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Preparation and some properties of porous alumina ceramics obtained by the gelatination of ammonium alginate

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This study was carried out to develop a new preparation process of porous alumina ceramics and to examine their porous properties. The gelatination of ammonium alginate by hydrochloric acid was used for the formation of a gel-like precursor composed of alumina particles and alginic polymer. By this simple chemical shaping process of green bodies, porous alumina ceramics with a very sharp pore size distribution and a porosity of 40 to 55% could be obtained after firing at 1000 to 1600 °C. The porosity showed an improvement of 15–20% compared with that of porous materials prepared from conventional procedures such as the pressing and slip-casting methods. The optimum concentrations of ammonium alginate and hydrochloric acid were 0.3–2.0 wt% and over 0.1 N, respectively, from the standpoint of the mixing treatment of raw materials and the gelatination.

1. Introduction

Porous ceramics have been increasingly used for industrial filters, catalyst supports and gas sensors. There are several methods to produce these porous ceramic materials. In particular, a process of burning off the added organic components from the green compact is often used because of the lower production cost. This process, however, has some problems such as the dispersibility of raw materials during the mixing and the uniformity of pore size distribution after the firing treatment.

Ammonium alginate is well known as an organic polymer, $-\!(C_5H_7O_4\ COONH_4)_{\overline{n}}$, which can be gelatinated by an ion-exchange reaction with protons or multivalent metal ions [1–7]. This polymer is widely used for the immobilization of yeasts and for the gel-like products of the food industry [8, 9].

In this paper, we tried to substitute ceramic powder for the yeast particles to develop a new shaping procedure and to obtain porous ceramics with a high porosity and sharp pore size distribution by burning off the ammonium alginate. The porous properties of alumina ceramics based on this method under several conditions were examined and compared with those of porous ceramics prepared by other methods.

2. Experimental procedure

Raw materials used in this study were α-type alumina (AES-12, average particle size 0.4 μm, Sumitomo Chemical Co.) and a commercial ammonium alginate powder (Wako Chemical Co., average molecular weight 860 000). The flow-chart to prepare porous alumina ceramics is shown in Fig. 1. Ammonium alginate (0.1–5 wt %), pure water and the deflocculant ammonium polycarboxylate (< 0.3 wt %) were fully mixed by a high-speed agitator. Alumina particles were then mixed with the alginate solution in a plastic pot-mill for 12 h. The mixture was dropped into 0.1 to 2 N HCl solution at 24 °C from a small burette nozzle to promote the ion-exchange reaction of NH_4^+ and H^+ ions. Droplets with a diameter of 1–3 mm were washed in pure water until the pH was 6–7. After drying at 60 °C for 12 h, droplets were fired at 1000–1600 °C for 2 h to form porous ceramics by the burning off of ammonium alginate.

Some properties of the resulting porous ceramics such as the porosity, average pore diameter, pore size distribution and morphology were investigated by a mercury porosimeter (Shimadzu Seisakusho, model 9310) and SEM (Jeol model 840) observation. Furthermore, some properties of porous ceramics prepared by the alginating method were compared with those of ceramics prepared by other processes such as pressing and slip-casting. In these processes, the same amount of ammonium alginate powder was added to alumina powder.

3. Results and discussion

The effect of several preparation methods on the porosity of porous alumina ceramics prepared at 1000–1600 °C for 2 h is shown in Fig. 2. The pore size distribution curves of porous ceramics prepared by alignation and slip-casting are shown in Fig. 3. The sintering of alumina particles was gradually promoted, so the porosity tended to decrease with increasing firing temperature. However, the porosity of

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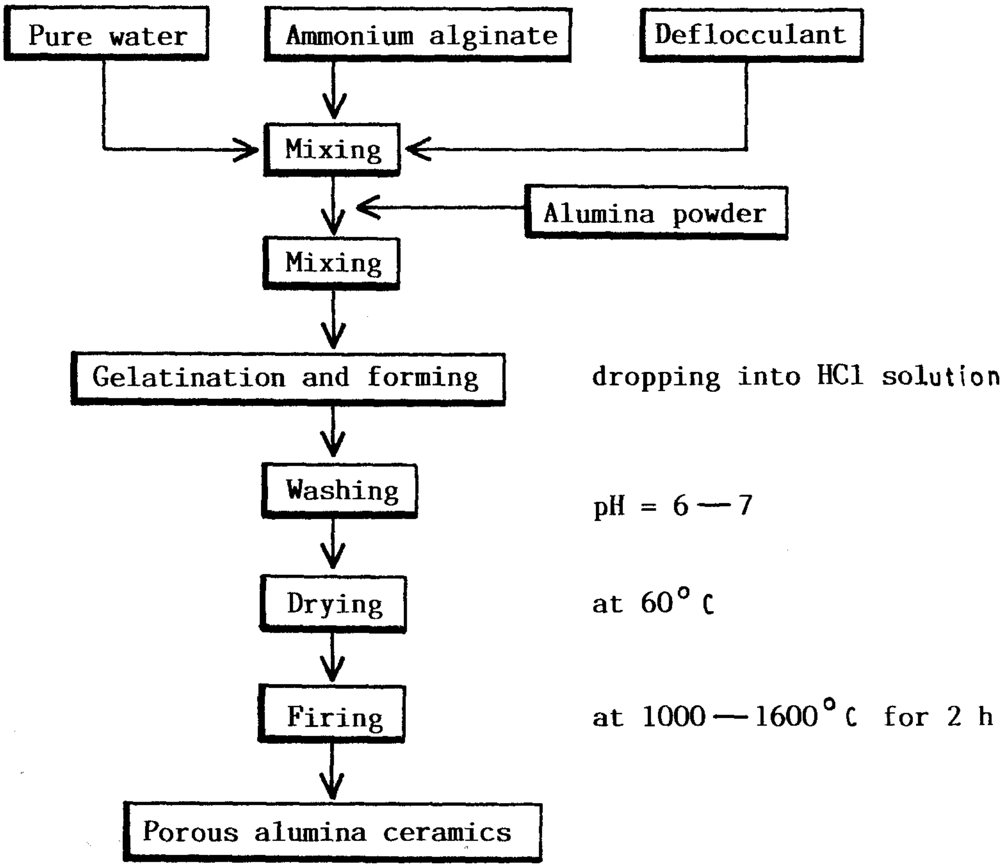

Figure 1 Preparation procedure of porous alumina ceramics by use of ammonium alginate.

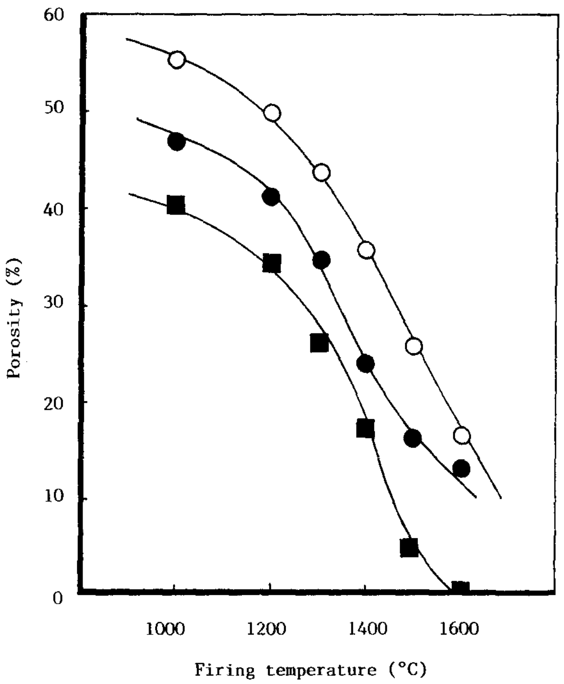

Figure 2 The effect of three kinds of preparation method on the porosity of porous alumina ceramics prepared at 1000 to 1600 °C for 2 h: (○) gelatination method, (■) slip-casting, (●) pressing.

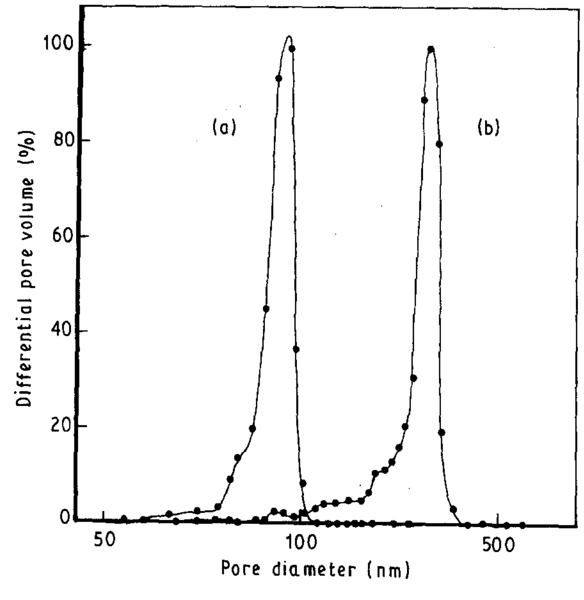

Figure 3 Pore size distributions of porous alumina ceramics obtained by (a) slip-casting and (b) algination methods.

ceramics prepared by this gelatination was higher than that of ceramics made by the pressing or slip-casting methods and showed an improvement of 15–20% up to 1500 °C. It is assumed that a very thin ammonium alginate film can envelop fine alumina particles together with water by the ion-echange reaction of NH_4^+ and H^+ ions, as in the reaction

$$-\!(C_5H_7O_4COONH_4)_n\!- + n\mathrm{HCl} \rightarrow -\!(C_5H_7O_4COOH)_n\!- + n\mathrm{NH_4Cl} \qquad (1)$$

and furthermore it is assumed that this film may be important to maintain the separation of the alumina particles.

In the pressing and slip-casting methods, alumina particles and ammonium alginate powders are mixed only mechanically but not gelatinated, so the porosity of porous ceramics is relatively lower due to the absence of a thin ammonium alginate film around each alumina particle.

Fig. 4 shows the effect of the concentration of ammonium alginate on the properties of porous alumina fired at 1200 °C for 2 h. Gel-like materials composed of alginic polymer, alumina particles and water could be produced in concentrations from 0.3 to 2.0 wt % and the porosity and pore diameter were constant after the firing. In this study, the concentration of ammonium alginate had many influences on the formation of droplets. When the concentration was below 0.3 wt % of ammonium alginate, shaping caused by the gelatination which was sufficient to form droplets in solution could not be observed, and it was very difficult to well mix the raw materials over 2.0 wt % because the ammonium alginate solution had too high a viscosity to form droplets from a small burette nozzle. Therefore, the concentration of ammonium alginate of 0.3 to 2.0 wt % was optimum to produce porous ceramics by use of the gelatination of ammonium alginate.

The effect of the gelatination time on the porosity of porous alumina ceramics fired at 1200 °C for 2 h is shown in Fig. 5. The concentration of HCl solution was 1 N. This result reveals that when a mixture of raw materials in solution is dropped into HCl solution, the rate of gelatination is expected to be high and ammonium alginate can immediately fully gelatinate inside a droplet. This phenomenon can be recognized from Fig. 6, which shows morphologies of the internal and outside parts of one droplet fired at 1200 °C for 2 h.

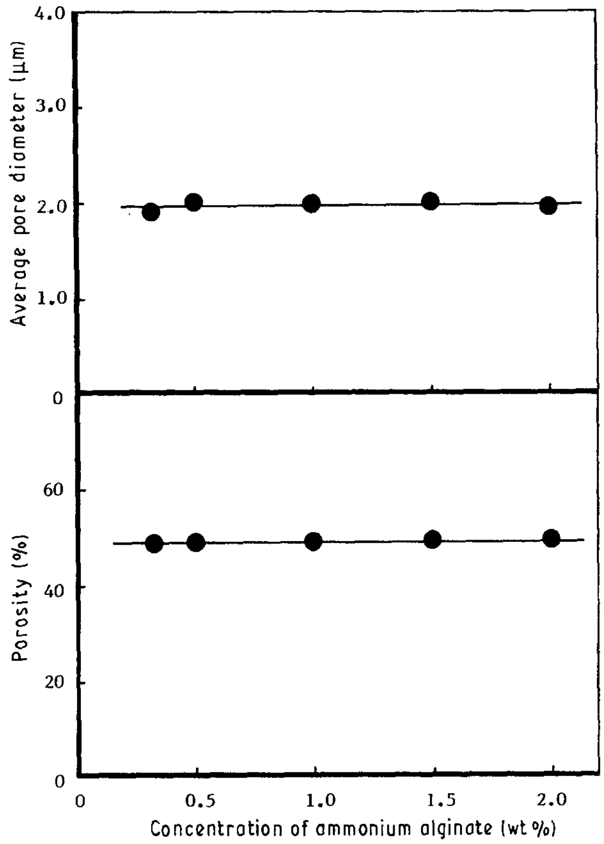

Figure 4 Effect of the concentration of ammonium alginate on the properties of porous alumina ceramics.

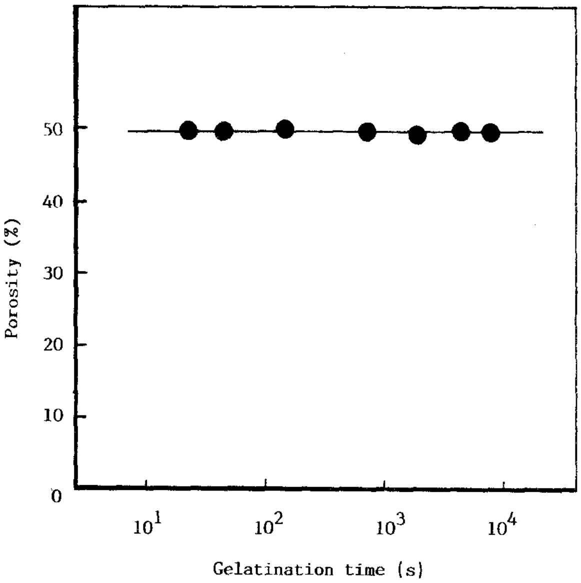

Figure 5 Effect of gelatination time on the porosity of porous alumina ceramics.

In addition, the concentration of HCl solution is a very important factor to initiate the gelatination of ammonium alginate, so the effect of the concentration of HCl on the properties of porous ceramics fired at 1200 °C is shown in Fig. 7. There were no changes in the porosity and average pore diameter above 0.1 N HCl. Below 0.1 N HCl, however, the porous properties could not be evaluated because no droplets could be formed in the solution. In this case, when one gel droplet (0.57 g) is formed by gelatination, it can contain about 5.7 mg (6.63×10^{-9} mol) of ammonium alginate. If the algination of one droplet is caused by the reaction of Equation 1, only 2.95×10^{-5} mol of HCl is needed to perform the ion-exchange reaction. However, a concentration of HCl over 0.1 N was needed to form one droplet in this study. This drastic difference of the theoretical and experimental concentrations of HCl solution to cause the gelatination is not yet fully examined.

4. Conclusions

Based on our studies, the following conclusions could be obtained.

1. Gel-like droplets which contained alumina particles and alginic polymer could be easily produced by using the gelatination of ammonium alginate and HCl solution. After firing at 1000–1600 °C, porous alumina ceramic with a sharp pore size distribution could be obtained, and its porosity showed an improvement of 15–20% compared with that of porous alumina ceramics prepared by conventional methods such as pressing and slip-casting.
2. In this alginating process, the optimum concentration of ammonium alginate was 0.3–2.0 wt % from the standpoint of the mixing procedure of raw materials and the shaping of droplets.
3. In the case of a droplet of 1–3 mm diameter, a very small amount of ammonium alginate could be

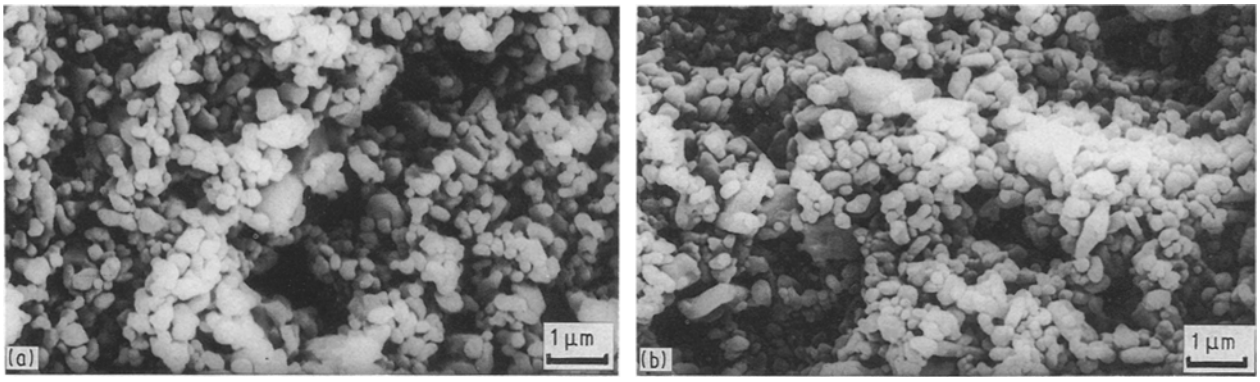

Figure 6 Morphologies of porous alumina ceramics obtained by the gelatination method: (a) fractured surface, (b) sintered surface area.

fully gelatinated inside a droplet by dilute HCl solution, and there existed uniform pore structures in the products fired at 1200 °C.

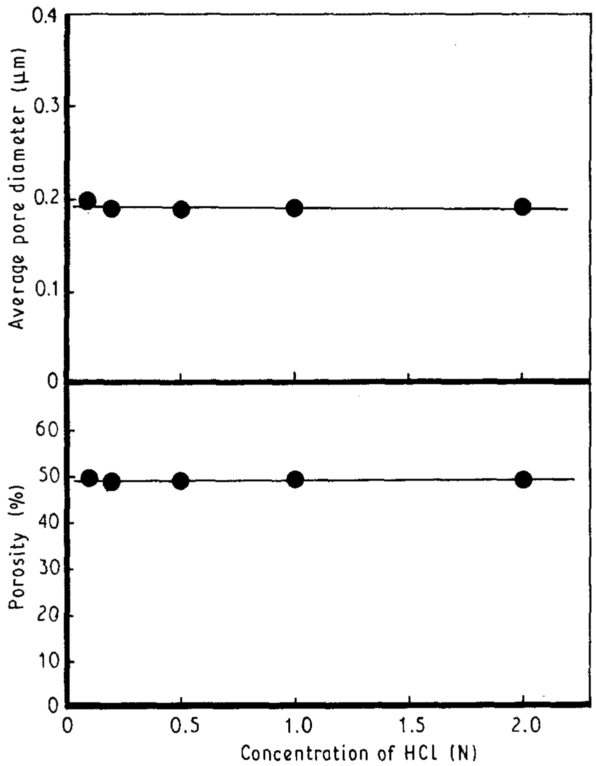

Figure 7 Effect of the concentration of HCl on the properties of porous alumina ceramics.

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