The effect of sacrificial templates on the pore characteristics of sintered diatomite membranes

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Recently, porous ceramic membranes have become an interesting subject due to their outstanding thermal and chemical stability. Among the many types of ceramics, as diatomite is inherently porous and irregular, it is worthwhile to investigate the relationship between the characteristics of sacrificial templates and porous microstructures after sintering. Therefore, sintered diatomite membranes were prepared with 8 μm solid polymer spheres, 20 μm solid polymer spheres, wheat starch, and light clusters of aggregated carbon nanotubes while varying the amount of sacrificial template material by dry pressing at 25 MPa. The results show that the characteristics of the sacrificial templates, e.g., the rigidity, directly affect the pore characteristics and accordingly determine the permeability of sintered diatomite membranes. Also, we discuss whether the largest pore sizes and average pore sizes of the sintered diatomite membranes reflect the actual permeability appropriately.

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1. Introduction

Porous ceramics are increasingly important¹⁾ as researchers seek to exploit their unique properties, such as high wear resistance,²⁾ low thermal conductivity,³⁻⁵⁾ and a low dielectric constant.⁶⁾ Notably, porous ceramic membranes⁷⁻¹¹⁾ are among the most feasible applications of porous ceramics. The driving force behind the development of porous ceramic membranes is mostly the need to produce membranes with greater thermal and chemical stability, as most polymeric membranes cannot withstand operating temperatures above 200°C or exposure to organic solvents such as benzene and toluene.¹²⁾

Recent developments related to porous ceramic membranes have heightened the need to investigate mass transport through a membrane. Although there have been various reports on commonly used materials for ceramic membranes, including γ - Al_2O_3 ,^{10,13)} α - Al_2O_3 ,^{9,14)} TiO_2 ,^{15,16)} ZrO_2 ,¹⁷⁾ SiO_2 ,¹⁸⁾ and composites of these materials,^{19,20)} there have been few studies on porous and irregular starting particles such as diatomite. Diatomite is a sedimentary rock originating from the siliceous fossilized skeletons of diatoms, which are composed of rigid cell walls called frustules.²¹⁻²³⁾ To date, no detailed studies regarding the use of a membrane made with inherently porous and irregular particles have been published.

One of the straightforward processing routes for the preparation of porous ceramic membranes is the sacrificial template method. This method usually consists of the preparation of a two-phase composite consisting of a continuous matrix of a ceramic phase and a dispersed sacrificial template phase that is initially homogeneously distributed throughout the matrix and is ultimately pyrolyzed to generate pores within the microstructure.¹⁾ The main advantage of a sacrificial template method in comparison with other methods is the ability to tailor the porosity, pore size distribution, and pore morphology of the sintered

ceramic membrane precisely through the appropriate choice of the sacrificial template. However, in particular, when the shapes of the starting particles are inherently porous and irregular, like diatomite particles, it is not certain as to whether the characteristics of sacrificial templates efficiently affect the final properties of a sintered diatomite membrane to the same degree as dense and uniform starting particles such as Al_2O_3 and ZrO_2 .

Therefore, to determine whether the shape of a sacrificial template can be transferred onto the pore structure of a sintered diatomite membrane effectively, different types of sacrificial templates were investigated. These were (i) 8 μm solid polymer spheres, (ii) 20 μm solid polymer spheres, (iii) wheat starch, and (iv) light clusters of aggregated carbon nanotubes. This study investigates in detail two factors that may dominate the pore characteristics of the sintered diatomite: the relative size and the rigidity of the sacrificial templates.

2. Material and methods

Diatomite (Celite 499, Celite Korea Co. Ltd., Korea) was used for the preparation of the sintered diatomite membranes. The average particle size of the as-received diatomite was 12.79 μm . To enhance the sinterability of the diatomite particles, the average particle size of the diatomite was reduced by ball-milling. Diatomite particles were mixed with distilled water as a solvent. The slurry was ball-milled for 24 h with an alumina ball-to-powder volume ratio of 2:1. The particle size of the ball-milled diatomite was analyzed by a particle size analyzer (LSTM 13 320 MW, Beckman Coulter, USA).

Diatomite particles ranging in quantity from 0 to 15 vol.% of PMMA (8 μm solid spheres, or 20 μm solid spheres, Sigma-Aldrich, USA), wheat starch (Wheat starch, Sigma-Aldrich, USA), or carbon nanotubes (CM95, Hanwha Chemical Co., Ltd., Korea) as a sacrificial template, and a polyethylene glycol binder were mixed, dry pressed at 25 MPa, and sintered at 1200°C for 1 h. Also, diatomite particles ranging in quantity from 0 to 25 vol.% of Expancel (hollow spheres, Expancel-920-DET-40-

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d25, Eka Chemicals AB, Sweden) as hollow polymer spheres, distilled water, and a polyethylene glycol binder were mixed, wet-pressed at 1 MPa, and dried for 24 h. Next, they were sintered at 1200°C for 1 h.

The pore characteristics of the sintered diatomite membranes were investigated by scanning electron micrography (JSM-5800, JEOL, Japan). Average pore sizes of the sintered diatomite membranes were measured by mercury porosimetry (Autopore IV 9510, Micromeritics, USA). The flow rate, Darcy's permeability constant and the largest pore size of the sintered diatomite membranes were characterized by capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., USA). Particularly, the largest pore size was measured by the bubble point method, which is the most widely used approach for evaluating pore sizes and which is capable of determining the largest pore size of a membrane. It is based on the feature, for a given fluid and pore size under constant wetting, that the pressure required to force an air bubble through the pore is inversely proportional to the size of the pore.

3. Results and discussion

Typical Scanning Electron Microscope (SEM) images of raw materials, i.e., diatomite particles after ball-milling for 24 h, as-received 8 μm solid polymer spheres, as-received 20 μm solid polymer spheres, as-received wheat starch, as-received light clusters of aggregated carbon nanotubes, and high magnification images of light clusters of aggregated carbon nanotubes, are shown in **Figs. 1(a)–1(f)**, respectively. In **Fig. 1(a)**, the diatomite particles maintained both the irregular shapes and inherent pores of the fossilized skeleton of diatoms after ball-milling for 24 h. **Figures 1(b) and 1(c)** depict the size difference between the 8 and 20 μm solid polymer spheres. The wheat starch in **Fig. 1(d)** has relatively irregular shapes as opposed to the solid polymer spheres.

Figures 1(e) and 1(f) depict light clusters of aggregated carbon nanotubes. Because carbon nanotubes tend to self-associate into micro-scale aggregates,^{24),25)} disaggregation and a uniform dispersion of individual carbon nanotubes are critical challenges that must be met to utilize the unique properties of carbon nanotubes successfully. However, in this study, carbon nanotubes were used without an aqueous colloidal dispersion by a surfactant such as sodium dodecyl sulfate (SDS), because, in our preliminary study, above 2.5 vol.% of sacrificial template, regardless of the type, was needed to enhance the permeability of the sintered diatomite membranes observably, and this amount of carbon nanotubes already far exceeded the criteria of a homogeneous dispersion of carbon nanotubes.²⁶⁾ Also, we only focused on the flexible and soft aspects of light clusters of aggregated carbon nanotubes in the comparison with the rigid solid polymer spheres.

Figures 2(a) and 2(b) show similar particle size distributions of sacrificial templates. The particle size distribution of the 8 μm solid polymer spheres corresponds to that of the wheat starch, and the particle size distribution of the 20 μm solid polymer spheres corresponds to that of light clusters of aggregated carbon nanotubes.

The diatomite membrane prepared by dry pressing at 25 MPa without any sacrificial template had an inherently porous microstructure, when sintered for 1 h at 1200°C, as shown in **Fig. 3(a)**. Although dry pressing methods generally introduce pores and voids into green bodies, subsequently degrading the densification of conventional ceramics,²⁷⁾ due to the highly porous microstructure of the diatomite matrix, it was difficult to find peculiar voids or pores in the sintered diatomite membrane prepared by dry pressing. The densities of diatomite membrane were dependent on the amount and the kind of sacrificial template addition, and were varied from 0.8 to 1.0 g/cm³. **Figures 3(b) and 3(c)** show a diatomite membrane prepared with the 8 μm solid polymer spheres and the 20 μm solid polymer spheres, respectively.

Fig. 1. Typical SEM images of raw materials: (a) diatomite particles after ball-milling for 24 h, (b) as-received 8 μm solid polymer spheres, (c) as-received 20 μm solid polymer spheres, (d) as-received wheat starch, (e) as-received light clusters of aggregated carbon nanotubes, and (f) a high-magnification image of (e).

Fig. 2. Particle size distributions of the (a) 8 μm solid polymer spheres, 20 μm solid polymer spheres, and diatomite after ball-milling for 24 h, and (b) light clusters of aggregated carbon nanotubes, wheat starch and diatomite after ball-milling for 24 h.

Fig. 3. Typical SEM images of diatomite membranes sintered for 1 h at 1200°C with (a) no addition of sacrificial template, (b) 10 vol.% of 8 μm solid polymer spheres, (c) 10 vol.% of 20 μm solid polymer spheres, (d) 10 vol.% of wheat starch, and (e) 10 vol.% of light clusters of aggregated carbon nanotubes.

As the average particle size of diatomite, which was ball-milled for 24 h, was 8.36 μm , the diatomite membrane had more distinct spherical pores in the diatomite matrix when prepared with the 20 μm solid polymer spheres as compared to the 8 μm solid polymer spheres. It is well known that micro-cracks can readily develop within the microstructure and act as escapee paths for the gas phase generated during the pyrolysis of a solid polymer template in a dense microstructure induced by uniform particles such as alumina and zirconia. However, in this study, we

successfully sintered the diatomite membrane at a heating rate of 5°C/min without a time-consuming burn-out process, unlike the conventional porous ceramics fabrication process. This can be explained by the highly porous diatomite matrix, which acts as an escape path for the gas phase which evolves during the pyrolysis of the sacrificial template without the generation of micro-cracks. While, even porous and irregular diatomite particles do not mitigate concerns over micro-crack generation completely, the inherent porous microstructure of the sintered diatomite can

Fig. 4. Pore size distributions of diatomite membranes with various amounts and different types of sacrificial polymer templates: (a) 8 μm solid spheres, (b) 20 μm solid spheres and 50 μm solid spheres, and (c) 45 μm hollow spheres, with all specimens subsequently sintered for 1 h at 1200°C.

withstand levels below a certain amount of gas phase locally generated during the pyrolysis process with an addition of up to 15 vol.% of the sacrificial templates.

In contrast to the solid polymer template case, the diatomite membrane prepared with wheat starch had more slit-like pores compared to that prepared with solid polymer spheres, as shown in Fig. 3(d). This can be explained by the difference in the degree of rigidity between the solid polymer spheres and the wheat starch. A solid polymer sphere, which consists PMMA, has an elastic modulus of approximately 3 GPa,^{28,29)} whereas the elastic moduli of various starches range from 0 to 500 MPa.³⁰⁾ Therefore, slit-like pores may be induced when the mixture of diatomite particles and wheat starch is exposed to external pressure during

dry pressing at 25 MPa. Figure 3(e) shows a diatomite membrane prepared with light clusters of aggregated carbon nanotubes. Although the average particle size of light clusters of aggregated carbon nanotubes was larger than that of the wheat starch, it is difficult to find a trace of light clusters of aggregated carbon nanotubes in the microstructure of the sintered diatomite. It may be that light clusters of aggregated carbon nanotubes tend to locate inside the inter-particle voids rather than in the continuous area of the diatomite matrix due to the flexibility of the carbon nanotube itself and the fragility of light clusters.

Figure 4(a) shows the pore size distributions of the sintered diatomite membranes prepared with 10 vol.% of 8 and 20 μm solid polymer spheres at a sintering temperature of 1200°C. The

Fig. 5. (a) Average pore sizes, and (b) the largest pore sizes of sintered diatomite membranes with various amounts and types of sacrificial templates as a function of Darcy's permeability constant.

pore size distributions of the sintered diatomite membranes prepared with 10 vol.% of 8 and 20 μm solid polymer spheres are in good agreement with the particle size distributions of the 8 and 20 μm solid polymer spheres, as shown in Fig. 2(a). Although the average size of the 20 μm solid polymer spheres is more than two times larger than that of the 8 μm solid polymer spheres, the main peak of 20 μm solid polymer spheres is slightly larger than that of 8 μm solid polymer spheres. This occurs because the main peaks of the 20 μm solid polymer spheres correspond to the throats³¹⁾ or entrance openings of the spherical pores approximately 20 μm in size, as mercury will enter the spherical pores at a pressure determined by the entrance size rather than the actual spherical pore size. Thus, the average pore sizes as measured by mercury porosimetry do not reflect the spherical pores induced by the sacrificial templates, and the average pore sizes are insufficient when seeking to understand the pore characteristics considering the permeability, which will be discussed again when referring to Figs. 5(a) and 5(b).

Figure 4(b) shows the pore size distributions of the sintered diatomite membranes prepared with 10 vol.% of wheat starch and light clusters of aggregated carbon nanotubes at a sintering temperature of 1200°C. Unlike the particle size distributions of the wheat starch, the pore size distribution of the sintered diatomite prepared with wheat starch shows a broad peak reflecting the various sizes of the slit-like pores. Also, the pore size distribution of the sintered diatomite prepared with light clusters of aggregated carbon nanotubes shows a negligible difference from the sintered diatomite prepared without any type of sacrificial template, as expected in Fig. 3(e).

The air permeation properties of sintered diatomite membranes prepared with 10 vol.% of different sacrificial templates at a sintering temperature of 1200°C are shown in Fig. 4(c). The permeability of the sintered diatomite membranes with 10 vol.% of 20 μm solid polymer spheres was the highest among the four types of sacrificial templates, and that of the sintered diatomite membrane with 10 vol.% of light clusters of aggregated carbon nanotubes was the lowest. To complement this result, the sintered

diatomite membranes were characterized by two different methods: average pore size measurements by mercury porosimetry and largest pore size measurements by capillary flow porosimetry.

Figures 5(a) and 5(b) show the average pore sizes and the largest pore sizes of the diatomite membranes prepared with various amounts of sacrificial templates ranging from 0 to 15 vol.% while varying the type of sacrificial template (8 μm solid polymer spheres, 20 μm solid polymer spheres, wheat starch, and light clusters of aggregated carbon nanotubes) as a function of darcy's permeability constant, with all samples sintered at 1200°C for 1 h. Although some specimens had higher Darcy's permeability constants than others, the average pore sizes of the sintered diatomite remained nearly unchanged. However, when a sintered diatomite membrane had a Darcy's permeability constant, it had a larger largest pore size. Moreover, for comparison, the data of the sintered diatomite membranes prepared with a 45 μm hollow polymer sphere wet pressed at 1 MPa while varying the amount of the 45 μm hollow polymer spheres ranging 0 to 25 vol.% were also plotted, as shown in Figs. 5(a) and 5(b). Although the largest pore sizes of the sintered diatomite membranes prepared with the 45 μm hollow polymer spheres wet pressed at 1 MPa show a distinctly different trend from those of the sintered diatomite membranes prepared with other templates dry pressed at 25 MPa in Fig. 5(b), the average pore sizes of these membranes show a negligible difference from the average pore sizes of the others in Fig. 5(a).

This occurs because the average pore size as measured by mercury porosimetry accounts for all open pores regardless of the pore type, including blind pores, cross-linked pores, and through pores,³¹⁾ whereas, in principle, the largest pore size measured by capillary flow porosimetry ensures that the pores are interconnected and act as pore channels. Thus, the measured largest pore size of the sintered diatomite membrane can not only provide the largest size of the solute that can pass through as a surface membrane but also can describe appropriately the permeability of the sintered diatomite membrane.

In the literature, the average pore size and the largest pore size of a track-etched polymeric membrane with a cylindrical pore structure and a very narrow pore size distribution, representing the ideal conditions for measuring the largest pore size, are essentially the same.³²⁾ However, the average pore size and the largest pore size of a metallic membrane with an asymmetrical pore structure³³⁾ are unambiguously different. One important consideration is that these studies³⁴⁾ focused on the discrepancies among the average pore size, the largest pore size, and pore size distribution as measured by either mercury porosimetry or capillary flow porosimetry. In the present study, we intended to determine experimentally which method is practically more appropriate when designing a membrane with a specific Darcy's permeability constant and a specific pore size, particularly a ceramic membrane prepared by the sacrificial template method.

Also, these results above show that the characteristics of the sacrificial templates, such as the shape and rigidity, directly affect the final pore characteristics after the sintering process and accordingly determine the permeability of the sintered diatomite membranes.

4. Conclusion

In summary, sintered diatomite membranes were prepared with the sacrificial templates of 8 μm solid polymer spheres, 20 μm solid polymer spheres, wheat starch, and light clusters of aggregated carbon nanotubes. The diatomite membranes were sintered at 1200°C for 1 h at a heating rate of 5°C/min, without a time-consuming burn-out process, unlike the conventional sacrificial template method. Although the diatomite membrane prepared with solid polymer templates had spherical pores, the diatomite membrane prepared with wheat starch had more slit-like pores as opposed to that created with solid polymer spheres due to the difference in the rigidity of the sacrificial templates. Furthermore, the diatomite membrane prepared with light clusters of aggregated carbon nanotubes had no particular pore shape owing to the flexibility of the carbon nanotube itself and the fragility of light clusters.

It is noteworthy that the characteristics of the sacrificial templates directly affect the pore characteristics after the sintering process, and accordingly determine the permeability of the sintered diatomite membranes. Also, the largest pore size of the sintered diatomite membrane can not only provide the largest size of the solute that can pass through as a surface membrane but can also appropriately describe the permeability of the sintered diatomite membrane.

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