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Preparation of SiO_2-ZrO_2-Na_2O Porous Glasses

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A new method for preparation of porous supports was investigated through heating the sol-gel derived SiO_2-ZrO_2 microspherical gel in the presence of NaCl. The products were composed of sponge-like structure similar to the porous glasses manufactured by the phase separation method.

Porous glasses containing ZrO_2 in their composition are received much interest since they are highly resistant to the alkaline solution. Eguchi et al. recently prepared the porous glasses composed of SiO_2-ZrO_2 skeleton by the phase separation method.[1] The resultant glasses had pore size in the range of about 100—10000 Å in radius, in contrast to the SiO_2-ZrO_2 porous glasses through the sol-gel method, whose pore size was smaller than 50 Å.[2] However, their process was quite complicated and troublesome since SiO_2 and ZrO_2 gel had to be removed in addition to phase separation and acid leaching. Therefore, the simple method is desired for manufacturing SiO_2-ZrO_2 based porous glasses, whose pore size is large enough for separation of biological materials. In this communication, we report a new preparation method of SiO_2-ZrO_2-Na_2O porous glasses.

A starting material in the present study was the SiO_2-ZrO_2 gel, which was prepared by dispersing a mixed alkoxide solution with organic solvent into aqueous solution and gelated with ammonia solution.[3] The gel consisted of nearly spherical particles of about 10 to 100 microns in diameter. Its composition after firing at 700 °C for 5 h was $83SiO_2$-$17ZrO_2$ based on wt%. To 2.0 g of the dried gel, 6.1 ml of 15 wt% NaCl solution was added and dried at 110 °C for 5 h. The impregnated gel was heated at 600 °C for 3 h under stream of air and heated again at designated temperature for 5 h. The calcined sample was washed with water followed by hot water of about 90 °C, then collected by filtration and dried at 110 °C.

Three products A, B, and C were prepared by the additional heating at different temperature 730, 760, and 800 °C, respectively. The surface area measured by nitrogen adsorption was 48, 37, and 28 m^2/g in product A, B,

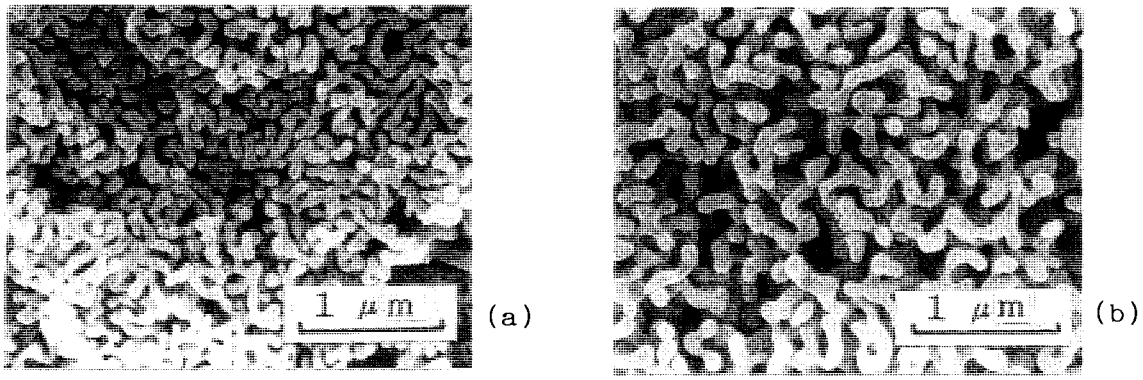

Fig. 1. SEM photographs of the porous glasses, (a) product B and (b) product C.

and C, respectively, whereas that of a product heated at 700 °C without addition of NaCl was 225 m^2/g. A large decrease in surface area was observed for products heated with NaCl. It reduced gradually as the calcination temperature increased. The peak of pore radius was became larger, in the order, A(804 Å) < B(892 Å) < C(1000 Å), and their pore volume also reduced as the calcination temperature increased, as measured by mercury penetration porosimetry. These results suggested that sintering and shrinkage of the microspherical particles were taking place as the heating temperature increased.

The SEM photographs of B and C were demonstrated in Fig. 1. Glassy skeleton analogous to porous glasses prepared by the phase separation method was clearly observed in both figures. In contrast, the surface of the starting particle was similar to texture of the gel. Therefore, this structure is believed to be formed via liquid phase viscous sintering process during heat treatment of the gel and NaCl. The oxide composition of the product C was $75SiO_2$-$16ZrO_2$-$8Na_2O$ based on the chemical analysis. The Cl content was about 0.1 wt%. It was suggested that Na cation was selectively incorporated into the product composition.

It is well-known that the salt impregnation of SiO_2 gel and the subsequent heat-treatment caused pore size enlargement together with crystallization of SiO_2 gel to α-cristobalite.[4] However, the results presented above indicated that porous glasses in the system SiO_2-ZrO_2-Na_2O were formed when the SiO_2-ZrO_2 gel was heated with NaCl. The present process is quite simple compared to the phase separation method, and especially suited for preparation of microspherical particles.

References

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