. Therefore the SiO_2 intermediate layer was coated on an asymmetric Al_2O_3 support. Figure 2 shows the cross section of the synthesized SiO_2 intermediate layers prepared by a sol-gel process. The thickness of the films was about 600 nm. In order to obtain crack-free membranes, the SiO_2 intermediate layers need to be crack-free and uniform in pore size. Figure 3 shows the cross section of the synthesized Pd/SiO_2 composite asymmetric membranes by the reverse micelle and sol-gel process. The thickness of the film was below 0.1 μm. Figure 4 shows the surface microstructure of the Pd/SiO_2 nano composite membranes sintered at 1000 °C for 2 h. The Pd/SiO_2 composite membranes showed a crack-free microstructure and a narrow particle size distribution even after heat treatment up to 1000 °C.

Conclusions

The supported Pd/SiO_2 composite membranes were prepared by dip-coating of a sol on an Al_2O_3 porous substrate and SiO_2 intermediate layer. The dip-coating solution was prepared by a reverse micelle and sol-gel process. The crack-free microstructure of the Pd/SiO_2 composite membrane layer was obtained by drying at 25°C for 24 h and heat treatment at 1000 °C for 2 h. The films demonstrated a narrow peak with a mean particle diameter at around 20 nm after a heat treatment at 1000 °C for 2 h. The top layer and its thickness were controlled by the number of dip-coatings. The thickness of the nano-composite top layer was about 0.1 μm. The particle size of Pd after heat treatment at 1000 °C was below 5 nm. The support layers and the intermediate layer will provide the mechanical stability and a separation, and the Pd/SiO_2 nano-composite membrane layer will provide a separation and catalytic selectivity.

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