Preparation of SiO_2–ZrO_2–Na_2O Porous Glass Supports

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A new method for preparing porous supports was investigated by heating a sol-gel-derived SiO_2–ZrO_2 and SiO_2–TiO_2 microspherical gel in the presence of NaCl. In the SiO_2–ZrO_2 system, the surface of the products comprised a sponge-like structure similar to the porous glasses manufactured by the phase-separation method. Their pore volume ranged from 1.48 to 3.18 $cm^3\,g^{-1}$ and the surface area ranged from 10 to 48 $m^2\,g^{-1}$. They contained a significant amount of Na_2O, whereas the Cl content was less than 0.1 wt%. The alkaline durability was excellent, as was expected from the composition of SiO_2–ZrO_2–Na_2O. On the contrary, a heat treatment of the sol-gel-derived SiO_2–TiO_2 microspherical gel, together with NaCl, caused crystallization of titania and silica, and the formation of glassy mixed oxide was not observed.

Porous glasses represent one type of well-known material having a beautiful texture, which originates from phase-separation. The size of the pores is quite uniform, and can be controlled by the heat-treatment conditions. They generally have high resistance to heat, as compared to that of the conventional silica gels. Various applied research has therefore been attempted, such as membrane separation, support for chromatography, carriers of enzymes and biomaterials, and catalysts.

Concerning the phase-separation method, non-porous mother glasses are manufactured, at first, by melting oxide materials at high temperature; they are then phase-separated, and a unique phase-separated glass texture is formed by a heat treatment of the mother glass. For example, Vycor glass, which is the typical porous glass, is manufactured from the SiO_2–B_2O_3–Na_2O mother glass. It is phase-separated and acid-leached in order to remove the B_2O_3–Na_2O-rich phase. However, the silica component in porous glass is dissolved, as in cases of silica gels, when they are used even in the weak alkaline solutions. This phenomenon is attributed to the fact that the silica gels remain between the porous glass skeletons.

To improve the alkaline-resistant property of porous glass, various trials to incorporate ZrO_2 into SiO_2 glass have been reported. One approach to obtain SiO_2–ZrO_2 porous glass was based on the conventional phase-separation technique, with an improvement in the mother-glass composition.[1—6] The addition of relatively large amount of alkaline-earth oxide, or zinc oxide, into the SiO_2–ZrO_2–Na_2O–B_2O_3 composition was found to be effective for leaving ZrO_2 in the porous glass skeletons. However, the amount of incorporated ZrO_2 was limited to about 5 wt%, since a part of the ZrO_2 was supposed to be in the acid-leaching phase. Moreover, a part of the ZrO_2 gel remained in the porous glass structure, which needed to be removed by a strong acid.

Another way to prepare a SiO_2–ZrO_2 porous glass was in line with the sol-gel process used to manufacture SiO_2–ZrO_2 gels.[7—10] After a heat-treatment of the gel, a SiO_2–ZrO_2 porous glass was formed. In this method, the ZrO_2 content could be easily controlled. However, the pore size of the resultant porous glass was usually small, around 40 Å in radius at maximum; their pore volumes were also small.

We investigated another process for preparing porous glass supports in the SiO_2–ZrO_2 system, whose ZrO_2 content was more than 5 wt%, and the pore size was larger than 100 Å. We also briefly reported on a new process for synthesizing SiO_2–ZrO_2–Na_2O porous glass supports from SiO_2–ZrO_2 gel and NaCl.[11] In the present paper we report on the results of the preparation and characteristics of these novel supports, and compare them with supports prepared from SiO_2–TiO_2 gel and NaCl.

Experimental

Preparation of Dried SiO_2–ZrO_2 Gel. The partial hydrolysis of ethyl silicate was performed by mixing ethyl silicate (250 g), ethanol (68.2 g), water (6.5 g), and a 0.1 M-HCl ethanolic solution (9.35 g) and refluxing at 60 °C for 30 min; the $H_2O/Si(OEt)_4$ and $H^+/Si(OEt)_4$ mole ratios were 0.3 and 0.001, respectively. To this mixture was added $Zr(OBu)_4$ (31.9 g), $P(OBu)_3$ (31.8 g), and ethanol (10 g). The resultant solution was heated at 120 °C for 1 h and 150 °C for 2 h under an Ar atmosphere to remove any volatile materials. The remaining solution (276.0 g) was used as an alkoxide solution for a mixed-oxide gel.

The alkoxide solution (44.5 cm^3), mixed with 7.5 cm^3 of cyclohexane and 22.5 cm^3 of *t*-amylalcohol, was added dropwise into an aqueous solution (433.9 g of water, ethanol (13.5 g) and Tween 20 (Polyoxyethylenesorbitan monolaurate) (3.4 g)) under stirring at about 400 rpm, to form an O/W emulsion. Then, 58.5 cm^3 of a 17.2% ammonia aqueous solution was added during 40 min; the resulting solution was stirred for 5 h and left standing over night. A white gel formed immediately upon the addition of an ammonia solution. After the supernatant solution was removed by decantation, the gel was washed with ethanol, collected by filtration and dried at 100 °C for 5 h. The dried gel was formed as nearly spherical particles of about 10 to 100 μm in diameter.

Preparation of SiO_2–ZrO_2–Na_2O Porous Glass. A weighed amount of 15 wt% sodium chloride aqueous solution was added to the dried gel described above, and dried at 110 °C for 5 h. Then, 2.0 g of the dried gel almost completely adsorbed 6.13 g of 15 wt% sodium chloride solution. The impregnated gel in the quartz tube was heated to 600 °C at a rate of 2 $°C\,min^{-1}$, and kept at 600 °C for 3 h under a stream of air. It was heated again in an alumina crucible at designated temperature for 5 h in a furnace. The calcined sample was added to 250 cm^3 of water, and the slurry was stirred for 3 h; the supernatant solution was then removed by decantation, and the same amount of water was added again. The slurry was heated at 90 °C for 3 h and left standing. After the supernatant solution was removed by decantation, 1000 cm^3 of water was added and the mixture was stirred. The samples were collected by filtration, then dried at 110 °C for 5 h. The dried gel in the SiO_2–TiO_2 system was prepared by the same procedure as that of the SiO_2–ZrO_2 gel, except that $Ti(OEt)_4$ was used instead of $Zr(OBu)_4$. The impregnation method of NaCl on the SiO_2–TiO_2 gel and the condition of the heat treatment was also the same as that described above.

Characterization of Products. The pore distribution and pore volume of the porous glasses were measured by a mercury penetration porosimetry using an Autopore 9200, Micrometrix. The maximum attainable pressure was 368 MPa, corresponding to 20 Å in pore radius. The surface area was obtained by a multipoint nitrogen-adsorption isotherm using the BET method by a Sorptomatic 1800, manufactured by Carlo Elba Co.

The X-ray diffraction (XRD) measurements were made using Cu *Kα* radiation and a diffraction device fitted with a graphite monochromatory using a Phillips PW 1700. A scanning electron microscope (SEM) observation was performed on gold-coated surfaces using a Hitachi S-900. The sample used for transmission electron microscope (TEM) was prepared according to a method described in Ref. 12, and it was observed using a JEOL JEM-100CX. The thermogravimetric-differential thermal analysis (TG-DTA) curves were measured using a Rigaku TG-DTA. The samples in the Pt cell were held at 200 °C for 40 min, and then heated to 1500 °C at a rate of 10 $°C\,min^{-1}$ under an air stream.

Chemical analyses of the products were performed as follows. For a SiO_2 analysis, the samples were dissolved by adding H_3BO_3–Na_2CO_3 and heating to melt. The amounts of SiO_2 were analyzed by weight loss after a HF treatment. The Cl contents were measured by ion chromatography after the samples had been dissolved by the method described above. For Zr, Ti, Na, and P analyses, the samples were dissolved by adding H_2SO_4–HF and heating. The Zr, Ti, and P concentrations were measured by inductively coupled plasma (ICP, JY-38P, Seiko Densi Kogyo), and the Na content was measured by atomic absorption spectrometry (AAS).

For a preliminary alkaline-resistant test, after about 100 mg of the sample had been dried at 120 °C to constant weight, it was weighed and then added to a Teflon® container, followed by a 0.1 M-NaOH solution. The Teflon container was shaken several times, and left standing at room temperature. After 24 h, the Si concentration of the solution was determined by ICP by sampling 5 cm^3 of the solution. Three reference samples (G1, G2, and S1) were prepared as follows. G1: the dried gel in the SiO_2–ZrO_2 system was calcined at 700 °C for 5 h. G2: the gel composed of $81SiO_2$–$19ZrO_2$ was made from the mixed oxide composition similar to the mixed alkoxide solution described above, except that prehydrolysis of $Si(OEt)_4$ was performed on the condition that $H_2O/Si(OEt)_4$ mole ratio was 1.0. This gel was heated at 800 °C for 5 h. S1: the SiO_2 gel was synthesized by the same procedure with that of G2, without using $Zr(OBu)_4$.

Results

Preparation of the SiO_2–ZrO_2 Gel. The unique procedure used to prepare microspherical silica gel was originally described by Unger, using an O/W technique.[13,14] The organic phase, comprising a prehydrolyzed solution of ethyl silicate and cyclohexane, was dispersed into an aqueous phase comprising water and ethanol; it was then gelled with an ammonia solution. The obtained silica gels were about 10 μm in size and possessed an average pore diameter in the range between 30 and 300 Å. A similar method was applied to the preparation of SiO_2–ZrO_2 gel.[15] The starting material in the present study, a SiO_2–ZrO_2 based gel, was also synthesized using an analogous procedure, except that a mixed alkoxide included $P(OBu)_3$, and the ratio of water to ethyl silicate was 0.3 (much smaller than 1.0). The SiO_2–ZrO_2 gel was formed as nearly spherical particles of about 10 to 100 μm in diameter. The mixed alkoxide solution used in the present study was $79SiO_2$–$11ZrO_2$–$10P_2O_5$ when it was calculated on the oxide-weight basis. However, a chemical analysis of the gel calcined at 700 °C for 5 h indicated that its composition was $83SiO_2$–$17ZrO_2$ by weight, and that the content of P_2O_5 was less than 1 wt%. This result indicated that $P(OBu)_3$, which existed in the mixed alkoxide solution, was scarcely incorporated into the gel composition, since the hydrolysis rate of $P(OBu)_3$ was very slow compared to that of $Zr(OBu)_4$. It behaved like organic solvents added to a mixed alkoxide solution, and contributed to the formation of larger size pores.

The surface of the SiO_2–ZrO_2 microsphere gel was generally smooth with a dense coated layer according to a SEM observation. Fairly large pores of up to 3 μm in size (Fig. 1(a)) were found in some parts of the particle surface. Inside of the particle was porous. It was assumed that the gel particles comprised a porous core and a dense outer skin. These particles were supposed to be highly porous, since more than 3.1 cm^3 of NaCl solution per 1.0 g of the gel was almost completely adsorbed. The pore formation was controlled by the amount of organic solvent added and the degree of prehydrolysis of ethyl silicate. The organic solvent remained inside of the microspherical emulsion until the gelling stage started, and played a role in pore formation. The very high porosity of SiO_2–ZrO_2 gel in this study was attributed not only to the small mole ratio of water to ethyl silicate, but also to $P(OBu)_3$, which behaved in a similar manner to that of cyclohexane and *t*-amylalcohol.

Characterization of SiO_2–ZrO_2–Na_2O Porous Glasses. Table 1 shows the synthetic conditions and surface areas of ten samples prepared under different conditions. In samples A1 to A5, 0.46 g of NaCl per 1.0 g dried gel was adsorbed and heated at different temperatures for 5 h. The surface areas of samples A2, A3, and A4, heated at between 730 and 800 °C, were less than 50 $m^2\,g^{-1}$, which was much smaller than that of A1, which was heated at 700 °C. In contrast, sample A5, which was heated at 820 °C, was nearly sintered. Sample A3-2 was prepared using a gel synthesized separately in double

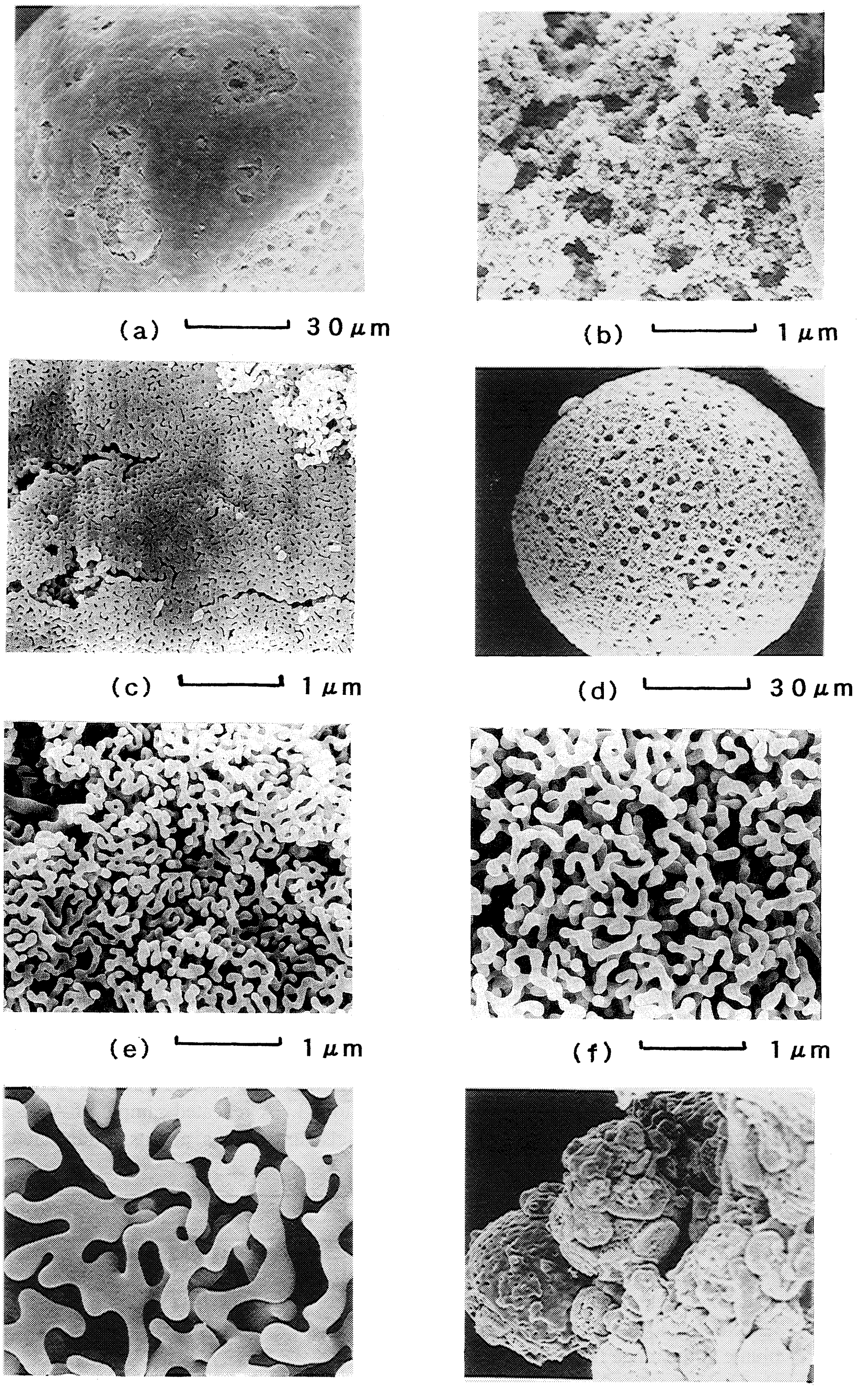

Fig. 1. SEM photographs of the porous supports, (a) the dried gel, × 1000 (b) sample A1 (0.46 g NaCl, 700 °C), × 30000 (c) sample A2 (0.46 g NaCl, 730 °C), ×30000 (d) sample A3 (0.46 g NaCl, 760 °C), × 1000 (e) the same sample with (d), ×30000 (f) sample A4 (0.46 g NaCl, 800 °C), × 30000 (g) sample B1 (0.29 g NaCl, 800 °C), ×30000 (h) sample A5 (0.46 g NaCl, 820 °C), ×1000 where (0.46 g NaCl, 700 °C) indicated that the sample was prepared by adding 0.46 g of NaCl per 1.0 g of the gel and heating the mixture at 700 °C.

Table 1. Effect of Synthetic Conditions on Physical Properties of Porous Supports in the SiO_2–ZrO_2 System

	Synthetic	condition	Surface	Pore	Peak top
Sample	NaCl/gel	Calcn. temp	area	volume[b)]	position
	g/g	°C	$m^2 g^{-1}$	$cm^3 g^{-1}$	Å
A1	0.46	700	153	—[c)]	—
A2	0.46	730	48	3.18	804
A3	0.46	760	37	2.93	892
A3-2	0.46	760	35	—	—
A4	0.46	800	28	2.43	1000
A5	0.46	820	<1	—	—
B1	0.29	800	10	1.48	2977
B2	0.29	800	23	2.65	1488
B3	0.29	900	<1	—	—
C1	0.59[a)]	800	10	1.80	2428,6095
G1	0	700	225	3.88	—

a) KCl (g)/1.0 (g) gel. b) Pore volume of pore radius in the range of 20 to 10000 Å. c) Not measured.

scale by the same procedure as that of A3, and heated under the same conditions as that of A3. The surface area of A3-2 was consistent with that of A3. Samples of B1 and B3 were prepared by heating a gel impregnated with 0.29g NaCl per 1.0 g of dried gel at 800 and 900 °C, respectively. B3 was almost sintered in a way analogous to A5 heat-treated at 820 °C. Sample B2, synthesized using gel pre-heated at 700 °C before mixing NaCl, had a larger surface area than B1, which was prepared by heating the dried gel together with NaCl under the same conditions. The degree of sintering was reduced when the gel, once heated, was applied as the starting material. The surface area of A1, heated at 700 °C with NaCl, was smaller than that of G1, heated at the same temperature without the impregantion of NaCl. This result indicated that a partial sintering of the gel, due to the presence of NaCl, was already advanced by heating at 700 °C. C1 was prepared by heating the dried gel with KCl instead of NaCl. The molar amount of KCl added was the same as that of samples containing 0.46 g of NaCl per 1.0 g of the dried gel, and the mixture was heated at 800 °C. C1 was formed as a result of a similar degree of sintering as that of B1. It was therefore suggested that KCl might behave in an analogous way as to NaCl. On the contrary, a substantial part of the dried gel was dissolved in the case that an aqueous solution of NaOH or Na_2CO_3 was added to the gel instead of a solution of NaCl; the products after the heat treatment were agglomerate and heterogeneous.

The pore size distribution curves of A2, A3, A4, and B1 are shown in Fig. 1, and the peak top position of the pore radius and the pore volume in the range from 20 to 10000 Å are tabulated in Table 1. The pore volume of the products became gradually reduced as the heating temperature increased, which corresponded to a reduction of the surface area. The pore size distribution curves were also shifted to the direction of the larger pore radius. These results suggested that shrinking and sintering of the particles took place as the heating temperature increased. Samples A2, A3, and A4 had a fairly large pore size, since their pores existed mainly above 500 Å in radius. The surface area and pore volume of B1 were much smaller than that of A3. Although B1 and A3 were prepared by the impregnation of different amounts of NaCl, the mixtures were heated at the same temperature. The pore distribution of B1 spread mainly above 1000 Å with the pore peak at 3000 Å (Fig. 2). The degree of sintering of B1 was more advanced than that of A3.

SEM photographs of samples A1 to A5, and B1 are shown in Fig. 1(b)—(h). A sponge-like structure similar to the porous glasses manufactured by the phase-separation method was clearly observed in samples A2, A3, A4, and B1. This structure was believed to be formed via a viscous sintering process in a liquid phase. Although the size of the sponge-like vitreous texture was almost the same within one microsphere, some difference were observed among the microspheres. The size of the sponge-like structure was in the decreasing order in the sample, B1 > A4 > A3 > A2, which was in accord with the order of degree of the viscous sintering. In contrast, the sponge-like structure was not observed in sample A1 heated at 700 °C. The texture of A1 was irregular, and comprised particles smaller than 300 Å, similar to that of dried gel, which was consistent with the result that its surface area was not much reduced from that of the original gel. The particles of sample A5 were nearly sintered, and mostly adhered to each other, as shown in Fig. 1(h). This observation also corresponded to the surface area of A5.

A TEM photograph of sample A3, shown in Fig. 3, was observed on a specimen prepared by impregnating a resin into A3 and slicing them. The black dots in the figure correspond to the glass skeleton and the light part to the pore. A vitreous microstructure was observed inside of the particle, and had a fairly uniform size. The inside of the particles was highly porous. Large voids of about 1 μm in size were observed, corresponding to the SEM observation of the particle, and originating from the dried gel. There existed no gel such as silica, which usually remained between the skeletons of the conventional porous glasses before an alkaline treatment.

The X-ray diffraction patterns of A3, A5, and B3 are shown in Fig. 4. Samples A2, A4, and B1 were all amorphous, similar to A3. A reheated sample of A3-2 at 860 °C for 4 h was also amorphous, and its surface area was 3 $m^2 g^{-1}$. In

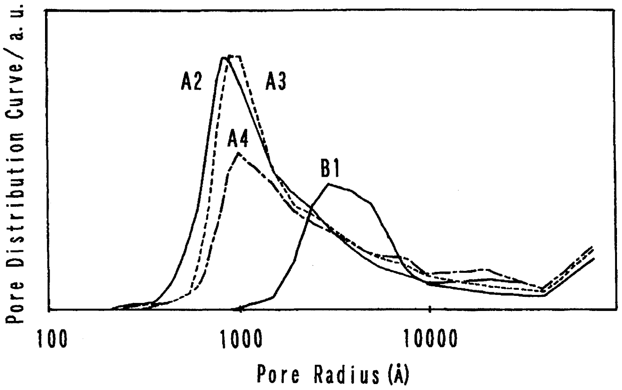

Fig. 2. Pore size distribution curves of the porous glass suports.

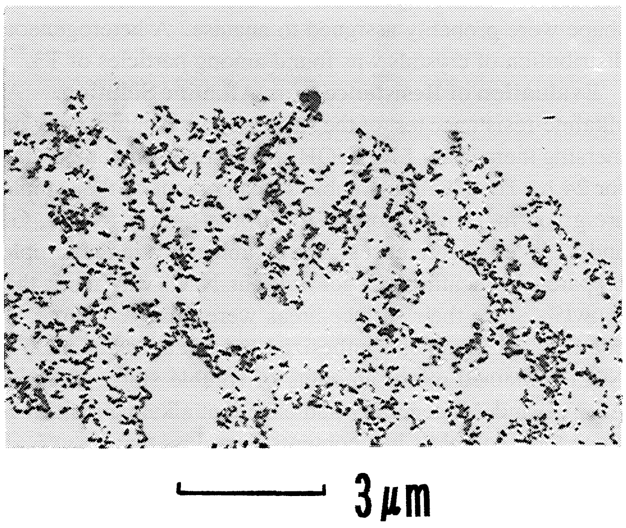

Fig. 3. TEM photograph of sample A3.

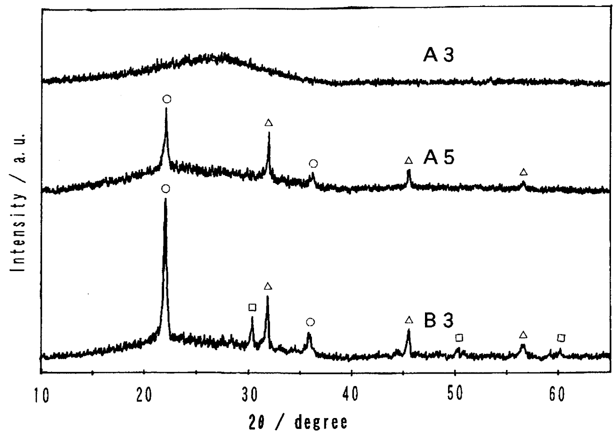

Fig. 4. X-Ray diffraction patterns of samples A3, A5, and B3. The peaks were assigned to ○: α-cristobalite, □: tetragonal zirconia, and △: NaCl.

samples of A2 to A5, and B1, added NaCl was removed in the process of washing, since the porosity of the products after a heat-treatment was maintained. However, the X-ray diffraction patterns of A5 and B3, both heated at the temperatures above 800 °C, indicated that the crystalline phases advanced. They were identified as α-cristobalite and NaCl in A5, and α-cristobalite, NaCl, and tetragonal zirconia in B3, respectively. The higher calcination temperature caused both sintering with the inclusion of NaCl and the crystallization of silica and zirconia. NaCl was not removed, even after washing the samples in hot water.

The results of a chemical analysis of A4 and B1 are tabulated in Table 2. Both products contained an appreciable amount of Na_2O, but a negligible content of chloride. This indicated that sodium ions were incorporated into the SiO_2–ZrO_2 gel, and formed SiO_2–ZrO_2–Na_2O glass. Excess NaCl added to the dried gel was removed during the washing process. The oxide compositions of both samples were similar to the values reported for the alkoxide derived nonporous glass fiber.[16)]

Table 2. Chemical Compositions of the Glasses[a)]

Sample	SiO_2	ZrO_2	Na_2O	P_2O_5	Cl	Total
A1	75	16	5.6	—	—	97
A3-2	75	14	7.0	—	—	96
A4	75	16	7.9	0.3	0.1	100
B1	76	16	8.8	0.3	0.1	101
R[b)]	76	17	7	—	—	100

a) Based on wt%. b) Sample 9 in Ref. 16.

The surface areas of the samples after being heated again are shown in Table 3. A sample reheated at 900 °C for 5 h was nearly sintered, and a sample reheated at 860 °C for 5 h underwent substantial sintering, judging from the result of their surface areas, as well as the SEM photographs. On the contrary, only a small change in the surface area was observed for a sample reheated at 760 °C for 5 h. The surface area of a sample reheated at 860 °C for 4 h was much smaller than that of a sample before reheating. No exothermic peak related to crystallization was observed in TG-DTA measurements of samples A2, A4, and B1 (Fig. 5).

Results of the SiO_2–TiO_2 System. The SiO_2–TiO_2 based gel was made from a mixed alkoxide solution, whose composition was $80SiO_2$–$10TiO_2$–$10P_2O_5$. $Zr(OBu)_4$ in the SiO_2-ZrO_2-based alkoxide solution was substituted to $Ti(OEt)_4$. The sample after heating the dried gel at 700 °C had

Table 3. Surface Areas of Porous Supports after Heat Treatment of Sample A3-2

Sample	Heat treatment condition		Surface
	Temp	Time	area
	°C	h	$m^2\,g^{-1}$
A3-2	—	—	35
R1	760	5	28
R2	800	5	27
R3	860	4	3
R4	860	5	<1

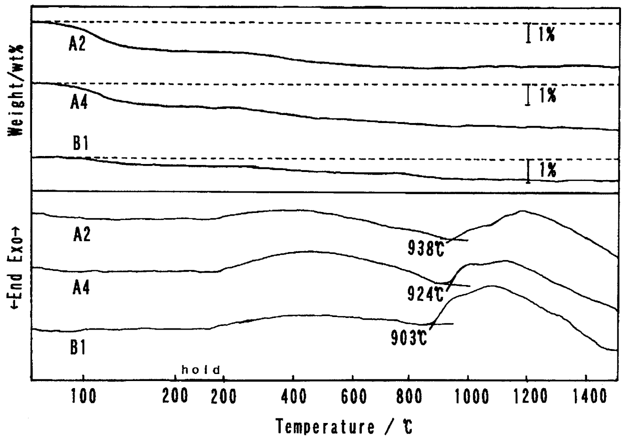

Fig. 5. TG-DTA curves of samples A2, A4, and A5. The samples were heated to 200 °C from room temperature and hold for 40 min. and then heated to 1500 °C at the rate of 10 °C min^{-1}.

a composition of $83SiO_2$–$15.6TiO_2$–$1.4P_2O_5$ according to a chemical analysis. The content of P_2O_5 in the gel was much smaller than that of the starting alkoxide solution, which was analogous to the SiO_2–ZrO_2 gel. This dried gel was heated together with NaCl at 700, 730, and 760 °C for 5 h. The pore characteristics are given in Table 4. The surface area of T3 indicated that it was nearly sintered. The pore peak position of T2 was shifted in a larger direction, and the pore volume was reduced compared to T1. It exhibited the same behavior as the SiO_2–ZrO_2 system, in which the sintering of particles was advanced along with increasing the heat-treatment temperature. However, the temperature at which the product was nearly sintered was lowered by approximately 60 °C in the SiO_2–TiO_2 system, compared to that of the SiO_2–ZrO_2 system.

The X-ray diffraction patterns of T1, T2, and T3 are shown in Fig. 6. The peaks of anatase were clearly identified, even in a sample heated at 700 °C. In T2 and T3, the peaks of α-cristobalite were observed in addition to those of anatase. This indicated that in the SiO_2–TiO_2 system, phase-separation and crystallization to silica and titania advanced when the gel was heated with NaCl at temperatures higher than 700 °C. However, the peaks of NaCl were not found, which existed in samples prepared by heating SiO_2–ZrO_2 gel with NaCl at temperatures above 820 °C. The SEM observation of particles of T3 indicated that the skeleton of the particles was generally squarish, and that many crystallines were observed, as shown in Fig. 7. The crystals having a needle-like shape were probably assigned to anatase. A heterogeneous distribution of crystals was found among particles of T3.

Table 4. Effect of Synthetic Conditions on Pore Characteristics of Porous Supports in the SiO_2–TiO_2 System

Sample	Synthetic conditions		Surface area	Pore volume	Peak top position
	NaCl/gel	Calcn. temp			
	g/g	°C	$m^2 g^{-1}$	$cm^3 g^{-1}$	Å
T1	0.29	700	21	2.04	1487
T2	0.29	730	10	1.19	1948
T3	0.29	760	<1	—	—
G3	0	700	153	2.32	—

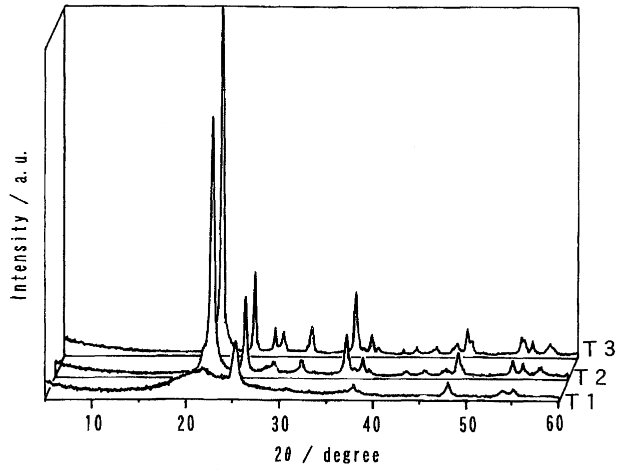

Fig. 6. X-Ray diffraction patterns of the SiO_2–TiO_2 based supports.

Evaluation of Resistance to an Alkaline Solution. An alkaline-resistance test of the supports was conducted by immersing them in a 0.1 M-NaOH solution at room temperature for 24 h. The alkaline-soluble silica content of the samples are given in Table 5, together with the figures for G1, G2, and S1 listed as references. The soluble silica in the samples prepared by heating the gel without NaCl was more than 20 wt%, since their surface areas were relatively large. In contrast, the samples synthesized by a heat treatment with NaCl contained minor amounts of soluble silica. Samples A2, A3, and A4 generally had excellent alkaline resistance, since their soluble silica contents were less than 1 wt%. In samples A2, A3, and A4, the amounts of soluble silica decreased, and those values divided by the surface area were also reduced as the degree of sintering advanced. The soluble silica in T1 was rather high, although its surface area was small. On the contrary, the soluble silica in T2 was relatively low. However, its amount divided by the surface area was higher than those of SiO_2–ZrO_2–Na_2O porous glass samples.

Discussion

The results described in the previous section demonstrate that the heat treatment of SiO_2–ZrO_2 gel with NaCl in the range of 730 to 800 °C and the subsequent washing of any NaCl remaining in the products formed porous glasses having SiO_2–ZrO_2–Na_2O compositions. As the heating temperature was increased, the skeleton of the SiO_2–ZrO_2–Na_2O glass grew and the pore distribution was also moved to a larger size. A glassy structure similar to porous glass manufactured by a phase-separation method was also observed inside the particle, and no gel remained in the glass structure. The alkaline durability was excellent, as expected from the composition of SiO_2–ZrO_2–Na_2O. The samples after a heat treatment of the porous supports again at 860 °C were still amorphous, although it was observed that some degree of sintering and a certain reduction in the surface areas oc-

Table 5. Results of Alkaline-Resistant Test

Sample	NaCl/gel	Calcn. temp	$D^{a)}$	Surface area	$D/S^{b)} \times 10^2$
	g/g	°C	wt%	$m^2 g^{-1}$	
A1	0.46	700	6.27	153	4.1
A2	0.46	730	0.97	48	2.0
A3	0.46	760	0.62	37	1.7
A4	0.46	800	0.20	28	0.7
B1	0.29	800	0.05	10	0.5
G1$^{c)}$	0	700	29.2	225	13.0
G2$^{d)}$	0	800	24.8	390	6.4
T1	0.46	700	3.8	21	18.1
T2	0.46	730	0.2	10	2.0
S1$^{e)}$	0	800	44.2	293	15.1

a) D: Percentage of soluble silica to sample weight after the sample was immersed in a 0.1 M-NaOH solution for 24 h. b) D/S: D value divided by surface area. c) G1: the SiO_2–ZrO_2 gel calcined at 700 °C without NaCl impregnation. d) G2: $81SiO_2$–$19ZrO_2$ composition. e) S1: $100SiO_2$ composition.

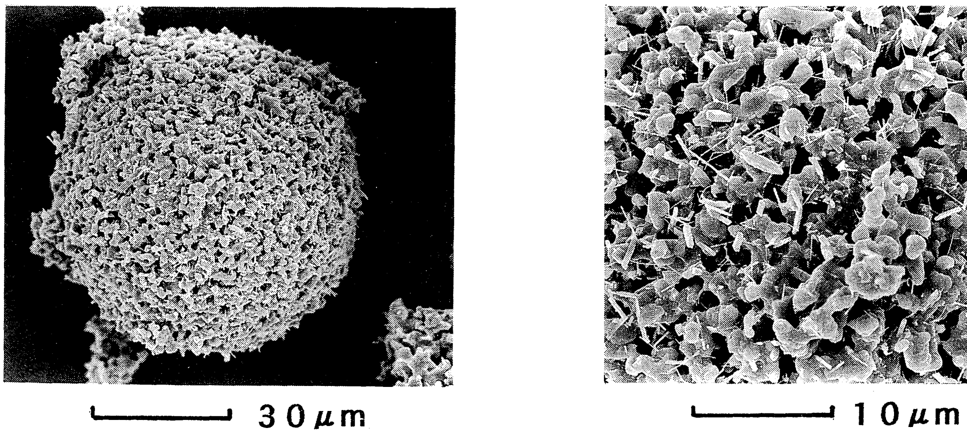

Fig. 7. SEM photographs of the SiO_2–TiO_2 based porous supports.

curred. To our knowledge, there seems to be no report which describes formation of porous glass by the heat treatment of a silica-based gel impregnated with NaCl. On the contrary, when dried gels in the SiO_2–TiO_2 system were heated together with NaCl, there occurred phase separation and crystallization into titania and silica. Thus, a glassy composition was not formed, although they sintered in a similar manner with the SiO_2–ZrO_2 system.

Porous glasses were prepared by various methods, for instances: phase separation, sol-gel, and etching salts from a sintered body formed by heating fine glass particles and milled salts. The pore size of the porous glasses obtained by the sol-gel procedure was small in the SiO_2–ZrO_2 system, below 100 Å in radius.(7—10) The porous glasses prepared by the fine glass particles and salts generally possessed pores larger than 1 µm.(17) On the contrary, the phase-separation method was able to control the pore size over a wider range. For porous glasses in the SiO_2–ZrO_2 system, it was described that the pore size of those glasses was in the range from 0.01 to 10 µm.(1—6) The pore radius of the porous glasses obtained in the present study were about 500 to 5000 Å in radius, which were in a similar range as that of porous glasses obtained by the phase-separation method.

Although the preparative method of the present study resembled the process of porous glasses and glass-ceramics from the fine glass powders and salts, the pore formation and equalization related to the 'template' effect of salt seemed not to be involved in this method.(17) The raw materials were a highly porous gel, which retained porosity, even after some reduction during the synthetic process.

The pore size distributions of the products were not sharp compared to the phase-separated glasses. It must originate from the pore characteristics of the SiO_2–ZrO_2 gel. The pore size distribution measurement of the SiO_2–ZrO_2 gel, after being heated at 700 °C for 5 h without impregnation of NaCl (sample G1), indicated that pore volume in the range from 20 to 10000 Å in radius was 3.88 $cm^3\,g^{-1}$, and that its pore distribution was quite broad. The dried gel heated at 700 °C in the SiO_2–TiO_2 system (sample G3) possessed a similar pore distribution, and its pore volume was 2.32 $cm^3\,g^{-1}$. Although there was fear that the strength of the gels was not strong enough for a Hg intrusion measurement, these data were not inconsistent with a SEM observation. In addition, a similar result was obtained in the two systems. It was therefore assumed that the pore distributions of the dried gels were similar to those described above. On the contrary, pores smaller than 500 Å in radius were diminished in samples A2, A3, A4, T1, and T2 as the result of partial sintering. Also, the pores of sample B1, smaller than 1000 Å in radius, disappeared, whereas larger pores remained. It was indicated that a certain pore equalization was observed due to liquid-phase sintering, which diminished the narrower pore in the starting gel.

The pore volume of the porous glasses prepared by phase separation was usually less than 1.0 $cm^3\,g^{-1}$. Their pores originated from the soluble phase during the etching process in the composition after phase separation. It seemed difficult to obtain microsphere particles smaller than 100 µm by this method. On the contrary, most of the samples obtained in this study had a microsphere shape and about 10 to 100 µm in size; also, their pore volume (more than 1.48 $cm^3\,g^{-1}$) was highly porous. The porosity attained more than 85% when the density of the glass skeleton was assumed to be 2.5.(18)

Inorganic salt impregnation of silica gel and heating the resultant mixture was reported to cause an enlargement in the pore size an a reduction of the surface area of silica gel.(19) This method is called 'salt impregnation of silica gel', or the 'salt method'. Silica microspheres with a defined pore size were similarly prepared by a salt-impregnation method.(13) Although supports with a sharp pore size distribution were obtained, due to densification of the silica gel, a porous structure was not observed on the surface of the particles by SEM.(12) It was supposed that there was a dense coat layer in the particles. The surface of the SiO_2–ZrO_2–Na_2O porous glass particles was definitely porous, and no surface coat layer was observed, as can be seen in Figs. 1 and 3. This difference might be attributed to the size of the surface-coated layer of the starting gel, and to the degree of viscous sintering of the support composition.

Heating silica gels together with NaCl was reported to form a liquid phase and to result in crystallization to α-cristobalite; NaCl behaved as a flux.(20,21) Similarly, silica crystallization was observed when the sol-gel derived SiO_2–Na_2O gel was heated at 500 °C.[22] These results indicated that the Na cation with silica gel generally promoted crystallization. It was reported that the crystallization of silica proceeded when silica gel with a trace amount of Na was heated at temperatures lower than 700 °C.[22] The same behavior was also observed in the present study. In the case that SiO_2–TiO_2 gel was heated with NaCl at 700 °C, the crystallization of titania was advanced. Also, silica, in addition to titania, was crystallized when the mixture was heated at 730 °C. A similar result was obtained for samples A5 and B3, heated at temperatures above 800 °C in the SiO_2–ZrO_2 system. On the contrary, the liquid phase of SiO_2–ZrO_2–Na_2O composition was formed during a heat-treatment, and a glassy system was formed, which inhibited the crystallization of silica when a mixture of the SiO_2–ZrO_2 dried gel and NaCl was heated in the range of 730 and 800°C. The peaks of NaCl were observed on the X-ray diffraction patterns in samples A5 and B3, which were heated at temperatures above 800 °C in the SiO_2–ZrO_2 system. On the other hand, there existed no peak of NaCl in sample T3, which similarly proceeded sintering in the SiO_2–TiO_2 system. Considering that all of the samples were washed with water after the heat-treatment, voids remained to remove NaCl in the SiO_2–TiO_2 system. In contrast, an excess amount of NaCl was not removed in the particles because of melting and occlusion into the glass in the case of the SiO_2–ZrO_2 system.

For the formation of SiO_2–ZrO_2–Na_2O glass from the SiO_2–ZrO_2 gel and NaCl, a kind of oxidation process of NaCl was required. The reaction of SiO_2 and NaCl was studied (Ref. 23), and the formation of a Na_2SiO_3 layer was identified by an X-ray microanalyzer. It was suggested that the following reactions took place:

$$2NaCl + SiO_2 + 1/2O_2 \longrightarrow Na_2SiO_3 + Cl_2 \quad (1)$$

$$2NaCl + SiO_2 + H_2O \longrightarrow Na_2SiO_3 + 2HCl \quad (2)$$

Similar reactions must be involved in the reaction of the present study. For the alkoxide-derived SiO_2–ZrO_2 gel, the reaction of (2) may be dominant, since the ion-exchange between the sodium cation and the hydroxyl proton led to the formation of HCl, as indicated in

$$-OH + NaCl \longrightarrow -ONa + HCl. \quad (3)$$

These porous glass supports were expected to have different surface properties from those of the well-known porous glasses, since they have Na_2O in their compositions. Further research on the mechanism of the formation of the porous glass supports will be reported elsewhere.

Conclusion

1. A porous glass support with the composition SiO_2–ZrO_2–Na_2O was obtained when a sol-gel-derived, microspherical, SiO_2–ZrO_2 gel was heated with NaCl.
2. The porous glass comprised microspherical particles of about 10–100 μm in size. These particles comprised sponge-like glassy structure analogous to the porous glass prepared by the phase-separation method. Inside of the particles were also glassy fine particles with larger voids of about 1 μm in size. Gel was not found between the glassy skeleton.
3. The surface area of the porous glass ranged from 10 to 48 $m^2\,g^{-1}$, and the pore volume (pore radius 20—10000 Å) ranged from 1.48 to 3.18 $cm^3\,g^{-1}$. The peak radius of the pore distribution was at 800—3000 Å.
4. The approximate composition of the porous glass was $SiO_2 : ZrO_2 : Na_2O = 82 : 8.6 : 8.4$—9.2 mol%, the Cl content being less than 0.2 mol%. The alkaline durability was excellent, as expected from the composition of SiO_2–ZrO_2–Na_2O.
5. Some pore equalization was observed during the process to form the glass structure. However, the pore size distribution was not sharp, which was attributed to the SiO_2–ZrO_2 gel characteristics. As the temperature of the heat-treatment increased, the viscous sintering was advanced and the surface area and pore volume of the products was reduced. They were amorphous when the heat-treatment temperature was below 800 °C.
6. In the SiO_2–TiO_2 system, the heat treatment of the sol-gel-derived SiO_2–TiO_2 microspherical gel together with NaCl caused a crystallization of titania and silica, and no formation of a glassy mixed oxide was observed.

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