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Preparation of porous supports in the SiO_2-ZrO_2-Na_2O system from microspherical silica gels

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Preparation of porous supports in the SiO_2-ZrO_2-Na_2O system was investigated using a commercially available silica gel as a starting material. The microspherical silica gel, impregnated with $ZrOCl_2$ and NaCl, was heated and subsequently washed with water. Porous supports, composed with sponge-like skeletons on the surface of the particles, were obtained owing to suppression of crystallization of the supports as well as their sintering. Similar supports were formed using a silica gel prepared from sodium silicate solution by the same procedure. In contrast, crystallization of silica proceeded in supports prepared by heating the mixture of silica gel and NaCl in the absence of $ZrOCl_2$. A new method for preparing the analogous supports was also investigated by heating a mixture of silica gel impregnated with $ZrOCl_2$ and Na_2CO_3 powder. © *2001 Kluwer Academic Publishers*

1. Introduction

SiO_2-ZrO_2 mixed oxides gained increasing attention in recent years because they have excellent properties for use as alkali-durable glasses and catalysts [1–3]. Moreover, many studies on the SiO_2-ZrO_2 system were also reported; two examples are zirconia dispersed on silica [4] and an application as a dental filler [5]. Porous material in the SiO_2-ZrO_2 system has been investigated for application as a chromatographic support with alkaline durability [6, 7] and as a heterogeneous catalyst [8].

Silica supports with large pores more than 10 nm in diameter have been used for chromatographic separation of bio-related materials, such as proteins and enzymes [9]. Supports of inorganic oxides have the advantages of mechanical strength and of stability to organic solvents and biomaterials, although they are dissolved even in weak alkaline solution, and control of their larger pore size is difficult. Porous supports of SiO_2-ZrO_2 system with spherical particles of 1 to 50 μm in size and their pore size in the range of 10 to 100 nm have been desired for the above applications, especially for high-performance liquid chromatography (HPLC).

The representative methods of preparation of porous materials in the SiO_2-ZrO_2 system are using a sol-gel method, a phase separation of glasses, and impregnation of ZrO_2 on porous silica. Various methods were investigated because it was rather difficult to prepare homogeneous SiO_2-ZrO_2 mixed oxide, while maintaining desired porosity. In the case of the sol-gel method, porous glasses with homogeneous distribution of ZrO_2 in the silica matrix were easily prepared. The ZrO_2 content of porous glasses could be controlled over a wider range, and their alkaline resistance was excellent in this procedure [10–13]. However, the pore radius of the sol-gel derived porous glass was less than 5 nm. Recently, porous gels with large pores in the range of 0.2–30 μm in size were reported using phase separation of polyethylene oxide and SiO_2-ZrO_2 gel [14].

In the case of the phase-separation method, the amount of ZrO_2 incorporated was limited because ZrO_2 mainly moved to the soluble phase during heat-treatment and thus it did not remain in the porous glass skeleton after etching in the soluble phase. The addition of an 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 [15–18]. However, the maximum amount of the ZrO_2 content was less than 8 wt% according to the recent report [19]. Also many steps were required for preparation of phase-separated porous glass; melting of starting oxides at high temperature, heat-treatment of phase separation, and a few etching steps.

On the other hand, impregnation or coating ZrO_2 onto porous silica was economical in comparison with the sol-gel method, and its preparation was quite simple. Improvements in alkali stability at pH 9 were reported for porous silica support impregnated with ZrO_2

for chromatographic separation [20], and impregnation of ZrO_2 into a porous silica glass was reported [21]. For the impregnated method, distribution of ZrO_2 was restricted to the surface of supports; therefore their alkaline durability seemed to be limited.

One of the present authors has already reported a new procedure for preparing SiO_2-ZrO_2-Na_2O porous 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 [22, 23]. Furthermore, an advanced preparative method was recently reported; the method involves heating a mixture of the microspherical silica gel prepared by a sol-gel procedure, $ZrOCl_2$ and NaCl at 760°C [24]. Microspherical porous supports less than 100 μm in particle size were easily obtained using this method. Most of the pores were distributed on more than 10 nm in radius and their pore volume was more than 1.0 cm^3/g.

It seemed that this method has potentially wide applicability to various kinds of silica gels, with ease of transformation of silica gel to porous-glass-like support, which contained a certain amount of ZrO_2, while maintaining particle shape. In this paper, we investigated application of a recently reported procedure to a commercially available silica gel used for HPLC supports, and to a silica gel prepared from sodium silicate solution. Pore size of these silica gels was small for separation of bio-related materials, and they could not be used in a mobile phase of higher than neutral pH [20]. We studied conversion of these silica gels to porous-glass-like supports with pore size of about 50 nm in diameter and with alkaline durability through incorporation of ZrO_2 in their compositions. Moreover, an improved method, using Na_2CO_3 instead of NaCl, is also reported. These supports might be suited for application as HPLC supports since they possess microspherical particles of 3 to 20 μm in size and sufficient porosity, and durability for alkaline solution. They also have the possibility of application for dental-filler, since they contain a certain amount of ZrO_2 in their composition.

Heat treatment of mixtures of silica gels and NaCl was reported to be used as practical technique for enlargement of pore size of silica gels for HPLC [25]. In addition, the treatment was also investigated from a point of view of the crystallization behavior of silica gel [26, 27]. Thus, in this paper, we also studied the influence of heat-treatment of the above mixtures and compared them with the mixtures together with $ZrOCl_2$.

2. Experimental procedure

2.1. Preparation of SiO_2-ZrO_2-Na_2O porous supports

Two types of microspherical silica gels were used in this study; one was Nucleosil 100-3 purchased from Chemco Scientific Co. Ltd., and the other was silica gel prepared from a sodium silicate solution [28]. Nucleosil 100-3 is manufactured by M. Nagel, and its particle size is 3 μm in diameter. The preparation scheme is shown in Fig. 1. Samples A to D and F to I were prepared as follows (Method A in Fig. 1). A 5 cm^3 aqueous solution containing a designated amount of $ZrOCl_2{\cdot}8H_2O$ and 0.58 g of NaCl was added to two grams of the dried gel, pre-heated and retained at 120°C until it maintained a constant weight. 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 200 cm^3 of water, and the supernatant solution was decanted to remove soluble salts such as excess NaCl. The same washing process was repeated one more time, and the supernatant solution was decanted. The product was collected by filtration and dried at 120°C for 5 h.

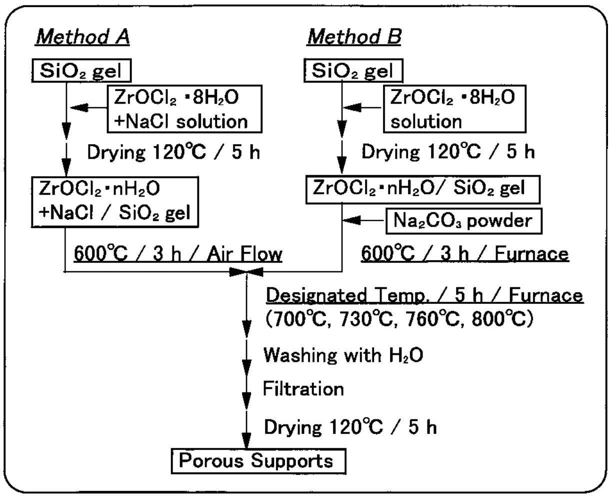

Figure 1 Preparation procedures of porous supports.

For samples K to P, silica gel impregnated with only $ZrOCl_2{\cdot}8H_2O$ was first prepared by the same procedure as described above (Method B in Fig. 1). The powder of pulverized anhydrous Na_2CO_3 and the impregnated gel were mixed together by shaking for 3 min in a sample tube. The mixture was heated in an alumina crucible at 600°C for a designated time and then at 760°C for 5 h in a furnace. The calcined sample was washed to remove soluble salts such as excess NaCl and dried by the same procedure as that of samples A to D. For sample R, the impregnated gel was mixed together with pulverized NaCl. For samples S and T, each mixture was heated in a crucible at 600°C for a designated time and then at 760°C for 5 h in a furnace. The resultant mixtures were treated by the same method as that described above.

2.2. Characterization of products

The specific surface areas (SSAs) were obtained by the Brunauer-Emmett-Teller (BET) single-point method with a Quantachrome Autosorb-6 using nitrogen as the adsorbate. The pore-size distributions and pore volumes of the porous supports were measured by mercury-penetration porosimetry using an Autopore 9200, Micrometrix. The X-ray diffraction (XRD) measurements were made using a Phillips PW 3710 diffractometer with Cu K_α radiation. The scanning electron microscope (SEM) observations were performed on gold-palladium-coated surfaces using a Hitachi S-900 and a Hitachi S-4500. Particle size distribution was measured by a Horiba LA-500. Chemical analyses of products were performed by X-ray fluorescence using a Rigaku System 3370.

2.3. 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 plastic container to which a 0.1 M NaOH solution was added. The plastic 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).

3. Results and discussion

3.1. Preparation of porous supports using Nucleosil as a starting gel

A Nucleosil 100-3 (Gel-n) was investigated first as a starting material. 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. The mixtures were heated by method A shown in Fig. 1; the same condition as that of the previous report [24].

SEM photographs of Gel-n and samples B, C and D are shown in Fig. 2. A SEM photograph of sample A was not shown since it was similar to that of sample B. The surface of microspherical particles of Gel-n was composed of a gel-like structure. In contrast, porous-glass-like skeletons were observed on the surface of the microspherical particles of samples A to D. In sample C, the vitreous skeletons were developed compared to those of sample A and B. Differences were clearly observed between the shape of microspherical particles in sample D, prepared by heating a mixture of Gel-n and NaCl without $ZrOCl_2$. It was composed of particles between the first and the final stage of sintering; some particles were almost sintered and the other particles

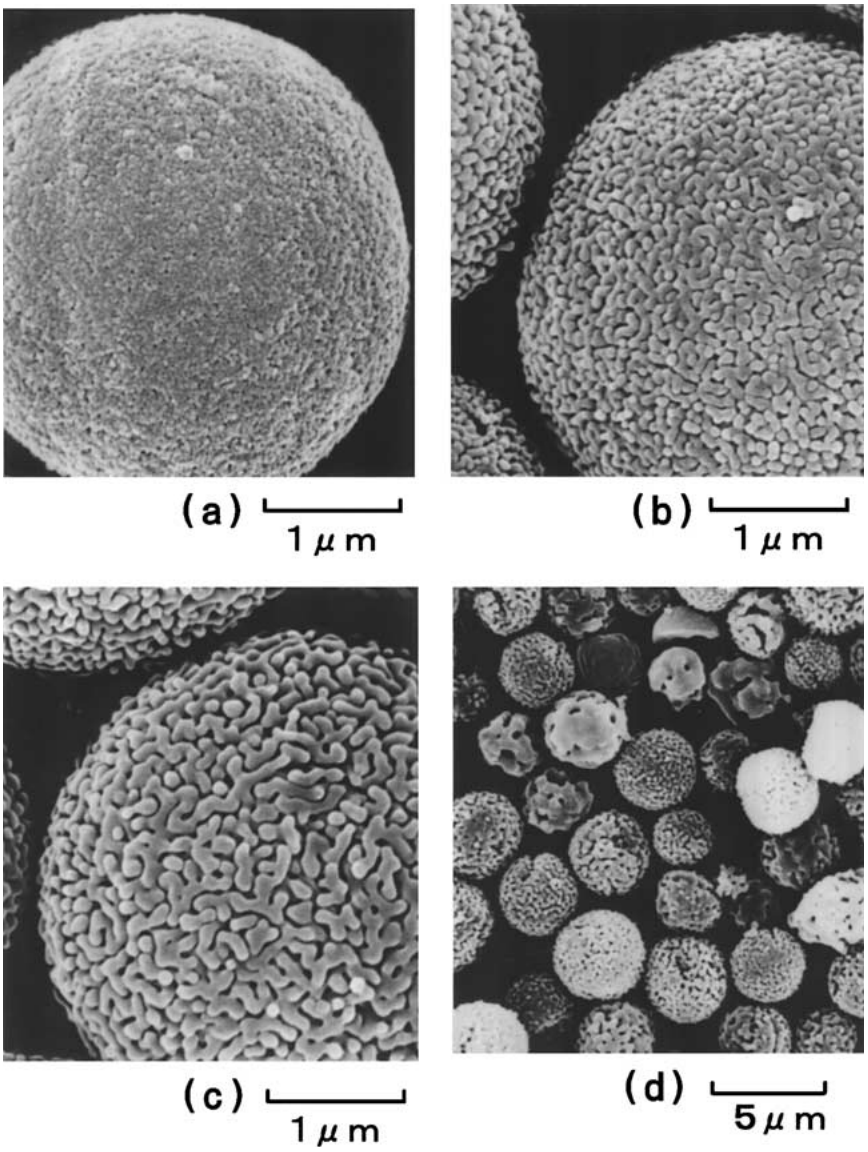

Figure 2 SEM photographs of samples Gel-n, B, C and D. (a) Gel-n, (b) sample B (0.10 g ZrO_2, 760°C), (c) sample C (0.05 g ZrO_2, 760°C), (d) sample D (0 g ZrO_2, 760 °C), where (0.10 g ZrO_2, 760°C) indicates that the sample was prepared by adding 0.10 g of ZrO_2 per 1.0 g of Gel-n in the form of $ZrOCl_2{\cdot}8H_2O$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

TABLE I Effect of synthetic conditions on pore characteristics of porous supports in the SiO_2-ZrO_2-Na_2O system

	Synthetic conditions				Product composition					
Sample	Silica gel type	ZrO_2/gel (g/g)	NaCl/gel (g/g)	Calcn. temp./°C	ZrO_2/SiO_2 (g/g)	Na_2O/SiO_2 (g/g)	SSA ($m^2 g^{-1}$)	Pore volume[a] ($cm^3 g^{-1}$)	Mode pore radius (nm)	Median particle size/μm
A	Gel-n[b]	0.15	0.29	760	0.14	0.044	40	0.69	24	3.0
B	Gel-n	0.10	0.29	760	0.09	0.037	36	0.65	24	2.9
C	Gel-n	0.05	0.29	760	0.05	0.032	26	0.59	32	3.1
D	Gel-n	0	0.29	760	0	0.011	8	0.24	82	4.9
E	Gel-n	0	–	150	–	–	309	1.04	3.3	3.1
F	Gel-m[c]	0.05	0.29	700	0.05	0.018	145	0.81	5.5, 18	11.2
G	Gel-m	0.05	0.29	730	0.05	0.021	53	0.79	23	11.4
H	Gel-m	0.05	0.29	760	0.05	0.034	38	0.69	30	11.1
I	Gel-m	0.05	0.29	800	0.05	0.054	$\leq$1	0.23	55	22.4
J	Gel-m	0	–	150	–	–	352	1.16	3.7	11.2

[a] Pore volume in the range from 2 to 100 nm.

[b] Nucleosil 100-3.

[c] Silica gel prepared from a sodium silicate.

retained porosity. The size of the skeleton and pores between skeletons (the darker parts of the photographs in Fig. 2) were in increasing order, A, B < C < D. As the amount of ZrO_2 added to Gel-n decreased, the pore size of the porous supports became larger and the degree of sintering of the porous supports increased accordingly.

Physical properties of four samples and sample E (Gel-n heated at 150°C) are listed in Table I, and pore-size distribution curves are shown in Fig. 3. The SSAs and pore volume of the supports decreased and pore size became larger as the amounts of ZrO_2 impregnated into the gel decreased. The SSA and pore volume of sample E was in accordance with data reported by the manufacturer. However, its mode pore radius (3.3 nm) was smaller than the 10 nm in diameter described in the catalogue, although pores larger than 10 nm in radius also existed in Sample E.

Almost all pores of samples A, B and C were in the range of 10 to 50 nm in radius; pores smaller than 10 nm had disappeared. In contrast, the mode pore radius of sample D was 82.4 nm and pores larger than 100 nm were observed. Its pore size distribution was broader than those of A, B and C. These results indicated that a degree of sintering of porous supports was reduced as the content of $ZrOCl_2$ added to Gel-n was increased, and heterogeneous sintering occurred in the absence of $ZrOCl_2$. These results were similar to those of porous supports obtained using a sol-gel derived silica gel [24]. However, pore volume in the range of 10 to 100 nm of samples A, B, and C was less than 0.7 cm^3/g; smaller than that of samples prepared using the sol-gel derived silica gel, whose pore volume was more than 1.0 cm^3/g. This difference originated from the porosity of two types of original silica gel, since porous supports were formed through sintering of the gel. Pore volume of sample E was smaller than that of the silica gel prepared by the sol-gel method. Pore size distributions of samples A, B and C were broader than those of porous supports obtained using the silica gel prepared by the sol-gel method. The heterogeneity of particles observed for sample D also existed to some extent in samples A, B and C, although difference between particles was much less clear than that in sample D. Thus, it seemed that homogeneity between particles of samples A to D in this study was inferior to that of samples in the previous study [24].

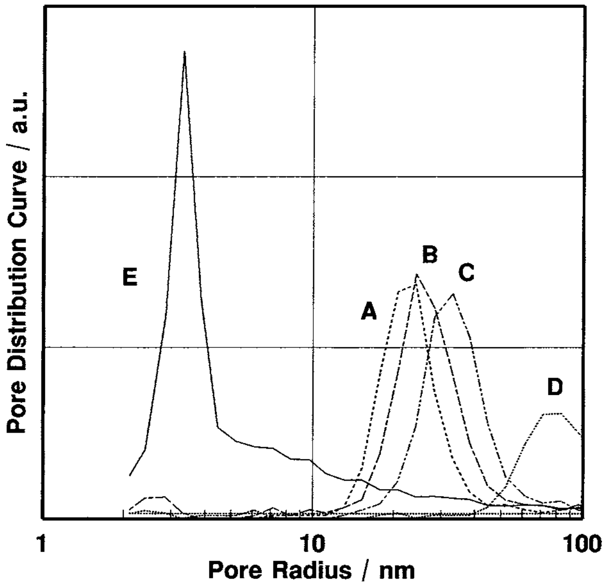

Figure 3 Pore-size distribution curves of samples A, B, C, D and E.

XRD patterns of samples A to D are shown in Fig. 4. The pattern of sample D was very different from those of the three other samples; its peaks were assigned to cristobalite. In contrast, a crystalline phase due to silica was not observed in samples A, B and C, although the peak intensity around $2\Theta = 21°$ increased in the order A < B < C. It was clear that crystallization of silica gel was suppressed as the amount of ZrO_2 added was increased. Extensive crystallization seemed to occur in sample D, because it was prepared by heating the gel and NaCl without the addition of $ZrOCl_2$. Peaks assigned to tetragonal ZrO_2 (t-ZrO_2, $2\Theta = 30°$, 35°, 50° and 60°) were identified in samples A and B. This result was consistent with those of products prepared from the sol-gel-derived silica gel.

The results of chemical analysis of samples A to D are shown in Table I. The content of ZrO_2 corresponded to that of ZrO_2 impregnated into Gel-n. The sodium content was dependent on the amount of ZrO_2 added. The sodium cation probably existed in the form of

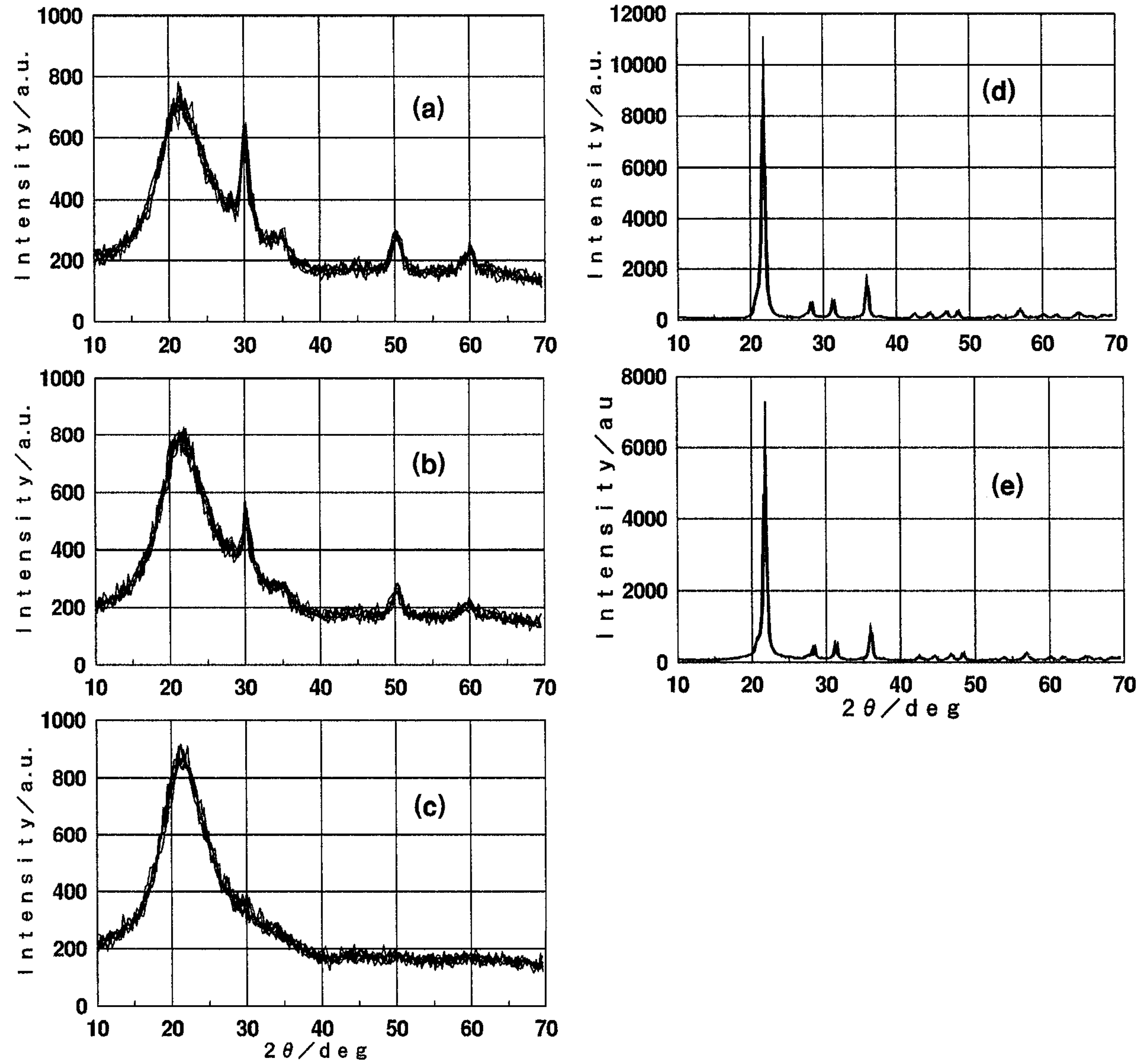

Figure 4 X-Ray diffraction patterns of samples A, B, C and D. (a) Sample A (0.15 g ZrO_2, 760°C), (b) sample B (0.10 g ZrO_2, 760°C), (c) sample C (0.05 g ZrO_2, 760°C), (d) sample D (0 g ZrO_2, 760°C), (e) Nucleosil 4000, where (0.15 g ZrO_2, 760°C) indicates that the sample was prepared by adding 0.15 g of ZrO_2 per 1.0 g of Gel-n in the form of $ZrOCl_2 \cdot 8H_2O$ in addition to NaCl and heating the mixture at 760°C.

SiO_2-ZrO_2-Na_2O in the support, since salt in the form of NaCl was removed by washing the supports with water.

These results demonstrated that crystallization and sintering of Gel-n occurred and sintering among particles was heterogeneous when the mixture of Gel-n and NaCl was heated in the absence of ZrO_2. The addition of ZrO_2 in the amount of 0.05 g per 1.0 g of Gel-n together with NaCl reduces crystallization of the support. As the amount of ZrO_2 increased, the reduction of crystallization was enhanced and the amount of Na_2O into the support was increased. Thus, the supports in the SiO_2-ZrO_2-Na_2O system, comparable those in the previous report [24], were obtained from commercially available silica gel by heating mixtures of the silica gel, $ZrOCl_2$ and NaCl; the same procedure using the sol-gel derived silica gel. This treatment induced sintering of the silica gel, reduction of SSA and pore volume, and enlargement of pore size. However, sintering could be controlled by the amount of ZrO_2 added to the gel. Pore volume of the supports obtained in this study was smaller than those prepared from the sol-gel derived silica gels, and their pore size was broader owing to a more heterogeneous composition than supports in the previous study. However, pore volume of the present supports was more than 0.5 cm^3/g and their pore size was distributed mainly 50 nm in diameter.

The results of XRD measurement of samples prepared by the same procedure with samples A to D are tabulated in Table II. These samples were synthesized

TABLE II Effect of synthetic conditions on degree of crystallization of porous supports

ZrO_2/SiO_2 (g/g)	Heating temperature/°C 700	730	760	800
0	Amorph.[a]	Crist.[b]	Crist.	
0.05		Amorph.	Amorph.	Crist.
0.10		Amorph.	Amorph.	Amorph. + Crist.
0.15		Amorph.	Amorph. + t-ZrO_2	Amorph. + t-ZrO_2
0.20			Amorph. + t-ZrO_2	Amorph. + t-ZrO_2

[a] Amorph.: Amorphous.
[b] Crist.: Cristobalite.

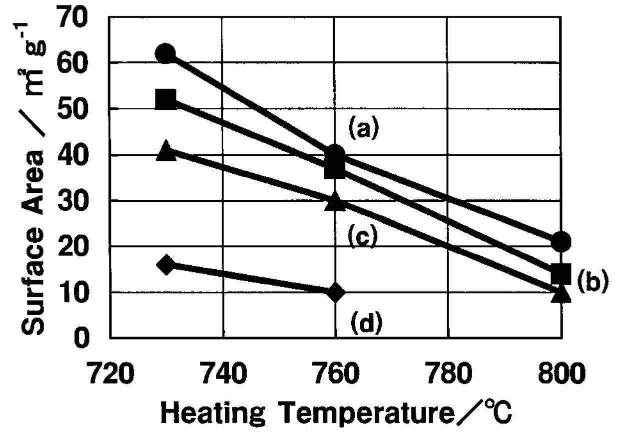

Figure 5 Relationship between specific surface areas, heat-treatment temperature, and amounts of ZrO_2 impregnated per 1.0 g of Gel-n. (a) 0.15 g, (b) 0.10 g, (c) 0.05 g, (d) 0 g.

with using different amount of ZrO_2 and by heating the mixtures at 700°C to 800°C. In the case of 0.05 g ZrO_2 added to 1.0 g of Gel-n ($ZrO_2/SiO_2 = 0.05$ g/g), the peaks assigned to cristobalite appeared in the sample prepared by heating the mixtures at 800°C. The peak intensity of $2\Theta = 21°$ was increased in the sample prepared by $ZrO_2/SiO_2 = 0.10$ g/g at 800°C. In contrast, the peak intensity of $2\Theta = 21°$ was weak in the case of 0.15 g/g and 0.20 g/g, although the peak intensity assigned to t-ZrO_2 increased. As the amount of ZrO_2 added to Gel-n was increased, the heat treatment temperature of the mixtures, at which supports transformed from amorphous to cristobalite, was raised. SSAs of these samples against heating temperature are plotted in Fig. 5. As the mixtures were heated at higher temperature, SSAs of supports were decreased and their sintering was initiated. The addition of ZrO_2 in the amount of 0.05 g to 1.0 g Gel-n was effective to reduce sintering, and larger amounts of ZrO_2 were even more effective.

Tanaka *et al.* [29] described that grades of large pore size of Nucleosil (1000, 4000) were composed of mixtures of at least two kinds of silica particles. They observed crystallization of Nucleosil 4000 using TEM. Gailliez-Degremont *et al.* [30] also reported that Nucleosil 1000 crystallized to cristobalite according to measurements using Raman spectroscopy and XRD. The XRD pattern of Nucleosil 4000, shown in Fig. 4e, clearly indicated its crystallization to cristobalite. Its SSA (12 m^2/g) was similar in value with that of sample D prepared by heating the mixture of Gel-n and NaCl without addition of $ZrOCl_2$. From the above result, the particles of sample D were heterogeneous due to different degrees of sintering and crystallization to cristobalite. Thus, Nucleosil with larger pore size was supposed to be manufactured, not by mixing different kinds of particles, but by the salt impregnation method [31, 32]. This result was consistent with the report [25] that wide-pore silica gels prepared by heating the silica gels impregnated with NaCl were composed of mixtures of different pore sizes.

For salt impregnation method, we demonstrated previously that pore formation in the case of salt impregnation of SiO_2-ZrO_2 gel was ascribed to sintering of the glassy phase of the support, and it was not formed by a template effect of NaCl [22, 23]. It was also suggested that pore fabrication in the case of salt impregnation of silica gel was not due to a template role of NaCl, but it was due to sintering of silica gel. Therefore, heterogeneity observed among particles of sample D was attributed to different degrees of sintering of particles, which probably originated from difference of sodium ion distribution among the particles. Addition of ZrO_2 to the mixtures of silica gel and NaCl might assist sodium ion diffusion and result in a more homogeneous composition of SiO_2-ZrO_2-Na_2O.

3.2. Preparation of porous supports using a silica gel derived from sodium silicate

The similar procedure described above was investigated using a microspherical silica gel (Gel-m) synthesized from a sodium silicate solution [28] as a starting material instead of Gel-n, whose preparation method was not known. Samples F, G, H and I were prepared by heating the mixtures of Gel-m, $ZrOCl_2$, and NaCl at 700, 730, 760, and 800°C; addition of ZrO_2 was 0.05 g per 1.0 g of Gel-m. The physical properties and chemical analysis of these samples are shown in Table I; SEM photographs and their pore size distribution are shown in Figs 6 and 7, respectively. Sintering of the support had scarcely proceeded in the case of Sample F since its SSA was 145 m^2/g and surface of particles was composed with gel-like texture, as observed in the SEM photograph. On the contrary, sample I was nearly sintered as its SSA was less than 1 m^2/g, and its particles adhered to each other and almost sintered. Porous glass-like structure was observed in sample G and H, as shown in Fig. 6c–e. No crystalline peak was identified in XRD patterns of samples F, G and H. In contrast, peaks assigned to cristobalite were clearly observed in that of sample I. These results indicated that sintering of supports proceeded as heat-treatment temperature of the mixtures was increased and that supports with porous-glass-like skeletons were obtained when the mixtures were heated at 730°C (sample G) and 760°C (sample H).

The physical properties of sample H were compared with those of sample C, prepared by the same conditions as those of sample H; the only difference was the starting silica gels. SSA and pore volume of sample H was larger than that of sample C, and pore size distribution of sample H was sharp compared to that of C. SSA and pore volume of Gel-m, the starting silica gel of sample H, was larger than that of Gel-n, the starting gel of sample C. The difference of physical properties of a starting material influenced those of the products.

The results described above demonstrated that similar supports were obtained in the case that Gel-m was used as a starting silica gel, with the supports using Gel-n as a starting gel. Porous supports synthesized from Gel-n and Gel-m possessed smaller pore volume and broader distribution of pore size than those of supports prepared using a sol-gel derived silica

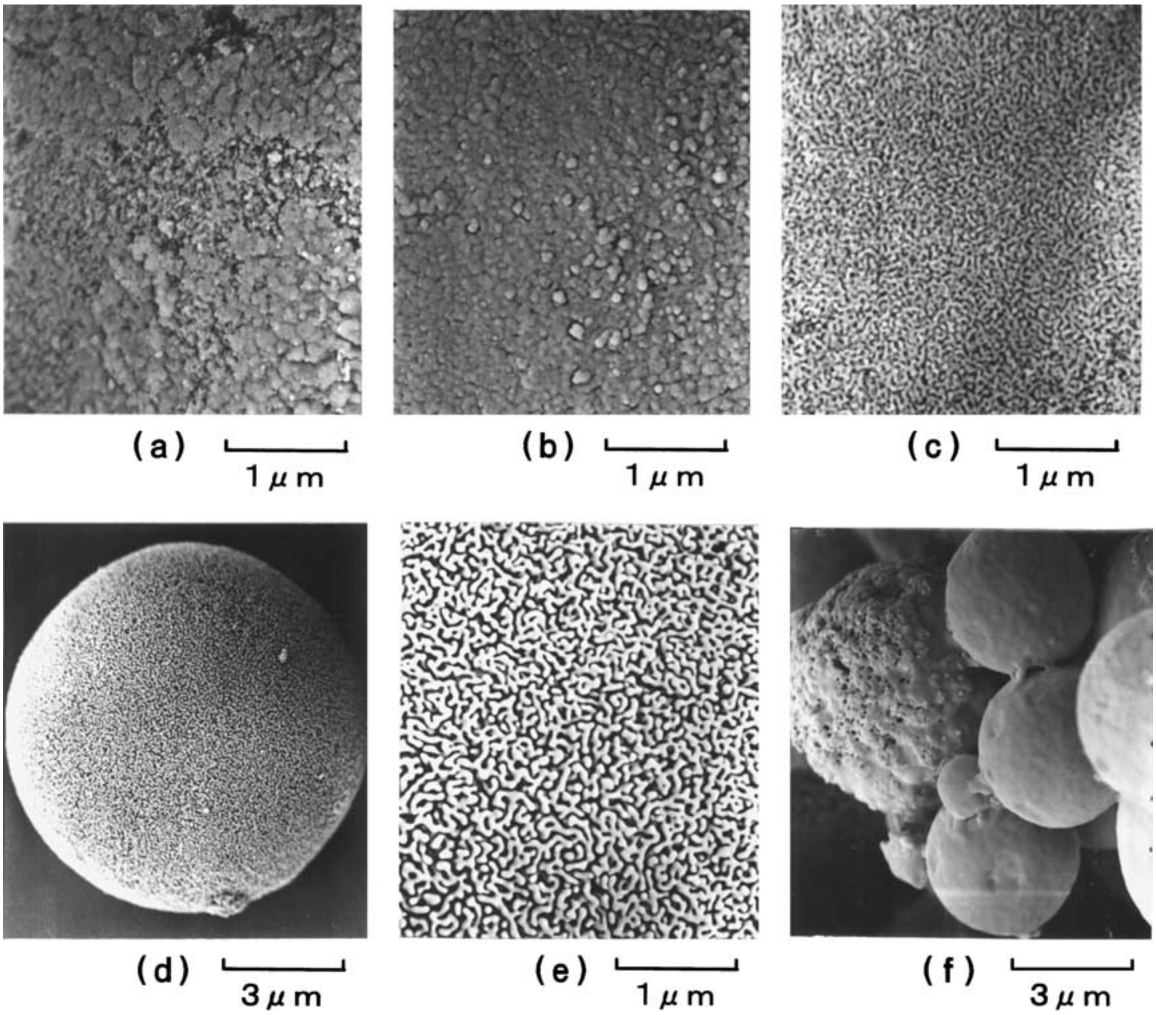

Figure 6 SEM photographs of samples Gel-m, F, G, H and I. (a) Gel-m, (b) sample F (0.05 g ZrO_2, 700°C), (c) sample G (0.05 g ZrO_2, 730°C), (d) and (e) sample H (0.05 g ZrO_2, 760°C), (f) sample I (0.05 g ZrO_2, 800°C), where (0.05 g ZrO_2, 700°C) indicates that the sample was prepared by adding 0.05 g of ZrO_2 per 1.0 g of Gel-m in the form of $ZrOCl_2{\cdot}8H_2O$ in addition to NaCl and heating the mixture at 700°C.

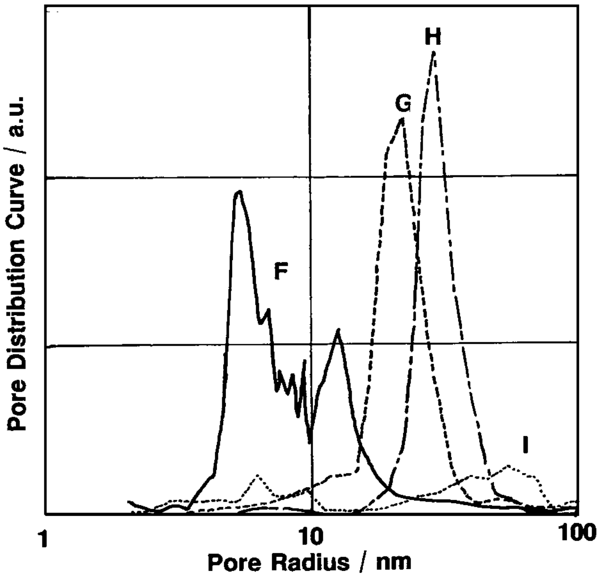

Figure 7 Pore-size distribution curves of samples F, G, H and I.

gel. However, pore volume of these supports was sufficiently large to be applicable as a HPLC separation support, since their pore volume was more than 0.5 cm^3/g.

3.3. Preparation of porous supports using Na_2CO_3 instead of NaCl

The above results and previous studies [24] were based on investigation using NaCl as an impregnation salt to a silica gel. We report here results of a preparation using Na_2CO_3 added to Gel-n as a solid state instead of NaCl. We investigated a procedure by heating mixtures of Gel-n impregnated with $ZrOCl_2$ and fine powder of Na_2CO_3 at 760°C, and washing the resultant supports with water (method B in Fig. 1). Four samples, K, L, M and N, were prepared from the mixtures, where the mole ratio of Na_2CO_3 to ZrO_2 was 1.0, 1.5, 2.0 and 3.0, respectively. SSAs of four samples are shown in Table III, and their XRD patterns are shown in Fig. 8.

In the case of Sample N, sintering of the support had proceeded and it had phase-separated to silica and zirconia crystals, since the peaks of α-cristobalite were identified in sample N and its SSA was 1 m^2/g. Median size of particles of sample N was more than 60 μm, which indicated that microsphere particles adhered to each other through sintering. Sample M was not sintered compared to sample N, although the peak of α-cristobalite appeared at $2\Theta = 21^\circ$ on the XRD pattern. In contrast, SSAs of samples K and L were more than 10 m^2/g, and in the XRD patterns, the peaks of

TABLE III Effect of synthetic conditions on physical properties of porous supports in the SiO_2-ZrO_2-Na_2O system

	Synthetic conditions[a]						
Sample	Type of Na salt	Na salt/Gel-n (g/g)	Na_2CO_3/ZrO_2 mole ratio	Calcn. time at 600°C	SSA (m^2g^{-1})	Median particle size/μm	Peak[c] intensity a.u.
K	Na_2CO_3	0.13	1.00	3 h	31	3.2	380
L	Na_2CO_3	0.20	1.49	3 h	14	4.1	350
M	Na_2CO_3	0.26	2.01	3 h	6	7.7	372
N	Na_2CO_3	0.39	2.96	3 h	1	62.1	346
O	Na_2CO_3	0.13	1.00	1 h	41	3.4	392
P	Na_2CO_3	0.13	1.00	10 h	36	3.1	342
Q	–	0	0	1 h	332	3.4	484
R	NaCl	0.29	2.05[b]	1 h	75	3.1	506
S	NaCl	0.29	2.05[b]	1 h	51	3.2	475
T	NaCl	0.29	2.05[b]	3 h	51	3.4	591

[a] ZrO_2/Gel-n weight ratio: 0.15 g/g, calcination condition: 760°C/5 h.

[b] $NaCl/ZrO_2$ mole ratio.

[c] Peak intensity of $2\Theta = 30°$.

α-cristobalite were not observed and only weak peaks of t-ZrO_2 were observed. SSA of sample K was the nearest among four samples to that of sample A, prepared by heating Gel-n impregnated with the same amount of $ZrOCl_2$ and NaCl at the same temperature.

SEM photographs of samples K, L and M are shown in Fig. 9. Porous-glass-like skeletons similar to that of sample A were observed in these samples. It was observed that samples L and M were composed of porous particles and non-porous ones completely sintered. The size of vitreous skeletons increased in the order $K < L < M$, and sintering proceeded in this order, also. Particle size of samples K, L and M had the same trend, and the increase of particle size was attributed to adhesion between particles. This result was due to formation of a Na_2O-SiO_2 phase, which enhanced sintering between particles. The Na_2O-SiO_2 phase was formed by decomposition of excess Na_2CO_3 in the mixtures of Gel-n impregnated with $ZrOCl_2$ and Na_2CO_3. The degree of sintering of samples M and N was more advanced than that of sample L, because an excess amount of Na_2CO_3 in the mixtures for preparation of samples M and N was larger than that of sample L.

XRD patterns of supports after heating at 600°C during the preparation step of samples K, L and M, are shown in Fig. 8e, f and g, respectively. Very sharp peaks were observed and identified as NaCl. NaCl peaks disappeared in the XRD patterns of samples K, L and M, compared with those of the mixtures after heating at 600°C. These samples were obtained by subsequently heating at 760°C and washing the mixtures with water. NaCl formation after heating the mixtures at 600°C was attributed to reaction of Na_2CO_3 and HCl evolved from $ZrOCl_2$ according to the following reaction in the case of sample K.

$$\begin{aligned} &SiO_2/xZrOCl_2 + xNa_2CO_3 \\ &\quad \rightarrow SiO_2/xZrO_2 + 2xNaCl + xCO_2 \uparrow \end{aligned}$$

In the case of the mixtures for samples L, M and N, it seemed that excess Na_2CO_3 ($Na_2CO_3/ZrOCl_2$ molar ratio more than 1) decomposed to Na_2O during heat treatment.

The above results indicated that the supports, analogous with those prepared by heating the mixtures of Gel-n impregnated $ZrOCl_2$ together with NaCl, were obtained by heating the mixtures of Na_2CO_3 and Gel-n impregnated with $ZrOCl_2$, in the range that Na_2CO_3/ZrO_2 molar ratio was between 1.0 and 2.0. HCl evolved during heat treatment was much reduced in this advanced procedure compared to that in the ordinary method. Therefore, the mixtures could be fired in crucibles from the first step of heat treatment at 600°C. Thus, the new process was a simpler preparative method than the ordinary one.

The following are results that some synthetic conditions were investigated from a point of view of NaCl distribution. Samples O and P were prepared by heating the same composition as that of sample K at 600°C for 1 h and 10 h, respectively, before heating them at 760°C for 5 h. Samples Q, R, S and T were synthesized by heating in crucibles mixtures under the same conditions as those of sample K. Sample Q was prepared from Gel-n impregnated with $ZrOCl_2$ without sodium salt addition, and sample R was prepared from the solid mixtures of the impregnated gel and pulverized NaCl. Samples S and T were synthesized by heating the same composition as sample A (Gel-n impregnated with $ZrOCl_2$ and NaCl), in crucibles from heat-treatment at 600°C. SSAs and peak intensities of $2\Theta = 30°$ assigned to t-ZrO_2 in XRD patterns are shown in Table III.

Sintering of the support had scarcely proceeded in the case of sample Q judging from its large SSA. Sample R possessed larger SSA (75 m^2/g) than that of sample S, which indicated that the sintering was not advanced in sample R compared to that of sample S. Both samples were prepared from the same composition and with the same heating temperature; the only preparation difference was in the NaCl addition method. The sintering of sample S was comparable to that of sample R, although its sintering was less than that of sample O; the degree of sintering was in the order $O > S > R$. Because the probable mechanism for the SiO_2-ZrO_2-Na_2O glassy composition was through reaction of the silica gel impregnated with $ZrOCl_2$

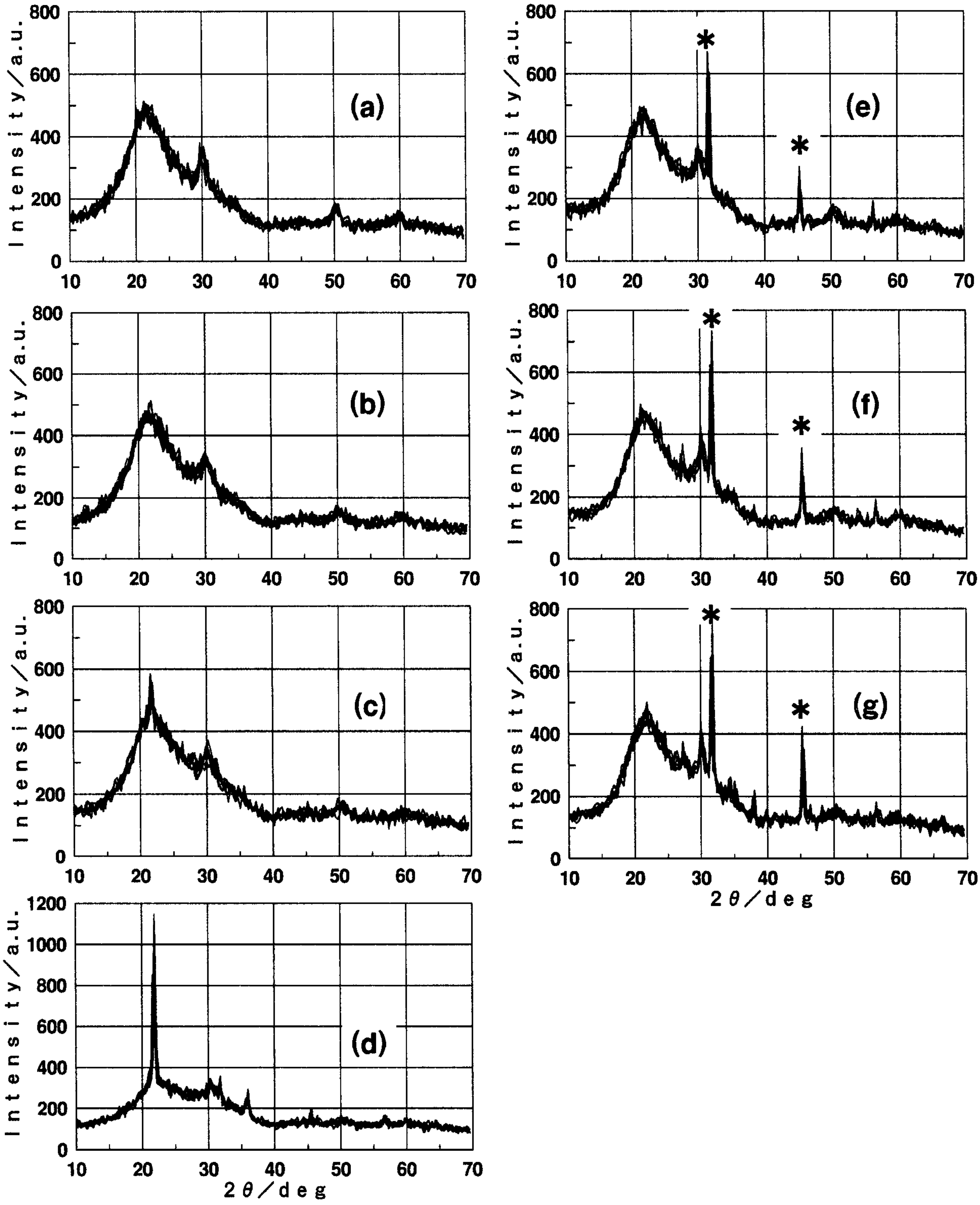

Figure 8 X-Ray diffraction patterns of samples K, L, M, N and those after heat-treatment at 600°C. (a) Sample K ($Na_2CO_3/ZrO_2 = 1.0$), (b) sample L ($Na_2CO_3/ZrO_2 = 1.5$), (c) sample M ($Na_2CO_3/ZrO_2 = 2.0$), (d) sample N ($Na_2CO_3/ZrO_2 = 3.0$), where $Na_2CO_3/ZrO_2 = 1.0$ indicates that the sample was prepared by heating the mixtures of Gel-n impregnated with $ZrOCl_2$ and Na_2CO_3 in the molar ratio of $Na_2CO_3/ZrO_2 = 1.0$. (e)–(g) intermediates examined during synthesis; the samples after heat-treatment at 600°C, (e) for sample K, (f) for sample L, (g) for sample M. * indicates the peaks assigned to NaCl.

and sodium cation diffused in particles, smaller size and more homogeneous distribution of NaCl crystals might promote sintering of the mixtures. The reactivity of NaCl formed from Na_2CO_3 and $ZrOCl_2$ during heat treatment was suggested to be higher than NaCl mixed in the solid phase. Compared with samples A and T, the sintering of the porous support had proceeded more and distribution of ZrO_2 was more homogeneous by heating the mixtures at 600°C in a furnace under an air stream than by heating it in a crucible.

3.4. Evaluation of resistance to an alkaline solution

Preliminary evaluation of the alkaline resistance of supports was investigated by immersing them in a

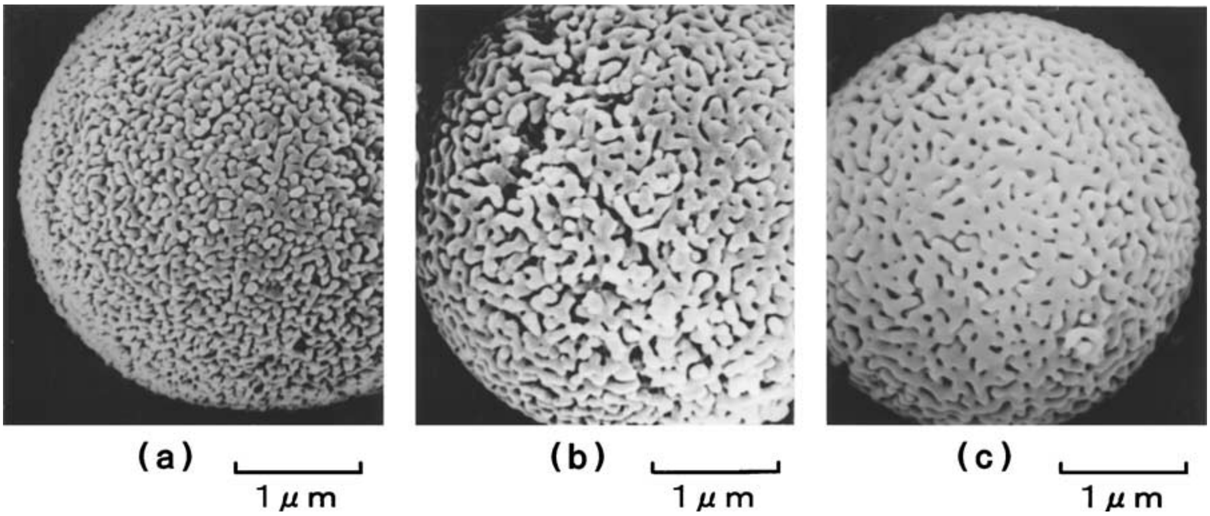

Figure 9 SEM photographs of samples K, L and M. (a) Sample K ($Na_2CO_3/ZrO_2 = 1.0$), (b) sample L ($Na_2CO_3/ZrO_2 = 1.5$), (c) sample M ($Na_2CO_3/ZrO_2 = 2.0$), where $Na_2CO_3/ZrO_2 = 1.0$ indicates that the sample was prepared by heating the mixtures of Gel-n impregnated with $ZrOCl_2$ and Na_2CO_3 in the molar ratio of $Na_2CO_3/ZrO_2 = 1.0$.

0.1 M NaOH solution at room temperature for 24 h and analyzing the amount of Si in the solution. Data on soluble silica content (*D*) and those values divided by the SSAs (*D/S*) are shown in Table IV for samples A to R and Nucleosil 4000.

The soluble silica content of samples A to C was slightly larger than that of sample D; however, D/S of samples A to C was less than a half value of that of sample D, indicating that alkaline resistance of the porous supports was improved by addition of ZrO_2. Compared with *D/S* of samples A, B and C, improvement of alkaline resistance was observed until the content of ZrO_2 was increased to 0.10 g ZrO_2/1.0 g of silica gel. Almost the same D/S of samples A and B implied that the increase of ZrO_2 content did not contribute to strengthening the structure probably due to its heterogeneous distribution; additional ZrO_2 had phase-separated and had not mixed well to form a homogeneous mixed-oxides composition. This trend was consistent with that of the porous supports prepared from sol-gel derived silica gel [24].

TABLE IV Results of alkaline-resistance test

Sample	D^a (wt%)	SSA ($m^2\ g^{-1}$)	$D/S^b \times 10^4$ ($g\ m^{-2}$)
A	5.6	40	14
B	5.8	36	16
C	6.1	30	20
D	4.1	10	41
E	91.0	309	29
F	50.1	145	35
G	9.9	53	17
H	6.5	38	19
I	0.8	1	81
J	85.7	331	26
K	4.6	31	15
L	2.8	14	20
M	1.5	6	26
N	0.8	1	81
O	5.5	41	14
P	4.7	36	13
Q	79.2	332	24
R	17.6	75	23
S	8.6	51	17
T	9.5	51	19
N4000[c]	8.1	12	68
Ref.[d]	0.6	35	1.7

[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] N4000: Nucleosil 3-4000.
[d] The porous support prepared by heating the mixture of the SiO_2-ZrO_2 gel and NaCl [22].

The soluble silica content and D/S of samples K, O and P had a value similar to that of sample A. These four samples were prepared from mixtures with the same amount of ZrO_2 added to silica gel and by subsequently heating the mixtures at 760°C. Therefore, the analogous porous supports were obtained using Na_2CO_3 instead of NaCl as Na salt, judging from result of alkaline resistance as well as physical properties.

The soluble silica content of nearly sintered samples I and N was small, although the D/S value was largest among the samples in Table IV. On the contrary, the soluble silica content of samples Q and E was high and almost the entire sample was dissolved due to their large SSAs. However, their D/S value was about twice as large as that of sample A. Thus, a certain improvement of alkaline resistance was observed by ZrO_2 impregnation to silica gel and by heat-treatment of the mixtures.

The soluble silica content and D/S of the SiO_2-ZrO_2-Na_2O porous support [22], which was synthesized by impregnation of NaCl into the SiO_2-ZrO_2 gel and a subsequent heat-treatment, was approximately 1/10 less than that of samples A, K, O and P. This result implies that the ZrO_2 distribution in the porous supports of this study was not as homogeneous as that of the SiO_2-ZrO_2-Na_2O porous support, although much improvement of alkaline resistance was observed in these samples compared to original silica gel or its ZrO_2 modification (sample Q). Alkaline durability of samples A, K, L and M was inferior, in some degree, to that of the porous supports prepared by the similar method reported previously [24] using the sol-gel derived silica gel. This might indicate that ZrO_2 distribution of the supports of this study was, in some degree, more heterogeneous than that of the supports obtained from the sol-gel derived silica gel. Also, it was consistent with the results of pore characteristics and X-ray diffraction patterns.

4. Conclusion

The preparative method of porous supports in the SiO_2-ZrO_2-Na_2O system was applied to commercially available silica gel and to silica gel prepared from sodium silicate solution. The mixtures of microspherical silica gel impregnated with $ZrOCl_2$ and NaCl were heated and subsequently washed with water. Porous supports, composed with sponge-like skeletons on the surface of the particles, were obtained owing to suppression of crystallization of supports as well as their sintering. Pore volume of the supports was smaller, and their pore-size distribution was broader than that of the supports prepared from the silica gel derived by the sol-gel method. This result originated from the different nature of the starting gels.

In contrast, crystallization of silica proceeded in supports prepared by heating the mixture of silica gel and NaCl in the absence of $ZrOCl_2$. This support was composed of different types of particles due to difference in sintering degree, which might be attributed to a heterogeneous distribution of the sodium cation. The heterogeneous shape among particles was similar to that of silica supports prepared by the salt-impregnation method.

An advanced method for preparing the analogous supports was also investigated by heating a mixture of silica gel impregnated with $ZrOCl_2$ and Na_2CO_3 powder. In the case that mole ratio of $Na_2CO_3/ZrOCl_2$ was in the range of 1 to 2, the porous supports so prepared had similar physical properties to the above supports through formation of NaCl during heat treatment. This method was superior to the ordinary one since HCl evolution from $ZrOCl_2$ was much reduced.

Alkaline durability of the supports in this study was improved compared with the original silica gel and its ZrO_2 modification although it did not exceed that of the supports prepared from the sol-gel-derived silica gel.

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