Preparation of Porous Microspheres in the SiO$_2$–ZrO$_2$–CaO–Na$_2$O System from Silica Gels

Yasushi TSURITA and Masayuki NOGAMI*

Science and Technology Center, Mitsubishi Chemical Corporation, 1000, Kamoshida-cho, Aoba-ku, Yokohama-shi 227-8502
*Department of Materials Science and Engineering, Nagoya Institute of Technology, Showa-ku, Nagoya-shi 466-8555

Abstract
Preparation of porous microspheres in the SiO$_2$–ZrO$_2$–CaO–Na$_2$O system was investigated by heating a mixture of fine Na$_2$CO$_3$ powder and commercially available, microspherical silica gel impregnated with ZrOCl$_2$ and CaCl$_2$, and by subsequently washing the product with water. Porous microspheres, whose surface was composed of sponge-like skeletons were obtained; their pore volume was up to 0.59 cm$^3$ g$^{-1}$ and the mode pore radius was in the range between 23 and 38 nm. The composition of the porous microspheres was SiO$_2$–ZrO$_2$–CaO–Na$_2$O, which contained ZrO$_2$ in the range between 11 and 17 mass%. Almost all amounts of Ca and Zr added and a certain amount of Na remained in the porous microspheres. Addition of CaCl$_2$ resulted in an increase in resistance to alkaline solution, compared to those of the microspheres prepared by the same procedure without CaCl$_2$ addition.

Key-words : SiO$_2$–ZrO$_2$, Sphere, Porous-glass, Support, Salt

1. Introduction
Various applications of porous glasses have been studied such as membrane separation, supports for chromatography, carriers of enzymes and biomaterials, and catalysts. They generally have high resistance to heat, quite uniform pore size and easy control of their pore size. Their application to support for HPLC (high performance liquid chromatography) has been reported. Vycor glass, which is a typical porous glass, is manufactured from a SiO$_2$–B$_2$O$_3$–Na$_2$O mother glass. It is phase-separated and acid-leached in order to remove the B$_2$O$_3$–Na$_2$O-rich phase. However, the silica gels remaining between the porous glass skeletons are dissolved when they are used even in weak alkaline solutions.

SiO$_2$–ZrO$_2$ mixed oxides have been known to have high alkaline resistance, and alkalai-durable glasses of the SiO$_2$–ZrO$_2$ system are used practically as fibers reinforcing cements. To improve the alkaline-resistant property of porous glass, therefore various trials to incorporate ZrO$_2$ into SiO$_2$ glass have been reported. The preparation of porous glasses with the SiO$_2$–ZrO$_2$ system is rather difficult because ZrO$_2$ does not remain in the porous glass skeletons with the phase-separation method. The addition of a relatively large amount of alkaline earth oxide, or zircon oxide, into the SiO$_2$–ZrO$_2$–Na$_2$O–B$_2$O$_3$ composition was found to be effective for allowing ZrO$_2$ to remain in the porous glass skeletons. Pore sizes in the improved porous glasses could be controlled in the range from 10 nm to 1 μm. However, the amount of ZrO$_2$ incorporated was less than 7 mass% according to a recent report. In the case of the sol–gel method, porous glasses with large amounts of ZrO$_2$ could be prepared, although it was difficult to control pore sizes larger than 5 nm.

These two methods are generally used for preparation of bulk glasses and a few studies were reported on microspherical porous particles in the SiO$_2$–ZrO$_2$ system. Improvements in alkali stability at pH 9 on chromatographic separation were reported for porous silica microspheres impregnated with ZrO$_2$. Their preparation was quite simple, although their alkaline durability seemed to be limited because distribution of ZrO$_2$ was restricted to the surface of supports. The sol–gel preparation of porous spherical beads in the system SiO$_2$–ZrO$_2$–TiO$_2$–Al$_2$O$_3$ was reported by González-Oliver et al. The particle size of the beads was generally larger than 100 microns and pore volume was close to 1.0 cm$^3$ g$^{-1}$, although no data were shown as to pore size, Garbassi et al. reported spherical ZrO$_2$–SiO$_2$ particles of 30–40 μm average diameter by the sol–gel method and their pore volume larger than 0.5 cm$^3$ g$^{-1}$ for catalyst supports. However, the pore size of the particles was small; only 4–7 nm in diameter.

We have investigated the preparation of porous microspheres in the SiO$_2$–ZrO$_2$ system with the following characteristics: 1) microspherical particles of 1 to 100 μm in size, 2) mode pore radius between 10 and 100 nm, 3) volume of the pores larger than 0.5 cm$^3$ g$^{-1}$, and 4) alkaline durability. These microspheres are expected to be used in the separation of large molecules, such as proteins, in liquid-phase chromatography. One of the present authors has already reported a new procedure for preparing SiO$_2$–ZrO$_2$–Na$_2$O porous glasses carried out by heating a mixture of the SiO$_2$–ZrO$_2$ gel and NaCl at temperatures between 730 and 800°C, followed by washing of the particles. Furthermore, a convenient preparative method was reported; the method involved heating a mixture of the microspherical silica gel prepared by a sol–gel procedure, ZrOCl$_2$ and NaCl at 760°C. We recently reported that this method could be applied to conventional silica gels, although the homogeneity of ZrO$_2$ distribution and alkaline durability of the microspheres prepared from conventional silica gels were inferior to those of the porous microspheres prepared from the sol–gel-derived silica gel. One of the advantages in the use of conventional silica gels as a raw material is commercial availability. Moreover, NUCLEOSIL used in the work has been applied to supports for liquid phase chromatography because it is microspherical and its size...
distribution is rather sharp. In this paper, we report that the homogeneity of ZrO$_2$ distribution and alkaline resistance of the porous microspheres obtained from NUCLEOSIL are much improved by addition of CaCl$_2$, together with ZrOCl$_2$, to the silica gels.

2. Experimental procedure

2.1 Preparation of SiO$_2$-ZrO$_2$-CaO-Na$_2$O porous microspheres

Two types of microspherical silica gels were used in this study; one was NUCLEOSIL 100-3 (Gel-n) purchased from Chemco Scientific Co., Ltd., and the other was SUNSPHERE L-31 (L-31) obtained from Asahi Glass Company. The first one was mainly used in this study. The physical properties of two silica gels are shown in Table 1.

A 5 cm$^3$ aqueous solution containing designated amounts of ZrOCl$_2$·8H$_2$O and CaCl$_2$·2H$_2$O was added to 2.5 g of the dried Gel-n, pre-heated at 120°C. The impregnated gel was heated at 120°C for 3 h. A pulverized powder of anhydrous Na$_2$CO$_3$ and the impregnated gel were mixed together by shaking for 3 min in a sample tube. The molar ratio of CaCl$_2$/ZrOCl$_2$ was 1.0 and that of Na$_2$CO$_3$/ZrOCl$_2$ was 2.0, and the ratios were the same for these samples.

The mixture was heated in an alumina crucible at 600°C for 1 h and then at a designated temperature between 700 and 800°C 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 3 h. Table 2 summarizes the preparation composition and temperature. In the sample notation, SZXCN-Y, X means the ZrO$_2$ content per 1.0 g of silica gel, and Y means calcination temperature.

For reference samples SZ15N-760 and SZ15-760, silica gel impregnated with only ZrOCl$_2$·8H$_2$O was first prepared by the same procedure as described above. In the case of sample SZ15N-760, the impregnated gel was treated under the same conditions as those described above. For sample SZ15-760, only the impregnated gel was heated at 600°C for 1 h and 760°C for 5 h, and then it was washed and dried by the same procedure. In the case of sample LSZ25CN-700, the starting silica gel used was L-31 instead of Gel-n.

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 Kα radiation. The scanning electron microscope (SEM) observations were performed on gold-palladium-coated surfaces using a Hitachi S–4500. Particle size was measured by a Horiba LA–500. For Zr, Ca and Na analyses of the products, the samples were dissolved by adding H$_2$SO$_4$–HF and heating. The Zr and Ca concentrations were measured by inductively coupled plasma (JY–38S, Johny Yvon), and the Na content was measured by atomic absorption spectrometry (AA40P, Varian). Cl contents of the products were measured semi-quantitatively by X-ray fluorescence using a Rigaku System.

Table 1. Physical Characteristics of Silica Gels

<table>
<thead>
<tr>
<th>Silica Gel</th>
<th>SSA (m$^2$/g$^{-1}$)</th>
<th>Pore Volume$^{a)}$ (cm$^3$/g$^{-1}$)</th>
<th>Mode Pore Radius (nm)</th>
<th>Median Particle Size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NUCLEOSIL 100-3</td>
<td>309</td>
<td>1.04</td>
<td>3.3</td>
<td>3.1</td>
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<tr>
<td>SUNSPHERE L-31</td>
<td>299</td>
<td>0.71</td>
<td>2.4</td>
<td>3.8</td>
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</table>

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

Table 2. Synthetic Conditions and Physical Characteristics of Porous Microspheres in the SiO$_2$-ZrO$_2$-CaO-Na$_2$O System

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZrOCl$_2$·8H$_2$O/Gel-n</th>
<th>CaCl$_2$·2H$_2$O/Gel-n</th>
<th>Na$_2$CO$_3$ /Gel-n</th>
<th>Calc. Temp. (°C)</th>
<th>SSA (m$^2$/g$^{-1}$)</th>
<th>Pore Volume$^{a)}$ (cm$^3$/g$^{-1}$)</th>
<th>Mode Pore Radius (nm)</th>
<th>Median Particle Size ($\mu$m)</th>
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<tbody>
<tr>
<td>SZ15CN-700</td>
<td>0.39</td>
<td>0.18</td>
<td>0.26</td>
<td>700</td>
<td>30</td>
<td>0.59</td>
<td>23.5</td>
<td>3.1</td>
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<tr>
<td>SZ15CN-730</td>
<td>0.39</td>
<td>0.18</td>
<td>0.26</td>
<td>730</td>
<td>23</td>
<td>0.48</td>
<td>30.3</td>
<td>3.1</td>
</tr>
<tr>
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<td>0.18</td>
<td>0.26</td>
<td>760</td>
<td>13</td>
<td>0.32</td>
<td>37.8</td>
<td>3.9</td>
</tr>
<tr>
<td>SZ15CN-800</td>
<td>0.39</td>
<td>0.18</td>
<td>0.26</td>
<td>800</td>
<td>4</td>
<td>0.09</td>
<td>60.0</td>
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<tr>
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<td>0.39</td>
<td>0</td>
<td>0.13</td>
<td>760</td>
<td>41</td>
<td>0.61</td>
<td>18.9</td>
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<td>SZ15-760</td>
<td>0.39</td>
<td>0</td>
<td>0</td>
<td>760</td>
<td>332</td>
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</tr>
<tr>
<td>SZ15CN-700</td>
<td>0.65</td>
<td>0.30</td>
<td>0.43</td>
<td>700</td>
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<td>0.38</td>
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<td>0.43</td>
<td>730</td>
<td>14</td>
<td>---</td>
<td>---</td>
<td>3.4</td>
</tr>
<tr>
<td>SZ15CN-760</td>
<td>0.65</td>
<td>0.30</td>
<td>0.43</td>
<td>760</td>
<td>5</td>
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</tr>
<tr>
<td>SZ15CN-800</td>
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<td>800</td>
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<tr>
<td>SZ35CN-700</td>
<td>0.92</td>
<td>0.42</td>
<td>0.60</td>
<td>700</td>
<td>12</td>
<td>0.19</td>
<td>---</td>
<td>9.5</td>
</tr>
<tr>
<td>LSZ25CN-700</td>
<td>0.68$^{b)}$</td>
<td>0.30$^{b)}$</td>
<td>0.43$^{b)}$</td>
<td>700</td>
<td>17</td>
<td>0.23</td>
<td>23.6</td>
<td>4.9</td>
</tr>
</tbody>
</table>

a) Pore volume in the range from 2 to 100 nm.
b) Silica gel: L-31.
3370, after the samples were diluted with cellulose. Preliminary evaluation of the alkaline resistance was investigated by immersing the samples in a 0.1 mol·kg⁻¹ NaOH solution at room temperature for 24 h.²¹,²²

3. Results

The synthetic conditions and physical properties of samples in SZ15CN series are shown in Table 2, and their SEM photographs and pore size distribution are shown in Figs. 1 and 2, respectively.

A sponge-like structure, similar to that of porous glasses prepared by the phase-separation method,¹,³ was observed in samples SZ15CN-700 to SZ15CN-800, as shown in Figs. 1(a) to (d). The size of the glassy skeletons on the particle surface increased with increasing the heating temperature of the mixture of the raw materials. This trend was consistent with the increasing order of the mode pore radius of the four samples. Adhesion among the particles was scarcely observed in sample SZ15CN-760 as shown in Fig. 3(a). This result corresponded with the measurements of particle size distribution; the median size of the particle distribution of samples SZ15CN-700, SZ15CN-730 and SZ15CN-760 was about 3 μm, which was similar to that of Gel-n. On the other hand, the particle size distribution of sample SZ15CN-800 could not be measured because its particles adhered to each other as shown Fig. 3(b).

SSAs of the four samples were less than 30 m²·g⁻¹, which indicated that the SSAs of the samples were considerably reduced compared with that of Gel-n (309 m²·g⁻¹). As the heat-treatment temperature of the mixtures was increased, the degree of sintering of the samples was enhanced; a reduction in the SSAs and pore volume, and an increase in the mode pore radius were observed. In sample SZ15CN-800, sintering of the microspheres proceeded, because its SSA was 4 m²·g⁻¹ and its pore volume was less than 0.1 cm³·g⁻¹.

The degree of sintering was considerably advanced in sample SZ15CN-760 compared with that of sample

![Fig. 2. Pore-size distribution curves of (a) SZ15CN-700, (b) SZ15CN-730, (c) SZ15CN-760, (d) SZ15CN-800 and (e) Gel-n.](image)

![Fig. 1. SEM photographs of samples (a) SZ15CN-700, (b) SZ15CN-730, (c) SZ15CN-760, (d) SZ15CN-800, (e) SZ25CN-700, (f) SZ35CN-700 and (g) LSZ25CN-700.](image)
SZ15N–760, which was prepared by heating the mixtures at the same temperature without addition of CaCl₂ and the same mole ratio of Na₂CO₃/ZrO₂ as that of sample SZ15CN–760. Even sample SZ15CN–700 (heat-treatment temperature: 700°C) possessed an SSA smaller than that of sample SZ15N–760. The mode pore radius of sample SZ15CN–700 was also larger than that of sample SZ15N–760. These results indicated that sintering of the microspheres was promoted by the addition of CaCl₂ to the mixtures of Gel-n and ZrOCl₂ together with an increased amount of Na₂CO₃.

Fig. 3. SEM photographs of samples (a) SZ15CN–760, (b) SZ15CN–800, (c) SZ25CN–800 and (d) LSZ25CN–700.

The physical properties of SZ25CN series samples and the SEM photograph of sample SZ25CN–700 with larger ZrO₂ amounts than SZ15CN–700 are shown in Table 2 and in Fig. 1 (e), respectively. A similar trend of sintering in samples SZ25CN–700 to SZ25CN–800 was also observed with that in samples SZ15CN–700 to SZ15CN–800, from the result of their SSAs; the degree of sintering was the increasing order, sample SZ25CN–700 < SZ25CN–730 < SZ25CN–760 < SZ25CN–800. Sample SZ25CN–800 was almost completely sintered because its SSA was less than 1 m²·g⁻¹; its particles adhered to each other and appeared almost sintered as shown in Fig. 3 (c).

In the case of sample SZ35CN–700, sponge-like skeletons were observed as shown in Fig. 1 (f), and a slight sintering between particles was identified. Its pore volume was less than 0.2 cm³·g⁻¹ and the pore size distribution was broad, although it was prepared by heating the mixtures at 700°C. This was due to the addition of larger amounts of the impregnation salts and Na₂CO₃; the ZrOCl₂ added was 0.35 g (on a ZrO₂ basis) per 1.0 g of Gel-n together with increasing amounts of CaCl₂ and Na₂CO₃. As the amount of added ZrOCl₂ was increased, the degree of sintering of the microspheres proceeded in increasing order, sample SZ15CN–700 < SZ25CN–700 < SZ35CN–700 < SZ35CN–800.

The change in pore size distribution curves with Zr content and with silica source is shown in Fig. 4. The pore size distributions of samples SZ15CN–700 and SZ25CN–700 were analogous; the only difference lay in the pore volume. For SZ35CN–700, clear peak in pore size distribution was not observed and not shown in Fig. 4. The pore distribution of LSZ25CN–700 shifted to larger size compared with that of L-31 and reduction of pore volume was about 0.5 cm³·g⁻¹. Sponge-like skeletons are also observed on the surface of sample LSZ25CN–700 as shown in Fig. 1 (g). The size of its spherical particles (Fig. 3 (d)) was not homogeneous compared to those of samples prepared from Gel-n.

The X-ray diffraction (XRD) patterns of selected samples are shown in Fig. 5. The XRD patterns of samples heat-treated at lower than 760°C were similar to those of samples heated at 760°C for SZ15CN and SZ25CN series. No apparent crystalline peak was identified in the XRD patterns of samples SZ15CN–760 and SZ25CN–760. In contrast, peaks assigned to α-cristobalite (2θ = 21°) were clearly observed in the XRD pattern of sample SZ15CN–800 and those assigned to α-cristobalite and tetragonal ZrO₂ (t-ZrO₂) in that of sample SZ25CN–800; both samples were prepared at 800°C. The XRD patterns of samples SZ35CN–700 and LSZ25CN–700 also indicated no apparent crystalline peak.

The peak intensities of t-ZrO₂ were in decreasing order, SZ15–760 > SZ15N–760 > SZ15CN–760. This result indicated that the distribution of ZrO₂ in the samples was improved by addition of Na₂CO₃ in the impregnated silica gel and even more by co-impregnation of CaCl₂. Peaks assignable to NaCl were not identified in all samples, although they were recognized in the all unwashed samples. Thus, NaCl was mostly removed by washing the mixtures with water twice.

The results of chemical analysis of the samples are shown in Table 3. From the analysis of Zr, Ca and Na concentrations, the weight percentage of these elements are indicated on an oxide basis. The contents of SiO₂ were calculated by subtraction of other oxides and Cl. A considerable amount (5–10 mass%) of Na₂O was incorporated in the samples as...
Fig. 5. X-ray diffraction patterns of (a) SZ15N-760, (b) SZ15-760, (c) SZ15CN-760, (d) SZ25CN-760, (e) SZ15CN-800 and (f) SZ25CN-800.

Table 3. Chemical Compositions of the Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$ (a)</th>
<th>Zr$_2$O$_3$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>Cl</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ15CN-700</td>
<td>78</td>
<td>11.4</td>
<td>5.1</td>
<td>5.3</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>SZ15CN-730</td>
<td>77</td>
<td>11.3</td>
<td>5.1</td>
<td>5.9</td>
<td>0.6</td>
<td>100</td>
</tr>
<tr>
<td>SZ15CN-760</td>
<td>76</td>
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<td>6.5</td>
<td>0.7</td>
<td>100</td>
</tr>
<tr>
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<td>5.2</td>
<td>8.4</td>
<td>2</td>
<td>100</td>
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<tr>
<td>SZ15N-760</td>
<td>83</td>
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<td>---</td>
<td>4.6</td>
<td>0.2</td>
<td>100</td>
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<tr>
<td>SZ25CN-700</td>
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<td>7.4</td>
<td>0.8</td>
<td>100</td>
</tr>
<tr>
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<td>100</td>
</tr>
<tr>
<td>LSZ25CN-700</td>
<td>69</td>
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<td>6.9</td>
<td>7.8</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>

(a) Based on mass %.

(b) Calculated by subtraction of other oxides and Cl.

The samples in this study contained 0.5–2 mass% of Cl, much larger than that of sample SZ15N-760. Its content increased in the samples prepared by heating the mixtures at higher temperature and in the case where larger amounts of ZrOCl$_2$ and CaCl$_2$ were used. However, the NaCl peaks were not observed even in the XRD pattern of sample SZ15CN-800; the largest amount of Cl was present, probably because NaCl content was below...
Table 4. Comparison of Molar Ratios between Synthetic Conditions and Product Compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthetic Conditions</th>
<th>Product Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZrO₂ / SiO₂</td>
<td>CaO / ZrO₂</td>
</tr>
<tr>
<td>SZ15CN-700</td>
<td>0.073</td>
<td>1.00</td>
</tr>
<tr>
<td>SZ15CN-730</td>
<td>0.073</td>
<td>1.00</td>
</tr>
<tr>
<td>SZ15CN-760</td>
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<tr>
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<td>SZ15N-760</td>
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<td>1.00</td>
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<td>LSZ25CN-700</td>
<td>0.12</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The dependence of SSAs, pore volume, and amounts of Na₂O on heat-treatment temperature of the mixtures is shown in Fig. 6. As the heating temperature of the mixtures became higher, the SSAs and amounts of Na₂O incorporated decreased, and the amounts of Na₂O incorporated increased almost linearly. The dependence of SSAs, pore volumes and the amounts of Na₂O incorporated in the products on the heat-treatment temperature of the mixtures is shown in Fig. 6. As the heating temperature of the mixtures became higher, the SSAs and amounts of Na₂O incorporated decreased, and the amounts of Na₂O incorporated increased almost linearly. In Table 4, the mole ratios of ZrO₂/SiO₂, CaO/ZrO₂ and Na₂O/ZrO₂ in the synthetic conditions and in product compositions are compared. The ratios of ZrO₂/SiO₂ and CaO/ZrO₂ for the synthetic conditions were nearly consistent with those in the products, which indicated that almost all of the Zr and Ca added were incorporated in the products. The Na contents in the products were in the range of 40 to 75% relative to the amounts of Na added to the silica gel. Results of the alkaline resistance of the samples are shown in Table 5. The soluble silica contents and the D/S values of the samples in this study were generally smaller than those of SZ15N-760 and much smaller than those of SZ15-760 and Gel-n. This result indicated that the alkaline resistance of the porous microspheres was much improved by co-addition of CaCl₂. This is consistent with the disappearance of peaks attributed to ZrO₂ on the XRD. With the increase in the heat-treatment temperature and amount of ZrOCl₂ added, both the soluble silica content and the D/S value were reduced, i.e., alkaline resistance was improved. The soluble silica content and the D/S value of sample LSZ25CN-700 were similar to those of sample SZ25CN-700. These two samples were prepared in the same condition except the used silica gel. Therefore, the
analogous porous microspheres were obtained using L-31 instead of Gel-n as silica gel, although the pore volume of sample LSZ25CN-760 was smaller than that of SZ25CN-760.

The soluble silica contents of samples SZ25CN-730, SZ25CN-760 and SZS5CN-700 were similar to those of the SiO₂-ZrO₂-Na₂O porous glass, which was synthesized by impregnation of NaCl into the SiO₂-ZrO₂ gel derived by the sol-gel method and a subsequent heat-treatment. However, they are mostly sintered and have small pore volume. Therefore, they don’t satisfy the goal of this study. The D/S values of the present samples were larger than that of the SiO₂-ZrO₂-Na₂O porous glass. This result indicated that homogeneity of the ZrO₂ in the present samples was not attained compared to that of the SiO₂-ZrO₂-Na₂O porous glass, although the ZrO₂ distribution was much improved compared with that of the microspheres prepared without CaCl₂ addition.

4. Discussion

The results described in the former section demonstrated that adequate pore characteristics were obtained for samples SZ15CN-700, -730, -760 and SZ25CN-700 without adhesion between the particles. The alkaline durability of these samples was much improved compared with the samples prepared without CaCl₂ addition. We reported in the previous paper²² that NaCl was converted after heating the mixtures at 600°C by reactions of Na₂CO₃ and HCl evolved from ZrOCl₂ according to the following Eq. (1).

\[
\text{SiO}_2/\text{ZrOCl}_2 + x\text{Na}_2\text{CO}_3 
\rightarrow \text{SiO}_2/\text{ZrO}_2 + 2x\text{NaCl} + x\text{CO}_2 \uparrow
\]  

(1)

In this study, we selected the molar ratio of CaCl₂/ZrOCl₂ of 1.0 and that of Na₂CO₃/ZrOCl₂ of 2.0. In the case where the mixtures of the impregnated gel and Na₂CO₃ were heated at 700°C, only the intense peaks assigned to NaCl were observed in the XRD patterns for the samples before washing them with water. Therefore, during heat treatment of the mixtures for samples in this study, the mixtures were first converted to SiO₂/μ(ZrO₂ + CaO) and NaCl. Thus, the reactions in Eq. (2) were assumed to proceed during heat treatment of the mixtures.

\[
\text{SiO}_2/\mu/\text{ZrOCl}_2 + \text{CaCl}_2 + 2x\text{Na}_2\text{CO}_3 
\rightarrow \text{SiO}_2/\mu/\text{ZrO}_2 + 4x\text{NaCl} + 2x\text{CO}_2 \uparrow
\]  

(2)

The Na cation was then assumed to be incorporated in the SiO₂-ZrO₂-CaO composition through sodium diffusion in the particles and the reaction of hydroxyl and NaCl (Si-OH + NaCl → Si-O- Na + HCl). Thus, sodium diffusion during heat-treatment might result in a homogeneous distribution of sodium in the particles of approximately 3 microns in size. Subsequently, the glassy composition of SiO₂-CaO-Na₂O enhanced the incorporation of ZrO₂, which was detected as a crystalline phase in the supports prepared without addition of CaCl₂. Addition of CaO in the mixtures seemed to contribute to lowering of the temperature of the beginning of viscous sintering.

From Fig. 6, the degree of sintering of the microspheres might be enhanced as the amount of Na₂O incorporated in the microspheres increased. The increase in heat-treatment temperature might contribute to strengthening the structure of glasses probably due to the homogeneous distribution of ZrO₂ from the result in alkaline-resistance test. However, in the case where the heat-treatment temperature of the mixtures was higher than 780°C, the glassy phase started phase separation to α-cristobalite and t-ZrO₂ and partial sintering with inclusion of a small amount of NaCl in the glassy phase, as in the case of sample SZ15CN-800. The peaks of α-cristobalite and t-ZrO₂ in the XRD patterns were also observed for the samples prepared under conditions similar to those of sample SZ15CN-800 without CaCl₂ addition.²²

Heat treatment of mixtures of silica powder and NaCl was reported to induce crystallization of silica.²³ Takeuchi et al. described that the onset temperature for the formation of quartz was lowered in the presence of Na₂CO₃ and CaCO₃.²⁴ Thus, the addition of alkali and alkaline earth salts generally promote crystallization of silica. In contrast, the presence of ZrO₂ in the mixtures of the silica gels together with alkali salts prevented crystallization of silica probably through formation of a SiO₂-ZrO₂-Na₂O glassy phase at temperatures between 700 and 800°C. This is consistent with a TG result reported by Wakasugi et al. in which ZrO₂ addition to a SiO₂-Na₂O system reduced crystallization in SiO₂-ZrO₂-Na₂O obtained by the sol-gel method.²⁷

The amounts of ZrO₂ in the samples in this study were 11 to 20 mass%, which were comparable to those of non-porous and alkaline-resistant glass fibers.²⁵ For SiO₂-ZrO₂ porous glasses prepared by phase separation of SiO₂-ZrO₂-B₂O₃-Na₂O glasses, ZrO₂ content reported in the products was about 8 mass% at maximum,²⁶ because ZrO₂ tends to move to a soluble phase during heat-treatment in phase-separation. The procedure reported in this study offered a very easy method for producing microspherical particles with high ZrO₂ content and a porous-glass texture. The samples also satisfied the goal of this study, although their pore volume except for sample SZ15CN-700 was smaller than 0.5 cm³·g⁻¹. Increase in the pore volume of the microspheres is assumed to be attained by using silica gel with higher porosity, such as the silica gel prepared by the sol-gel method.²¹

5. Conclusion

A convenient method was developed for conversion of microspherical silica gels to porous microspheres with SiO₂-ZrO₂-CaO-Na₂O composition. Only a one-step heat-treatment at a temperature analogous to that of phase separation in the conventional process for porous glass and washing only with water were required; repeated washing with acidic solution was not needed. The samples SZ15CN-700, SZ15CN-730, SZ15CN-760 and SZS5CN-700 possessed the following characteristics.

(1) The median particle size of the microspheres was about 3 microns. Pore volume was 0.3–0.6 cm³·g⁻¹ and the mode pore radius was in the range of 23 to 38 nm.

(2) The composition of the porous microspheres was SiO₂-ZrO₂-CaO-Na₂O, which contained ZrO₂ in the range of 11–17 mass%.

(3) No apparent crystalline phase was observed by conventional XRD.

(4) Soluble silica contents were less than half of those of the supports prepared without CaCl₂ addition and were much improved compared to that of the silica gel.

Addition of CaCl₂ to the mixtures resulted in a more homogeneous distribution of ZrO₂ and an increase in resistance to alkaline solution, compared to that of the microspheres prepared by the same procedure without CaCl₂ addition.

References
5) Yazawa, T., Tanaka, H., Eguchi, K. and Yokoyama, S., J.