The preparation and pore characteristics of an alumina coating on a diatomite-kaolin composite support layer

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Recently porous ceramic membranes have received great interest due to their outstanding thermal and chemical stabilities. In this paper, we investigated whether we could prepare an alumina coating to be deposited over a diatomite-kaolin composite support layer to reliably tailor the permeability by controlling the heat-treatment temperature of the alumina coating. The pore characteristics of an alumina coating on a diatomite-kaolin composite support layer were studied by scanning electron microscopy, mercury porosimetry, and capillary flow porosimetry.

Key-words: Diatomite-kaolin composite support, Alumina coating, Pore characteristics

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1. Introduction

In recent years, porous ceramics have attracted great interest as researchers seek to exploit their unique properties such as low density, low thermal conductivity, and a low dielectric constant. In particular, ceramic membranes are among the most feasible applications of porous ceramics.

It is generally agreed that the most important features of a porous ceramic membrane are its permeation and separation properties. Therefore, the precise tailoring of the pore characteristics of a porous ceramic membrane while retaining an acceptable level of permeability is interesting as a topic of scientific research. Although much research has been dedicated to the study of materials commonly used for porous ceramic membranes such as γ-alumina, α-alumina, titania, zirconia, silica, and composites of these materials, more detailed studies are necessary for porous ceramic membranes prepared from natural clays such as diatomite or kaolin.

Previously, we reported possible approaches for fabricating a sintered diatomite membrane that allow control over the membrane characteristics such as largest pore size and high mechanical strength, while retaining an acceptable level of permeability. These approaches enabled (1) the enhancement of the permeability of the diatomite support layer beyond that achieved by controlling the sintering temperature, (2) the reduction of the largest pore size of the diatomite support layer by forming a diatomite-kaolin composite, and (3) the reduction of the largest pore size of the diatomite support layer by depositing a diatomite-kaolin composite coating.

If an inexpensive natural material composite support layer, such as the diatomite-kaolin composite support layer used in this study, can be coated with a limited amount of an expensive high-purity alumina, an alumina-coated diatomite-kaolin composite support layer can be used as an intermediate platform to replace the expensive high-purity alumina support layer. Moreover, it may be possible to apply the accumulated database of alumina-based membranes to the design of diatomite-based membranes as future coatings for catalytic or filtration applications.

Notably, because the previous reports demonstrated that the diatomite-based support layers exhibit higher permeability than that of typical alumina support layers, it might be possible to compensate for the inevitable reduction in the overall permeability after applying an alumina coating onto diatomite-based support layers. However, there are a number of issues regarding the permeability of an alumina-coated diatomite-kaolin composite support layer. Here, we report the results of investigations that are quite different from either of the results reported previously.

In this study, the main focus was to evaluate the feasibility of coating an alumina layer onto a diatomite-kaolin composite support layer. We determined whether we could control the permeability of the diatomite-kaolin composite layer by adopting an alumina coating prepared under different heat-treatment temperatures.

2. Material and methods

Diatomite (Celite 499, Celite Korea Co. Ltd., Korea) and kaolin (Kaolin, Sigma-Aldrich, USA) were used to prepare a diatomite-kaolin composite support layer. The average particle sizes of the starting powders were determined by a particle size analyzer (LSTM 13 320 MW, Beckman Coulter, USA). The average particle sizes of the as-received diatomite, as-received kaolin, and as-received alumina (AKP-30, α-alumina, Sumitomo Chemical, Japan) were 12.79, 1.53, and 0.45 μm, respectively.

To enhance the sintering of the diatomite particles, the average particle size of the diatomite was reduced to 7.43 μm by ball-milling. In the ball-milling process, distilled water was used as the solvent, and the slurry was ball-milled for 24 h with an alumina ball-to-powder volume ratio of 2:1. To incorporate kaolin into the diatomite matrix, diatomite particles were mixed with 10 wt.% kaolin for 3 h by ball-milling with an alumina ball-to-powder volume ratio of 2:1. Using polyethylene glycol as the binder, the diatomite-kaolin composite specimens were dried at 18.7 MPa and then sintered at 1200°C for 1 h.

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To compare the pore characteristics of the diatomite-kaolin composite support layer with those of a typical alumina support layer, a commercial alumina support layer (disk type alumina membrane, 0.1-μm pore size, Nano Pore Materials, Korea) was purchased. The bulk densities of an as-sintered diatomite-kaolin composite support layer and an as-received commercial alumina support layer were 1.63 and 1.81 g/cm³, respectively.

A dip-coating process was used to deposit an alumina coating onto the diatomite-kaolin composite support layer. For the coating process, alumina, distilled water, an organic binder (HS BD-25, San Nopco Korea, Korea), and an inorganic binder (AS-40, Sigma-Aldrich, USA) were mixed, dip-coated on a pre-sintered diatomite-kaolin composite support layer, dried at room temperature for 24 h, and then heat-treated at 500–1200°C for 1 h.

The pore characteristics of the diatomite membranes were examined by scanning electron microscopy (JSM-5800, JEOL, Japan). The air flux was measured by capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., USA). All specimens (diameter 4 cm, and thickness 0.4 cm) were fitted between the O-rings in the bottom of the chamber and the bottom of the chamber insert used for capillary flow porosimetry. The flux was then measured automatically by sensors while incrementing the diameter of the motorized valve and the pressure of the regulator.

The largest pore size of the diatomite membrane was measured by the bubble point method, which is the most widely used approach for pore size determination and is capable of determining the largest pore size of a membrane. The method is based on the fact that, for a given fluid and pore size with constant wetting, the pressure required to force an air bubble through the pore is inversely proportional to the size of the pore.

3. Results and discussion

As previously reported,22) the interconnected pore structure of the diatomite-kaolin composite support layer was gradually shaped and defined, as the sintering temperature increased from 1000 to 1200°C. Although, the flexural strength sharply increased as both the sintering temperature and the amount of kaolin were increased, the permeability of diatomite-kaolin composite support layers were inversely proportional to the amount of kaolin addition. Therefore, in this study, all of the diatomite-kaolin composite support layers used were prepared with 10 wt.% kaolin, and the sintering temperature was set to 1200°C, to yield the appropriate permeability and mechanical strength. In addition, the mullite phase appeared as the amount of kaolin reached 25 wt.%.

At least microscopically the diatomite-kaolin composite support layer has a well-defined interconnected pore structure similar to that of a commercial alumina support layer. However, the feasibility of the application of a diatomite-kaolin composite support layer as a porous ceramic membrane must also be rationalized on the basis of the pore characteristics data.

Therefore, using mercury porosimetry, the pore size distribution and the pore structure of a diatomite-kaolin composite support layer were compared with those of a commercial alumina support layer. Figure 1 shows the pore size distributions of the diatomite-kaolin composite support layer and the as-received commercial alumina support layer. The average pore size of the diatomite-kaolin composite support layer and the as-received commercial alumina support layer were 1.085 and 0.104 μm, respectively, and both of them exhibited sharp pore size distributions, which positively affect the selectivity of a porous ceramic membrane.

Figure 2 presents the mercury intrusion-extrusion behavior of the diatomite-kaolin composite support layer and an as-received commercial alumina support layer. Obvious intrusion-extrusion hysteresis and mercury entrapments were observed, which implies that the microstructures of the aforementioned specimens consisted of a highly interconnected pore structure.26–28)

The image in Fig. 3(a) is a SEM cross-section of the alumina coating on the diatomite-kaolin composite layer, which was coated and then heat-treated at 500°C for 1 h. Defects, cracks, or delamination between the alumina coating and the diatomite-kaolin composite support layer were rarely observed. The images in Figs. 3(b) and 3(c) are SEM cross-sections of the alumina coating on the diatomite-kaolin composite layer, which was coated and then heat-treated at 700, and 900°C for 1 h, respec-
tively. These two figures clearly reveal the randomly distributed micro-cracks on the alumina coating layer, which are in contrast to the image shown in Fig. 3(a). Furthermore, the alumina coating on the diatomite-kaolin composite support layer that was heat-treated at 1100°C for 1 h exhibited severe micro-cracks, as shown in Fig. 3(d). This behavior is due to the difference in the linear shrinkage rate between the alumina-based coating and the silica-based support layer, which abruptly increases at temperatures above 1000°C. Moreover, the diatomite-kaolin composite support layer was pre-sintered prior to the alumina coating process, leaving very little shrinking potential to match the shrinkage of the alumina coating when they were later heat-treated together.

Figures 4(a) and 4(b) show the specific flow of the alumina coating deposited onto the diatomite-kaolin composite support layer as a function of the heat-treatment temperature. The permeability of the as-sintered diatomite-kaolin composite support layer is higher than that of the as-received commercial alumina support layer, which makes it possible to operate efficiently in industrial applications. The difference in permeability can be explained by the average pore size and the inter-connected pore structure of the diatomite-kaolin composite support layer compared to those of the alumina support layer, as previously shown in Figs. 1 and 2.

Note that the specific flow of all of the specimens does not increase linearly as the applied pressure increases, which can be understood as follows. At low pressure (<100–200 kPa), the specific flow is controlled by the Knudsen diffusion; at high pressure (>200–300 kPa), the specific flow is governed by the viscous flow; and at intermediate pressures, all of the Knudsen, slip, and viscous flows contribute to the specific flow. This trend is well-matched with the results previously reported by other researchers. 31,32

Figure 4(a) shows that the specific flow of the alumina-coated diatomite-kaolin composite support layer heat-treated at 500°C for 1 h follows the specific flow trend of the as-received alumina support layer at low pressure. As the applied pressure increases, an inflection point on the specific flow curve is observed. After this point, the response begins to follow the specific flow of the as-sintered diatomite-kaolin composite support layer. As the heat-treatment temperature increases from 500 to 1000°C, the inflection point gradually shifts to a higher pressure.

In contrast to Figs. 4(a), 4(b) indicates that the specific flow of the alumina-coated diatomite-kaolin composite support layer heat-treated at 1100°C for 1 h nearly matches the specific flow trend of the as-sintered diatomite-kaolin composite support layer, regardless of the applied pressure. Furthermore, the specific flow of the alumina-coated diatomite-kaolin composite support layer heat-treated at 1200°C for 1 h nearly matches the specific flow trend of the as-sintered diatomite-kaolin composite support layer. It can be suggested that the alumina coating cannot affect the overall permeability of the alumina-coated diatomite-kaolin composite support layer as the heat-treatment temperature reaches 1100°C due to the severe micro-cracks of the alumina coating, as observed in Fig. 3(d).

Because we observed an abrupt increase in the specific flow as the applied pressure increased, repeated permeability measurements were performed. A difference in the specific flow curve between the first measurement and subsequent measurements, and/or a continuous deterioration of the permeability during the repetitive measurements can be explained by the presence of the inflection point on the specific flow curve, which occurs as a consequence of the brittle fracture of the alumina coating at a certain pressure.

Figure 5 shows repetitive permeability measurements of the alumina-coated diatomite-kaolin composite support layer heat-treated at 700°C for 1 h. From the first measurement to the fifteenth measurement, all of the specific flow curves are found to overlap, which indicates a low measurement error. Although the data are not plotted, the repetitive permeability measurements...
of the alumina-coated diatomite-kaolin composite support layer exhibit a similar response with the abovementioned results, regardless of the heat-treatment temperature.

To complement the repetitive permeability measurements, the largest pore size was measured before and after the permeability measurement. The overall permeability can be affected by even a large pore or crack generated by the applied pressure during the permeability measurement. Unlike the average pore size measured by mercury porosimetry, the largest pore size measured by the bubble point method can be useful for the detection of a newly generated large pore or crack.

However, the largest pore sizes before and after the permeability measurement do not vary significantly, regardless of the heat-treatment temperature of the alumina coating, as shown in Fig. 6. This result shows that the largest pore size can be controlled by adjusting the heat-treatment temperature of the alumina coating.

Based on the aforementioned experiments, it can be suggested that the presence of an inflection point on the specific flow curve is not the result of an irreversible brittle fracture on the alumina coating. Instead, the inflection point may be caused by the influence of the complex blending of permeation through the bilayer structure, which consists of two materials with different permeability. Although the permeability of a diatomite-kaolin composite support layer does not depend on the heat-treatment temperature because it was already sintered at 1200°C, the
permeability of the alumina coating can be affected by the heat-treatment temperature. Thus, the specific flow curve gradually behaves more alumina-like as the heat-treatment temperature increases to 1100°C, and then, as the heat-treatment temperature increases further, the formation of severe micro-cracks in the alumina coating begins to dominate the overall permeability. Therefore, the specific flow curve behaves more diatomite-kaolin composite-like as the heat-treatment temperature reaches 1100°C.

In summary, we could tailor the pore characteristics of a low-cost diatomite-kaolin composite support layer to a commercial alumina support layer by depositing alumina coatings prepared under different processing conditions on diatomite-kaolin composite support layers. We also discussed that the linear shrinkage difference between an alumina-based coating and a diatomite-kaolin composite support layers. The permeability and the largest pore size of the diatomite-kaolin composite support layer by depositing alumina coatings prepared under different processing conditions on diatomite-kaolin composite support layers. Therefore, the permeability of the alumina coating can be affected by the heat-treatment temperature.

4. Conclusions

We prepared alumina-coated diatomite-kaolin composite support layers, and compared them with a commercial alumina support layer. The permeability and the largest pore size of the alumina-coated diatomite-kaolin composite support layer could be controlled by varying the heat-treatment temperature of the alumina coating, which provided an effective means of tailoring the pore characteristics.

Furthermore, note that the permeability and the largest pore sizes of the diatomite membranes could be maintained reliably during repetitive measurements. These findings demonstrate the feasibility of using a modified diatomite membrane as a porous ceramic membrane for microfiltration.

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References