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Fabrication and characterization of silver-doped silica composite membranes by a reverse micelle and Sol-Gel process

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Ag-doped SiO₂ composites nano-powders were synthesized by a reverse micelle and sol-gel process. The average particle size of the mixed sol was below 25 nm and was well dispersed in the solution. TEM results show the microstructure of Ag- doped SiO₂ nanoparticles was homogeneous and Ag was below 5 nm and Ag was well dispersed in the ceramic nano-particles. Ag-doped SiO₂ composite membranes were fabricated by a sol-gel process. Ag-doped SiO₂ composite membranes showed a crack-free microstructure and a narrow particle size distribution even after heat treatment up to 500 °C. The average particle size of the membrane was 30-40 nm, and the pore size of Ag-doped SiO₂ nano composite membranes was below 10 nm. The particle size of Ag after heat treatment at 500 °C was below 5 nm.

Key words: Ag doped SiO₂, Membranes, Reverse micelle, Sol-Gel processes.

Introduction

Ceramic membranes, owing to their novel properties, are important devices 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 colloidal suspension [3]. Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by the 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, Leenaars and Haibot 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 the reverse micelle and the sol-gel process. Among the many catalysts that have been reported for soot oxidation, Ag exhibits a high level of catalytic activity. Silver is an increasingly important material in many technologies. It displays unique properties such as chemical stability, excellent electrical conductivity, catalytic activity, while still being reasonably priced [8]. Therefore, a Ag-doped SiO₂ nano-composite system was selected for nano membranes in this study. The object of this study was to prepare SiO₂ membranes containing nano silver particles by a combined reverse micelle and sol-gel technique. Ag-doped silica composite membranes were prepared on porous Al₂O₃ supports (asymmetric membrane structure) and SiO₂ intermediate layers. The nano-composite membranes were prepared not densely packed or had cracks due to the differences in the structure and thermal incompatibility between the nano-composite membrane material and the porous support.

Experimental Procedures

The experimental procedure used to prepare Ag-doped SiO2 composite membranes is illustrated in Fig. 1. Typically, micro-emulsions of total volume 150 ml were prepared at an 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(Tetraethyl orthosilicate) was added into the stirred micro-emulsion. The microemulsion was mixed rapidly, AgNO₃ solution was added and after 5 minute of equilibration, hydrazine hydrate(9 M N₂H₄·xH₂O, Aldrich Chemical Co.) was added as a reducing agent. Multi-layer Al₂O₃ tubes were used as an asymmetric support. The tubular support was prepared by extruding α -alumina with a mean particle size of 20-40 µm, followed by slip casting α -alumina with a mean size of 0.3-10 µm. Multilayer support was about 12 mm in outer diameter and about 2 mm in thickness. Multi-layer support was immersed in a mixed sol for 5 to 300 s. The support with a gel layer

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Fig. 1. Flow chart of the fabrication of Ag-doped SiO₂ ncomposite membranes by a reverse micelle and sol-gel processing.

was dried for 24 h at 25 °C. The support with an intermediate layer was calcined at 900 °C for 2 h. Ag-doped SiO₂ composite membranes were heat treated at 500 °C for 1 h. The supported membranes was heat treated at a slow heating rate of 5 Kminute⁻¹ up to the objective temperature and holding for 1-2 h, followed by cooling down to room temperature at a rate of 5 Kminute⁻¹. Ag-doped silica 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 [9]. It is expected that the membranes having a smaller pore diameter and a narrower pore size distribution can be prepared from a sol whose particle size is smaller. The slip-casting process is one of the common techniques 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 [10]. For efficient separations, porous inorganic membranes need to be crackfree and uniform in pore size. Spherical silver-doped silica nano-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. Nanoparticles are formed by a homogeneous nucleation and growth process. The nucleation and growth of Ag 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 [11, 12].

Fig. 2 shows a TEM micrograph of synthesized Ag-doped SiO_2 nanoparticles by a reverse micelle and sol-gel process. The average size and size distribution of the synthesized Ag doped SiO_2 particles were below 30 nm and broad, respectively. The shape of the synthesized particles was



Fig. 2. HRTEM micrograph of synthesized Ag-doped SiO_2 nanosized powders by a reverse micelle and sol-gel process.

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Fig. 3. Microstructure of the cross section of a Ag-doped SiO_2 membrane by a reverse micelle and sol-gel process.



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

nearly spherical. For most of the particles lattice images of Ag were shown in the HRTEM micrographs. These results clearly mean that the synthesized particles of Ag were crystallized. The average size and size distribution of the synthesized Ag particles were below 10 nm and narrow, respectively. Fig. 3 shows the cross section of a synthesized Ag-doped SiO₂ composite asymmetric membrane by a reverse micelle and sol-gel process. The thickness of the film was below 1 μ m.

Fig. 4 shows the surface microstructure of a Ag-doped SiO_2 nano-composite membrane sintered at 500 °C for 2 h. The Ag-doped SiO_2 composite membranes showed crack-free microstructures and narrow particle size distribution even after heat treatment up to 500 °C.

Conclusions

Supported Ag-doped SiO₂ composite membranes were prepared by dip-coating of a sol on an Al₂O₃ porous substrate and a SiO₂ intermediate layer. The dip-coating solution was prepared by a reverse micelle and sol-gel process. A crack-free microstructure of the Ag doped SiO₂ composite membrane layer was obtained by drying at 25 °C for 24 h and heat treatment at 500 °C for 2 h. The top layer and its thickness were controlled by the number of dip-coating steps. The thickness of the composite membrane top layer was about 1 μ m. The particle size of Ag after heat treatment at 500 °C was below 5 nm. The support layers and the intermediate layer will provide the mechanical stability and separation, and Ag-doped SiO₂ composite membrane layer will provide separation and catalytic selectivity.

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References

- 1. Y.S. Lin and A.J. Burggraaf, J. Am. Ceram. Soc., 74 (1991) 219-224.
- 2. M. Cheryan, in "Ultrafiltration Handbook" (Technomic Publishing Company, Lancaster, PA, 1986) p. 7.
- R.J.R. Uhlhorn, H.I. Veld, M.H., B.J., K. Keizer and A.F. Burggraaf, J. Mat. Sci., 27 (1992) 527-537.
- X. Qunyin and A. A. Marc, J. Am. Cera. Soc., 76 (1994) 2093-2097.
- J. Sabate, M.A. Anderson, H. Kikkawa, M. Edwards and C.GA. Hill, J. Cata., 127 (1991) 167-170.
- A.F.M. Leenaars, K. Keizer and A.J. Burggraaf, J. Mat. Sci., 19 (1984) 1077-1088.
- A. Larbot, J.P. Fabre, C. Guizard and L. Cot, J. Am. Cer. Soc., 72 (1989) 257-261.
- I. Sondi, D.V. Goia and E. Matijevic, J. Collid & Inter. Sci., 260, (2003) 75-79.
- C.H. Chang, R. Gopalan and Y.S. Lin, J. Mem. Sci., 91 (1994) 27-45.
- H. Schaper and L.L. Van Reijen, Mater. Sci. Monogr., 14 (1982) 173-176.
- 11. T. Li, J. Moon, A.A. Morrone, J.J. Mecholsky, D.R. Talham and J. H. Adair, Mater. Sci. & Eng., R23 (1998) 139-242.
- K. Osseo-Asare, "Handbook of microemulsion science and technology" (Edited by Promod Kumar, K. L. Mittal, Basel, New York, 1999) p. 5.