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Preparation of Porous Supports in the SiO_2–ZrO_2–Na_2O System

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A new method for preparing porous supports in the SiO_2–ZrO_2 system was investigated. A microspherical silica gel impregnated with $ZrOCl_2$ and NaCl was heated and subsequently washed with water. Crystallization of silica proceeded in supports prepared by heating the mixture of silica gel and NaCl. In contrast, crystallization of supports as well as their sintering was suppressed in the case of the gel impregnated with $ZrOCl_2$ in addition to NaCl, and porous supports with the SiO_2–ZrO_2–Na_2O composition were formed. A porous-glass-like texture similar to the texture resulting from the phase-separation method was observed inside the microspherical particles as well as on their surface. Microspherical supports, whose pore volume was more than 1 $cm^3\,g^{-1}$ and whose mode pore radii ranged from 270 to 640 Å, were obtained by controlling the synthetic conditions for the silica gel, the amount of $ZrOCl_2$ added to the gel, and the temperature of the heat-treatment of the mixture.

SiO_2–ZrO_2 mixed oxides are excellent materials for use as alkali-durable glasses and catalysts.[1—4] Alkali-durable glasses of the SiO_2–ZrO_2 system are used practically as reinforcing cements.[3] The mixed oxide, like SiO_2–ZrO_2, is strongly acidic; hence, many studies have been reported on the catalytic chemistry of SiO_2–ZrO_2.[4] Moreover, the application of SiO_2–ZrO_2 to dental fillers was investigated, because ZrO_2 has a highly efficient radiopacity.[5]

The preparation of porous glasses in the SiO_2–ZrO_2 system has been investigated because components have both porosity and alkaline durability.[6] The porous glasses are stable not only at high temperatures but also to organic solvents and biomaterials. Many applied studies have reported their use in membrane separations and as chromatographic carriers, supports for biomaterials, and catalysts.[6] However, conventional porous glasses have a significant drawback in that they are soluble in alkaline solutions.

An improvement in mother-glass compositions has been investigated in an effort to retain ZrO_2 in porous glass skeletons. The addition of a relatively large amount of alkaline earth oxide or zinc oxide to a SiO_2–ZrO_2–Na_2O–B_2O_3 composition was found to be effective for leaving ZrO_2 in porous glass skeletons.[7—10] Pore sizes in the improved porous glass can be controlled in the range from 100 Å to 1 μm, and the glass is scarcely soluble even in a 0.1 M NaOH solution ($1\ M = 1\ mol\,dm^{-3}$). Another way to obtain SiO_2–ZrO_2 porous glasses is based on the sol–gel method. In this procedure, the ZrO_2 content of porous glasses can be controlled over a wider range, and their alkaline resistance is excellent.[11,12] The preparation of the glasses was quite simple. Two preparative methods, the phase-separation and the sol–gel method, are known for the synthesis of porous glasses in the SiO_2–ZrO_2 system. However, in the case of the phase-separation method, the amount of ZrO_2 incorporated was less than 7 wt% in spite of the rather complicated preparation. In the case of the sol–gel method, the pore radius of the sol–gel derived porous glass was less than 50 Å.[13,14] Thus, it is our goal to develop a simple method for the preparation of alkaline-resistant porous glasses, whose pores are more than 100 Å in radius. Moreover, microspherical supports less than 100 μm in size are preferred because of their performance in separations.

On the other hand, impregnation or coating ZrO_2 onto porous silica gels was proposed as another preparative method for SiO_2–ZrO_2 mixed oxides.[15] Improvements in alkali stability were reported even though ZrO_2 distribution was not homogeneous compared to porous glasses prepared by the phase-separation method. This procedure is economical in comparison with the sol–gel method. Impregnation of ZrO_2 into silica gel was also reported for catalyst preparations. However, its acidity was weaker than in the SiO_2–ZrO_2 system in which ZrO_2 was distributed homogeneously.[4,16] Recently, impregnation of ZrO_2 into a porous glass was reported.[17]

We have already reported a new synthesis of SiO_2–ZrO_2–Na_2O porous glass supports carried out by heating the mixture of the SiO_2–ZrO_2 gel and NaCl at temperatures between 730 and 800 °C, followed by washing of the supports.[18,19] Microspherical porous supports less than 100 μm in size are easily obtained using this method. Moreover, their pores are more than 100 Å in radius and their pore volume is large, although the pore size distribution is not sharp. Furthermore, we briefly reported an advanced preparative method; the method involves heating a mixture of a microspherical silica gel, $ZrOCl_2$ and NaCl at 760 °C.[20] These supports are expected to be used as protein separations on liquid-phase chromatography. In this paper, we report the results of this most recent synthetic method in detail.

Experimental

Preparation of Silica Gel. The microspherical gel was prepared according the method reported by Unger et al.,[21] with some modification of the organic phase and addition of a surfactant. Partial hydrolysis of ethyl orthosilicate was performed by mixing ethyl orthosilicate (500 g), ethanol (136.3 g), water (43.2 g), and a 0.1 M ethanolic HCl solution (18.7 g) and heating the mixture at 60 °C for 30 min; $H_2O/Si(OEt)_4$ and $H^+/Si(OEt)_4$ mole ratios were 1.0 and 0.001, respectively. The resultant solution was heated at 120 °C for 2 h and 150 °C for 2 h under Ar atmosphere to remove volatile materials. The remaining solution (337.3 g) was used as the alkoxide solution for the silica gel.

The alkoxide solution (45 cm^3), mixed with cyclohexane (7.5 cm^3) and *t*-pentyl alcohol (22.5 cm^3), was added dropwise to an aqueous solution with stirring at about 1000 rpm. The aqueous solution was composed of water (433.9 g), ethanol (13.5 g) and 3.4 g of Tween 20 (polyoxyethylenesorbitan monolaurate). Then an aqueous ammonia solution (58.5 cm^3) was added dropwise to an O/W emulsion; the white gel formed immediately upon its addition. The resultant slurry was stirred for 5 h and left standing overnight. The supernatant solution was removed by decantation. The gel was washed with ethanol by decantation, collected by filtration and dried at 100 °C for 8 h. The dried gel was formed as nearly spherical particles roughly 10 to 20 μm in diameter.

Preparation of SiO_2–ZrO_2–Na_2O Porous Supports. Two grams of the dried gel, pre-heated and retained at 120 °C until it maintained a constant weight, almost completely adsorbed a 5 cm^3 aqueous solution containing 0.80 g of $ZrOCl_2\cdot8H_2O$ and 0.58 g of NaCl (for samples A and F). The impregnated gel was heated at 120 °C for 5 h and then at 600 °C for 3 h under a stream of air in a quartz tube. It was heated again in an alumina crucible at a designated temperature for 5 h in a furnace. The calcined sample was added to 500 cm^3 of water, and the supernatant solution was decanted to remove soluble salts such as excess NaCl. The same washing process was repeated two more times, and the supernatant solution was decanted. The product was collected by filtration and dried at 120 °C for 5 h.

For impregnation of $ZrO(NO_3)_2$–$NaNO_3$, $ZrO(NO_3)_2$–NaCl, and $ZrOCl_2$–KCl, the amount of $ZrO(NO_3)_2\cdot2H_2O$ added was 0.15 g based on ZrO_2, and that of the alkaline salt was 0.29 g per 1.0 g of the dried gel based on NaCl; the molar amounts of KCl and $NaNO_3$ used were equivalent to that of NaCl. A reference (Sample Z) was prepared by heating the mixture of the silica gel and $ZrOCl_2\cdot8H_2O$ at 760 °C.

Characterization of Products. The pore-size distributions and pore volume of the porous supports were measured by mercury-penetration porosimetry using an Autopore 9200, Micrometrix. The maximum pressure attainable was 368 MPa, corresponding to a pore radius of 20 Å. The specific surface areas (SSAs) were obtained by the Brunauer–Emmett–Teller (BET) single-point method with a Shimadzu Rapid Surface Area Analyzer 2200 using nitrogen as the adsorbate. The X-ray diffraction (XRD) measurements were made using a Phillips PW 1700 diffractometer with Cu $K\alpha$ radiation. The scanning electron microscope (SEM) observations were performed on gold-coated surfaces using a Hitachi S-900 and a Hitachi S-4500. For observation of the inside of the support, the sample was crushed between two glass slides. Chemical analyses of products were performed by X-ray fluorescence using a Rigaku System 3370.

For a preliminary test of alkaline resistance, after about 100 mg of a sample was dried at 120 °C to a constant weight, it was weighed accurately and transferred to a Teflon® container, to which a 0.1 M NaOH solution was added. The Teflon® containers were shaken several times and allowed to stand at room temperature. After 24 h, the Si concentration of the solution was determined by sampling 5 cm^3 of the solution using inductively coupled plasma (ICP, JY-38P, Seiko Densi Kogyo).

Results and Discussion

Effect of Variable Amounts of ZrO_2 and NaCl. The effect of varying the amounts of ZrO_2 and NaCl added to the gels was investigated first, using the standard silica gel (S-1) as a starting material. The silica gel was highly porous; 1.0 g of the gel adsorbed 2.5 $cm^3\,g^{-1}$ of the aqueous solution. Four samples were prepared by changing the amount of $ZrOCl_2$ while maintaining a constant amount of NaCl on impregnation. The amount of $ZrOCl_2$ added per 1.0 g of the dried gel was 0.15, 0.10, 0.05, and 0 g based on ZrO_2 for samples A, B, C, and D, respectively. Physical properties of four samples are listed in Table 1, and pore-size distribution curves are shown in Fig. 1. The SSAs of the supports decreased and their pore size became larger as the amounts of ZrO_2 impregnated into the gel decreased. The pore-size distributions of samples A, B, and C were sharp, and their pores were around 500 Å in radius. In contrast, the mode pore radius of sample D was 1481 Å, which was much larger than those of samples prepared by heating the silica gel impregnated with ZrO_2. Samples A, B, and C possessed rather high porosity because their pore volumes were more than 1.0 $cm^3\,g^{-1}$. On the other hand, the pore volume of sample D in the size range from 20 to 1000 Å was 0.17 $cm^3\,g^{-1}$.

SEM photographs of samples A, B, C, and D are shown in Fig. 2. Porous-glass-like skeletons were observed on the surface of the microspherical particles. The size of their vitreous skeletons was, in increasing order, A < B < C < D. The darker parts of the photographs in Fig. 2 correspond to pores between skeletons, the size of which was similar to that of the skeleton. Pore sizes in samples A, B, and C were estimated to be around 0.1 μm, and that of sample D was about 0.3 μm. These values were roughly in accord with the pore sizes measured by the mercury intrusion method. Thus,

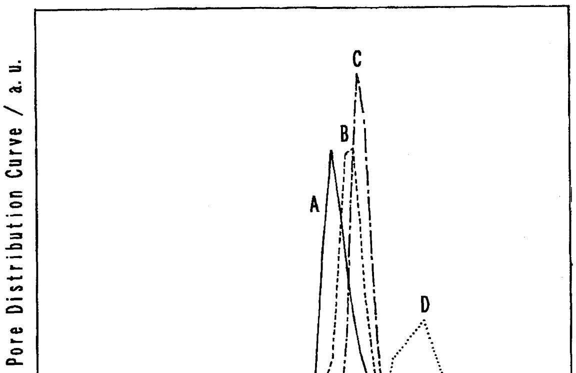

Fig. 1. Pore-size distribution curves of samples A, B, C, and D.

Table 1. Effect of Conditions of Synthesis on Pore Characteristics of Porous Supports in the SiO_2–ZrO_2 System

Sample	Synthetic conditions			SSA	Pore volume$^{a)}$	Mode pore radius
	ZrO_2/gel	NaCl/gel	Calcn. temp			
	g/g	g/g	°C	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	Å
A	0.15	0.29	760	38	1.44	451
B	0.10	0.29	760	32	1.35	602
C	0.05	0.29	760	22	1.46	643
D	0	0.29	760	13	0.17	1481
E	0.15	0.20	760	31	1.43	447
F	0.15	0.29	760	45	1.42	447
G	0.15	0.40	760	46	1.33	449
H	0.15	0.50	760	41	1.39	449
I	0.15	0.29	800	13	0.48	549
J	0.15	0.29	820	1	0.09	—
Z	0.15	0	760	271	1.76	—$^{b)}$

a) Pore volume in the range from 20 to 1,000 Å. b) The pore-size distribution was broad.

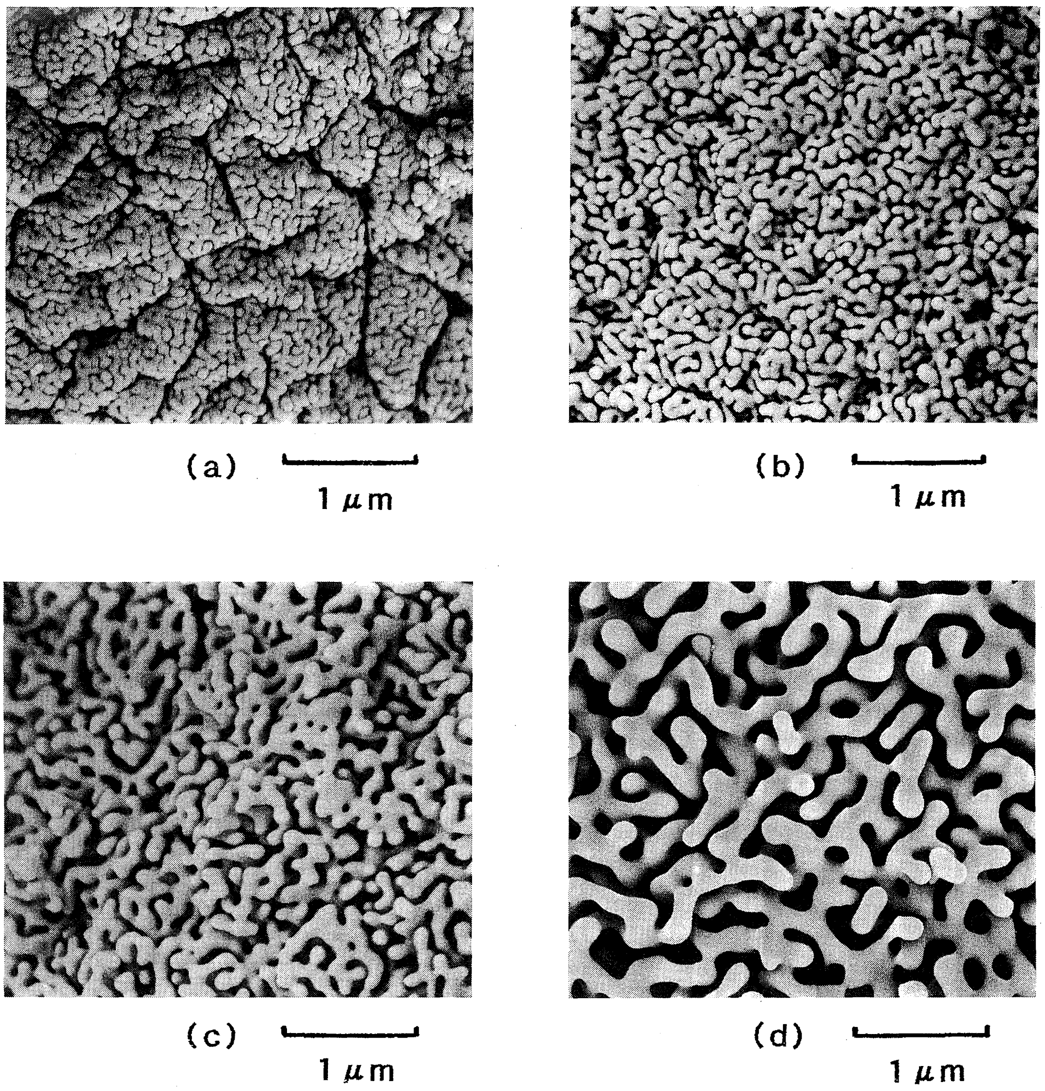

Fig. 2. SEM photographs of samples A, B, C, and D, (a) sample A (0.05 g ZrO_2, 760 °C), (b) sample B (0.10 g ZrO_2, 760 °C), (c) sample C (0.05 g ZrO_2, 760 °C), (d) sample D (0 g ZrO_2, 760 °C), where (0.15 g ZrO_2, 760 °C) indicates that the sample was prepared by adding 0.15 g of ZrO_2 per 1.0 g of the gel in the form of $ZrOCl_2\cdot 8H_2O$ in addition to NaCl and heating the mixture at 760 °C.

as the amount of ZrO_2 added to the silica gel decreased, the pore size of the porous supports became larger and the degree of sintering of the porous supports increased accordingly.

Variable amounts of NaCl impregnated into the gel were investigated next. Four samples were prepared by heating the mixtures of silica gel, $ZrOCl_2$, and NaCl, using 0.20, 0.29, 0.40, and 0.50 g of NaCl per 1.0 g of the dried gel. Samples E to H were synthesized using silica gel prepared as a different batch from the gel used for samples A to D. Sample F was obtained by a similar impregnation and heat-treatment to that of sample A. The mode pore radii of the pore-size distributions and pore volumes of two samples were consistent with each other, although their SSAs were slightly different, as shown in Table 1. The differences in physical properties among samples E to H were small compared to the differences among samples A to D. Specifically, the pore-size distributions were almost the same. Samples E to H possessed a porous-glass-like texture, and virtually no differences in size and shape of skeletons were observed on SEM photographs. Thus, the influence of the amount of NaCl added to the gel was much smaller than that of ZrO_2 over the range evaluated.

XRD patterns of samples A to D are shown in Fig. 3. The pattern from sample D was very different from those of the three other samples. Its peaks were assigned to cristobalite. Extensive crystallization seemed to occur in this support, because it was prepared by heating the gel and NaCl without the addition of $ZrOCl_2$. This result was consistent with the literature; NaCl acting as a flux promoted silica crystallization.[22] In contrast, a crystalline phase due to silica was not observed in samples A, B, and C, although the peak strength around $2\Theta = 22°$ increased in the order $A < B < C$. Peaks assigned to tetragonal ZrO_2 ($2\Theta = 30°$, $51°$, and $60°$) were identified in samples A and B. Their intensity increased as the amount of ZrO_2 added increased.

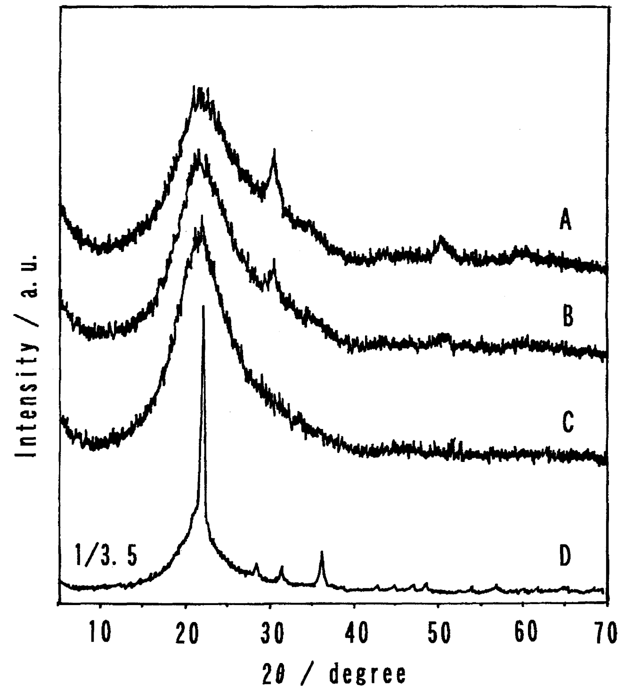

Fig. 3. X-Ray diffraction patterns of samples A, B, C, and D.

The relationship between the content of ZrO_2 or Na_2O in products and ZrO_2 impregnated into silica gel is plotted in Fig. 4. The SSAs of four samples are also plotted in Fig. 4 vs. the amount of impregnated ZrO_2. The results indicate that the amount of Na_2O as well as that of ZrO_2 in the support increased as the amount of ZrO_2 added to the gel increased. Sodium cations probably existed in the form of SiO_2–ZrO_2–Na_2O in the support, because salt in the form of NaCl was removed by washing the supports with water, and the chloride content in the supports was less than 0.2 wt% as determined by X-ray fluorescence. The presence of ZrO_2 in the mixture resulted in an increase in the Na_2O content of the supports. On the contrary, sample D contained very little Na_2O (0.2 wt%), which was consistent with the crystallization of the silica gel into cristobalite.

These results demonstrate that crystallization and sintering of the silica gel occurred when the mixture of silica gel and NaCl was heated in the absence of ZrO_2. This procedure was analogous to the 'salt method' previously reported.[21,23] The addition of ZrO_2 together with NaCl to the silica gel reduces crystallization of the support and induces the incorporation of Na_2O into the support. Incorporation of sodium cations in the form of Na_2O into the supports was similar to the result obtained by heating the mixture of the SiO_2–ZrO_2 gel and NaCl to produce SiO_2–ZrO_2–Na_2O.[18] However, the ZrO_2 distribution in the supports evaluated herein prepared by heating at 760 °C was not homogeneous compared to

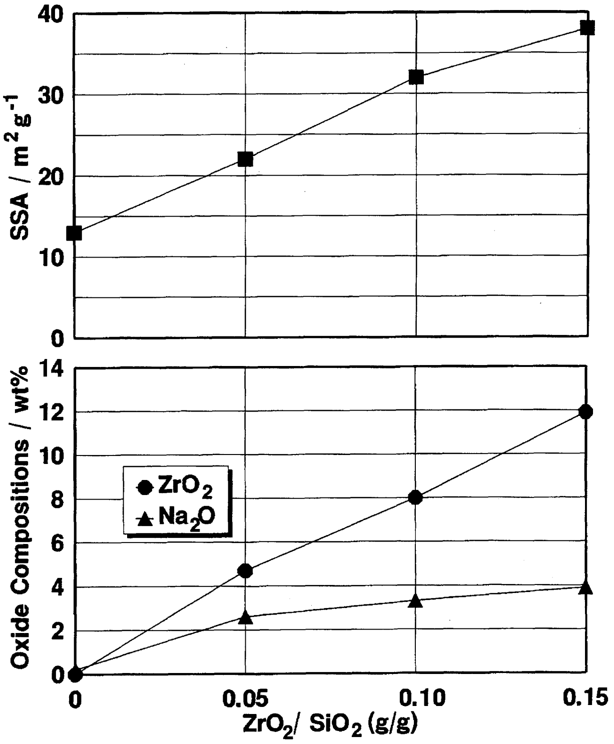

Fig. 4. Relationship between specific surface areas, oxide compositions and amounts of ZrO_2 impregnated per 1.0 g of the gel.

that in the supports made from the SiO_2–ZrO_2 gel and NaCl. This result originated from the ZrO_2 distribution in the mixture. Its distribution in the SiO_2–ZrO_2 gel prepared using the sol–gel method was more homogeneous than in the mixture of silica gel and $ZrOCl_2$.

Temperature of Heat Treatment and Salt Type. Samples I and J were prepared by adding the same amounts of $ZrOCl_2$ and NaCl to the gel as were used to prepare samples A and F and by heating the mixtures at temperatures higher than 760 °C; samples I and J were heated at 800 and 820 °C, respectively. The physical data are shown in Table 1. Sample J was almost sintered, because its SSA was 1 $m^2\,g^{-1}$ and its pore volume was nearly zero. The degree of sintering was more advanced in sample I than in A, because the SSA and pore volume of sample I was nearly one-third smaller than A. The XRD patterns of samples I and J together with A are shown in Fig. 5. Peaks attributed to cristobalite are clearly observed in sample J, which indicates that crystallization advanced and phase separation into silica and zirconia occurred. This result resembled that for the product obtained by heating a mixture of SiO_2–ZrO_2 gel and NaCl at temperatures higher than 820 °C.[18] The peak due to NaCl was not clearly observed in the pattern of sample J, which suggests that the liquid phase of the mixture upon heat-treatment was not soft enough to occlude NaCl into the vitreous composition. The peak intensity of tetragonal zirconia in sample I was much weaker than that in sample A. The amount of crystalline ZrO_2 decreased as the glassy composition of the SiO_2–ZrO_2–Na_2O system was formed. Thus, the glassy phase of the SiO_2–ZrO_2–Na_2O system of the support developed when the mixture was heated at 800 °C, compared to that of the support prepared by heating the mixture at 760 °C.

These results were evaluated for the mixtures of $ZrOCl_2$ and NaCl as impregnating salts in the silica gel. The following result was obtained using three different salt combinations. Sample K ($ZrO(NO_3)_2$–$NaNO_3$) was nearly sintered, as its SSA was less than 1 $m^2\,g^{-1}$. The weak peak around $2\Theta = 22°$ assigned to cristobalite was identified in sample K. Partial crystallization of the support occurred in sample K. The SSAs of sample L ($ZrO(NO_3)_2$–NaCl) and sample M ($ZrOCl_2$–KCl) were 37 and 54 $m^2\,g^{-1}$, respectively. Peak intensity around $2\Theta = 30°$ attributable to zirconia in the XRD pattern of sample M was nearly the same as that of sample A, whereas the intensity of the comparable peak in sample L was slightly lower.

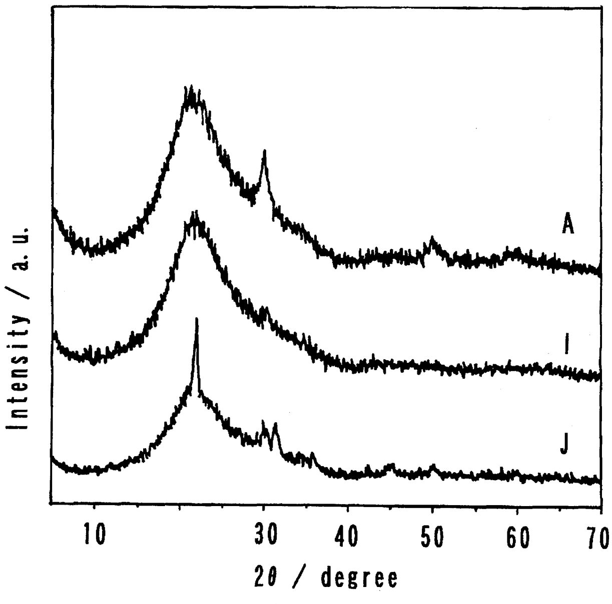

Fig. 5. X-Ray diffraction patterns of sample A, I, and J.

The results demonstrated that analogous supports were obtained when $ZrO(NO_3)_2$–NaCl and $ZrOCl_2$–KCl were used as impregnating salts instead of $ZrOCl_2$–NaCl. In contrast, in the case of $ZrO(NO_3)_2$–$NaNO_3$, sintering the mixture caused the loss of substantial porosity. A mixture of SiO_2–ZrO_2 gel and Na_2CO_3 or NaOH was sintered upon heating to 700 °C.[18] The formation of Na_2O and/or NaOH in the gel below 700 °C probably caused the sintering of the mixture at the lower temperature. For $ZrO(NO_3)_2$–$NaNO_3$ impregnation into silica gel, $NaNO_3$ was supposed to decompose at a lower temperature than NaCl and to turn into Na_2O, which would induce a complete sintering of the silica gel.

Effect of the Silica Gel Properties. We describe here an attempt to reduce the pore size by changing the preparative conditions of the silica gel. Three dried gels, S-2, S-3, and S-4, were prepared under the conditions listed in Table 2. S-1 was prepared by the standard procedure. The SSAs, pore volume and mode pore radii of the pore-size distributions of calcined samples are tabulated in Table 2. The gels were calcined at 600 °C for 3 h, and then at 760 °C for 5 h without addition of salt. The pore-size distribution curves of the gels of S-1 and S-4 are shown in Fig. 6; those of S-2 and S-3 were similar to that of S-1 and are not shown. The mode pore radius of the pore-size distribution of S-4 was 100 Å, much smaller than that of S-1; the pores of S-4 distributed mainly in the range from 20 to 200 Å in radius. In addition, the SSA of S-4 was larger than those of other gels.

The SSAs and pore volumes of the samples N to S prepared by heating the mixtures of silica gel and salt are shown in

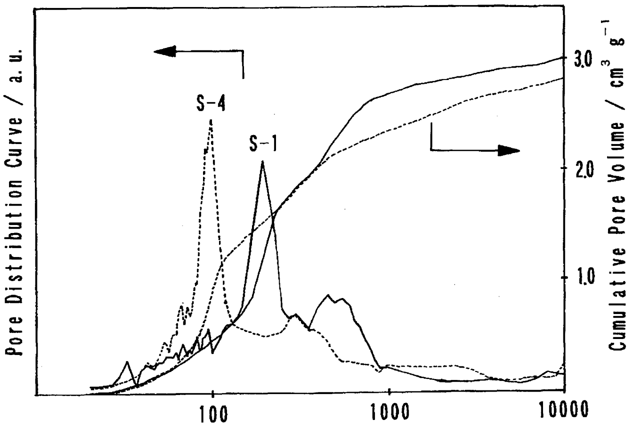

Fig. 6. Pore-size distribution curves of the silica gel after calcination at 760 °C.

Table 2. Conditions of Synthesis of Dried Gel and Their Effect on Pore Characteristics of Dried Gel Heated at 760 °C

Sample	Synthetic conditions			SSA	Pore volume[a]	Mode pore radius
	Addition of CyH[b]	Stirring time/h	Aging	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	Å
S-1	Yes	5	Yes	258	2.68	198
S-2	No	5	Yes	251	2.70	170
S-3	Yes	1.5	Yes	288	2.74	170
S-4	No	0.25	No	321	2.35	100

a) Pore volume in the range from 20 to 1,000 Å. b) CyH : Cyclohexane.

Table 3. The pore-size distribution curves of samples O and Q were analogous to that of sample A, although their mode pore radii were slightly different. Thus, the supports prepared by the salt impregnation method using S-2, S-3, and S-1 gels possessed similar pore-size distributions. This result was consistent with the finding that the pore-size distributions of two calcined samples were similar to that of S-1. The absence of cyclohexane in the organic phase and shortening the stirring time from 5 to 1.5 h did not seriously influence the pore characteristics of the silica gel. Unger et al. described that the addition of cyclohexane to the pre-hydrolysis solution of $Si(OEt)_4$ greatly affected the pore volume of products.[21] In this study, the organic phase of the standard method was composed of *t*-pentyl alcohol in addition to the pre-hydrolysis solution of $Si(OEt)_4$ and cyclohexane. Therefore, whether cyclohexane was added to the organic phase or not had little influence on the pore characteristics of the silica gel.

The pore-size distribution curves of samples N, O, and R are shown in Fig. 7. The pore-size distribution of sample N (730 °C) was shifted toward a smaller size compared to that of sample O (760 °C). This is attributed to a lower degree of sintering in sample N than in sample O. The mode pore radii of the pore-size distribution curves of the three samples were, in decreasing order, O (440 Å) > N (345 Å) > R (269 Å). The pore size of sample R (prepared using S-4) was the smallest among the supports prepared by salt impregnation in this study, and its pore volume was also much smaller than that of other samples. However, its pore volume was larger than those of porous glasses prepared by the phase-separation method (less than 0.9 $cm^3\ g^{-1}$).[24] The SEM photographs of samples N, O, and R are shown in Fig. 8. The skeleton size of the porous-glass-like texture in the support prepared by heating the mixtures at 730 °C (sample N) was smaller than that of the support prepared by heating at 760 °C (sample O). It is clear that voids between porous-glass-like skeletons were narrow in sample R, as shown in Fig. 8(c).

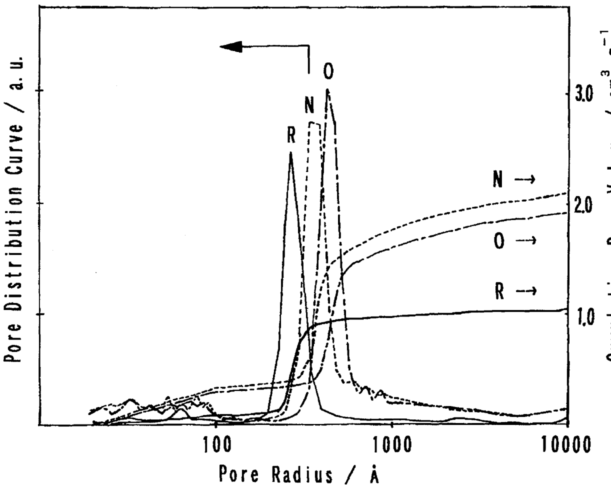

Fig. 7. Pore-size distribution curves of samples N, O, and R.

These results indicate that the physical properties of S-4 were quite different from those of S-1, S-2, and S-3. Shortening of the standing time after gelation was effective to prepare silica gel with small pore size. Standing after gelation causes growth of primary particles in the gel and the enlargement of the pore size. Silica particles grow through aging or through repeated dissolution-precipitation in an alkaline solution.[25]

This study demonstrated that mode pore radii of the porous supports ranged from 350 Å (730 °C) to 450 Å (760 °C) and

Table 3. Effect of Silica Gel on Pore Characteristics of Porous Supports in the SiO_2–ZrO_2 System

Sample	Synthetic conditions				SSA	Pore volume[a]	Mode pore radius
	Silica gel	ZrO_2/gel	NaCl/gel	Calcn. temp			
		g/g	g/g	°C	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	Å
N	S-2	0.15	0.29	730	54	1.74	345
O	S-2	0.15	0.29	760	37	1.58	440
P	S-3	0.15	0.29	730	59	1.71	350
Q	S-3	0.15	0.29	760	39	1.62	497
R	S-4	0.15	0.29	760	48	0.97	269
S	S-4	0.05	0.29	760	30	1.14	494

a) Pore volume in the range from 20 to 1,000 Å.

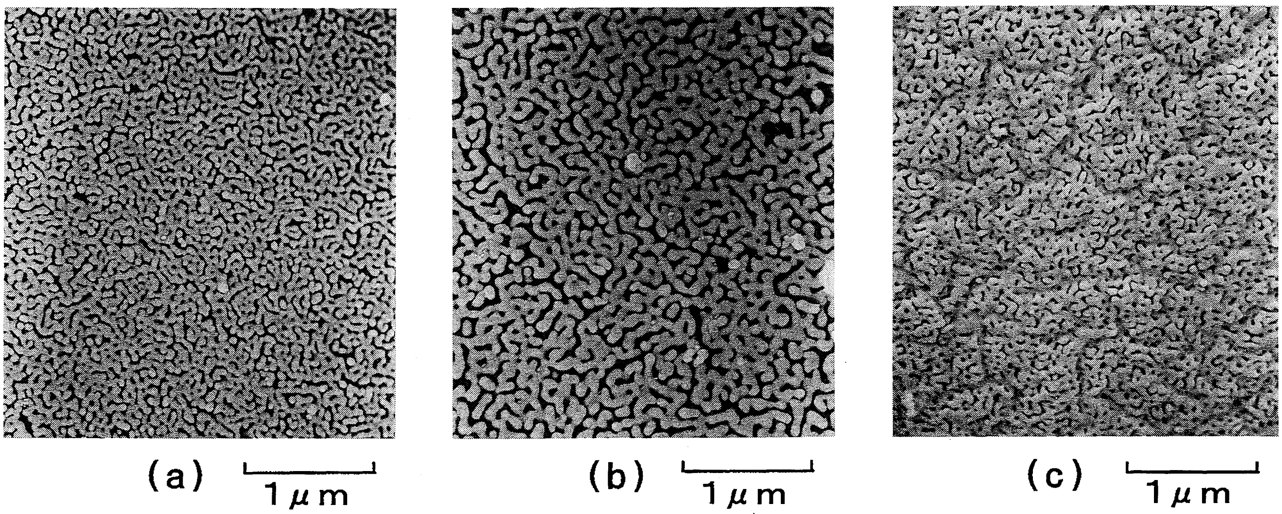

Fig. 8. SEM photographs of samples N, O, and R, (a) sample N (S-2/0.15 g ZrO_2, 730 °C), (b) sample O (S-2/0.15 g ZrO_2, 760 °C), (c) sample R (S-4/0.15 g ZrO_2, 760 °C), where (S-2/0.15 g ZrO_2, 730 °C) indicates that the sample was prepared by adding 0.15 g of ZrO_2 per 1.0 g of the S-2 gel in the form of $ZrOCl_2 \cdot 8H_2O$ in addition to NaCl and heating the mixture at 730 °C.

to 550 Å (800 °C) depending on the temperature of the heat treatment of the mixtures. The radii decreased to 270 Å (760 °C) by altering the silica gel as a result of adding 0.15 g/g ZrO_2. The radii ranged from 500 Å (sample S, prepared from S-4) to 640 Å (sample C, from S-1) as a result of adding 0.05 g/g ZrO_2. Accordingly the porous support with the mode pore radius in the range from 270 to 640 Å with a sharp pore-size distribution could be prepared by this method.

Changing Morphology from the Dried Gel to the Support. SEM photographs of the dried gel (S-4) are shown in Fig. 9(a), (b), and (c). The surface of the dried gel was generally a dense structure; however, cracks were observed in some parts of the particle surface, as shown in Fig. 9(b). In some particles, part of the surface was uncovered (the left upper side of Fig. 9(a)) and the inside of the particle was observed (Fig. 9(c)). The interior of particle was porous, and its texture was typical of the gel. The gel particles consisted of a porous core and a dense outer skin. This composite structure of particles was analogous to that of the SiO_2–ZrO_2 gel.[18] The coated surface layer seemed to originate from the interface of water and the organic phase of an O/W emulsion during preparation of the silica gel. The texture of the gel calcined without salt impregnation was similar to that of the dried gel. Thus, the pore-size distributions of the calcined gel measured using the Hg intrusion method probably reflected those of pores inside the particles.

The photographs of sample S (prepared from S-4 gel) shown in Fig. 9(d) and (e) indicate that the thin surface layer disappeared and the sample structure was converted into the porous-glass-like texture. In comparison with the morphology of the dried gel, the texture of the particle surface was changed considerably after heat treatment of the mixture of the gel and salt. SEM photographs of sample Q are shown in Fig. 9(f), (g), and (h); that of (f) shows crushed particles of sample Q for observation of inside structure, and those of (g) and (h) are broken particles found in sample Q. Obviously a similar texture to that of porous glasses was observed inside all particles. The insides of the support were supposed to be more porous than the pore openings between the skeletons observed on its surface. In the supports prepared by heating the mixtures at the lower temperature (730 °C), the influence of the thin oxide layer of the silica gel remained; the surface layer of the support was wrinkled, as shown in Fig. 9(i).

Evaluation of Resistance to an Alkaline Solution. The alkaline resistance of supports was evaluated preliminarily by immersing them in a 0.1 M NaOH solution at room temperature for 24 h and analyzing the amount of Si in the solution. Samples A, B, C, D, I and S were examined together with two references. The first one was sample Z, and the other was the porous support in the SiO_2–ZrO_2–Na_2O system, which was synthesized by impregnation of NaCl into the SiO_2–ZrO_2 gel and a subsequent heat-treatment.[18] Data on soluble silica content and those values divided by the SSAs are shown in Table 4. The soluble silica content of sample Z was high, and almost the entire sample was dissolved. This result presumably originated from its large SSA. In contrast, the soluble silica content of SiO_2–ZrO_2–Na_2O was approxi-

Table 4. Results of Alkaline-Resistance Test

Sample	ZrO_2/gel	Calcn. temp	$D^{a)}$	SSA	$D/S^{b)} \times 10^4$
	g/g	°C	wt%	$m^2 g^{-1}$	$g m^{-2}$
A	0.15	760	3.4	38	9.0
B	0.10	760	3.3	32	10
C	0.05	760	3.6	22	17
D	0	760	8.4	13	64
I	0.15	800	1.0	13	7.9
S	0.05	760	3.2	30	11
Z	0.15	760	73.5	271	27
Ref.$^{c)}$	—	760	0.6	35	1.6

a) *D*: Percentage of soluble silica to sample weight after a sample was immersed in a 0.1 M NaOH for 24 h. b) *D/S*: *D* value divided by SSA. c) SiO_2–ZrO_2–Na_2O : prepared by heating the mixture of the SiO_2–ZrO_2 gel and NaCl.

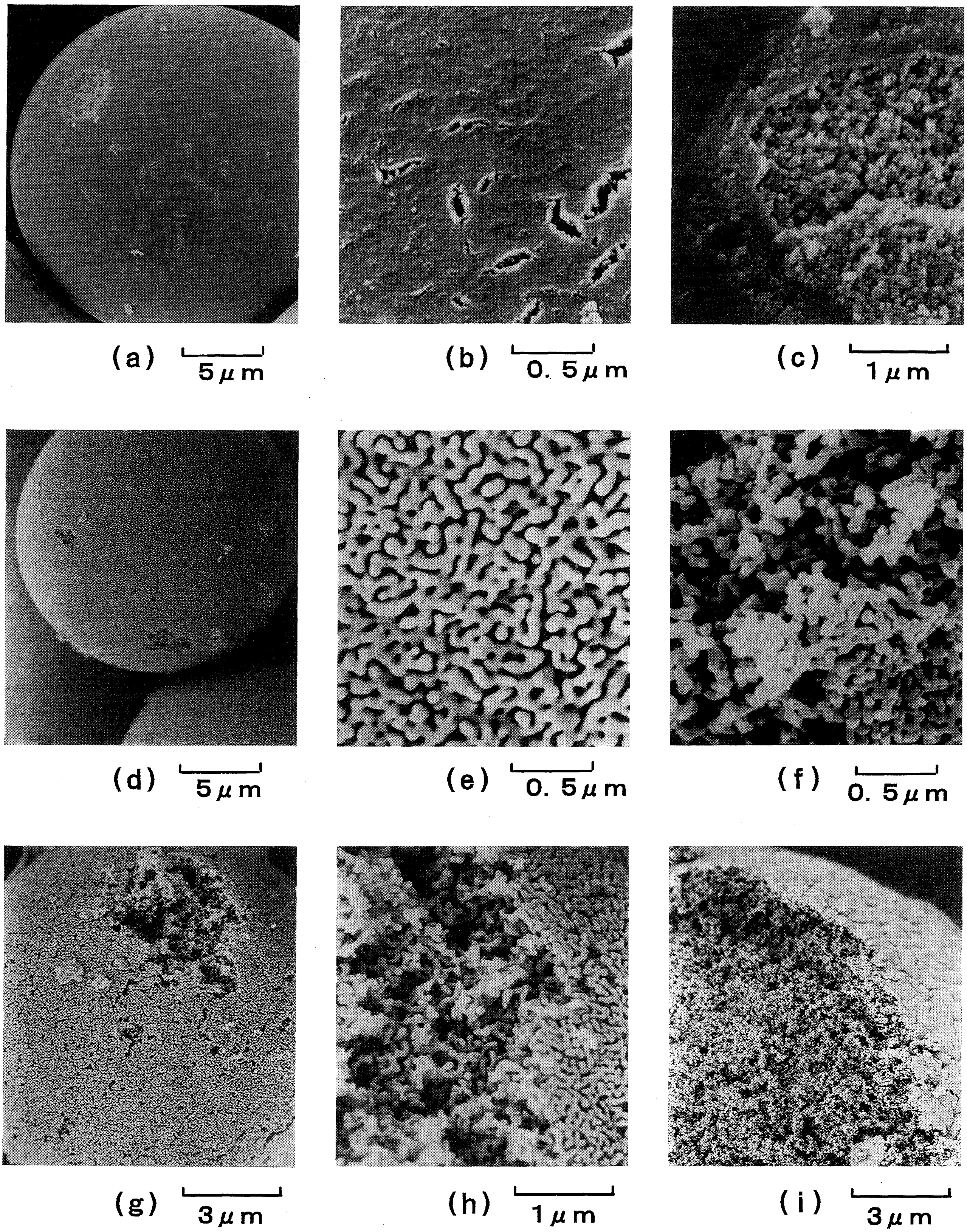

Fig. 9. SEM photographs of samples S-4, S, Q, and P, (a), (b), and (c) S-4 (dried gel), (d) sample S (S-4/0.05 g ZrO_2, 760 °C), (e) the same sample with (d), (f) a crushed particle of sample Q (S-3/0.15 g ZrO_2, 760 °C), (g) sample Q, (h) the same sample with (g), (i) sample P (S-3/0.15 g ZrO_2, 730 °C), where (S-4/0.05 g ZrO_2, 760 °C) indicates that the sample was prepared by adding 0.05 g of ZrO_2 per 1.0 g of the S-4 gel in the form of $ZrOCl_2 \cdot 8H_2O$ in addition to NaCl and heating the mixture at 760 °C.

mately 1/100 less than that of sample Z. The soluble silica content of samples in this study ranged from 1.0 to 8.4 wt%, which is between those of the two references. The soluble silica content of sample D (8.4 wt%), which did not contain ZrO_2, was high compared to those of samples A, B, and C, prepared from the silica gel impregnated with ZrO_2. The soluble silica content divided by the SSA of sample D was also high. The soluble silica content of sample I (prepared by heating at 800 °C) was much less than that of sample A (prepared by heating at 760 °C), although both used the same amount of ZrO_2. This was partially attributed to its small SSA ($13\ m^2\ g^{-1}$). However, the soluble silica content of sample I was much larger than that of porous supports in the SiO_2–ZrO_2–Na_2O system, which were manufactured by heating a mixture of the homogeneous SiO_2–ZrO_2 gel and NaCl. The soluble silica content per SSA was five times larger than that of the reference. This result implies that the ZrO_2 distribution in the porous supports in this study was not homogeneous even in sample I, which was prepared by heating the mixture at 800 °C.

Conclusions

A new preparative method for porous supports was investigated by impregnating $ZrOCl_2$ and NaCl into a microspherical gel, heating the mixture at temperatures ranging from 730 to 800 °C, and subsequently washing the mixture with water. The following results were obtained.

1. The presence of ZrO_2 in the mixture suppressed sintering and crystallization of the supports and promoted incorporation of Na_2O. The porous-glass-like texture similar to that produced by the phase-separation method was observed not only on the surface of the microspherical support but also in its interior.

2. Peaks of tetragonal ZrO_2 were observed in XRD patterns of the supports prepared by heating the mixtures of silica gel, NaCl and $ZrOCl_2$; the amounts of $ZrOCl_2$ were 0.15 g or 0.10 g per 1.0 g of the silica gel based on ZrO_2. The impregnation of $ZrOCl_2$ into silica gel resulted in the heterogeneous distribution of ZrO_2 in the supports, compared to porous glass supports prepared by heating the mixture of the SiO_2–ZrO_2 gel and NaCl.

3. Peak intensities of ZrO_2 in the supports were reduced by raising the temperature of the heat-treatment of the mixture from 760 to 800 °C. Ternary oxides in the SiO_2–ZrO_2–Na_2O system were partially formed.

4. Analogous supports were obtained by heating mixtures of silica gel and $ZrO(NO_3)_2$–NaCl or $ZrOCl_2$–KCl instead of $ZrOCl_2$–NaCl. In contrast, the support sintered and lost porosity by heating the mixture of silica gel and $ZrO(NO_3)_2$–$NaNO_3$.

5. Shortening the standing time after gelation was effective to prepare silica gel with small pore size. Pore sizes of the supports prepared using this gel as the starting material were smaller than those synthesized using the standard gel. Mode pore radii in the range from 270 to 640 Å were prepared with maintaining a sharp pore-size distribution.

6. The porous supports obtained in this study possess an alkali durability higher than the supports prepared by impregnation of $ZrOCl_2$ into silica gel and heating the mixture, although their resistance was inferior to the supports prepared from the SiO_2–ZrO_2 gel and NaCl.

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