Formation Process of $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ Porous Glass Supports

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$\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ 多孔質ガラス担体の生成機構

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The formation process of porous glass supports in a $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ system was investigated. The porous glass supports were prepared by impregnation of NaCl into a microspherical $\text{SiO}_2\text{-ZrO}_2$ gel, heating the mixture at temperatures ranging from 760 to 800°C, and washing it with water. Scanning electron microscope (SEM) observations indicated that porous glass skeletons were formed through sintering of the gel even before removal of NaCl, with the porosity of the gel partially retained. Heat treatment at a temperature higher than 760°C enhanced diffusion of sodium cations in the microspherical gel, which resulted in their homogeneous distribution. It was also confirmed that HCl was formed during reaction of the $\text{SiO}_2\text{-ZrO}_2$ gel and NaCl. Therefore, a liquid phase in a $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ system was probably formed through ion exchange between sodium cations and protons of hydroxy groups on the $\text{SiO}_2\text{-ZrO}_2$ gel, and the gel was partially sintered to form the porous glass supports.

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1. Introduction

Porous glasses are stable materials which retain their porosity even at high temperature.¹⁾ They are prepared not only by a conventional phase-separation method, but also by a sol-gel method as recently reported.²⁾ Porous glasses manufactured by a phase-separation method possess beautiful texture originating from glass skeletons. Pore size can be controlled by heat treatment conditions. On the other hand, porous glasses obtained through a sol-gel method were more flexible in their composition than those prepared by phase separation, although their pore size is generally small. Porous glasses are stable to organic solvents, bacteria and heat, and their mechanical strength is high. Therefore they are used in various fields of applied research as separation membranes, supports for chromatography, carriers of enzymes and biomaterials, and catalysts.²⁾

Conventional porous glasses with a high silica composition have the significant drawback that the silica component is dissolved even in a weak alkaline solution. To improve the alkaline resistance of high-silica porous glasses, a skeleton composed of $\text{SiO}_2\text{-ZrO}_2$ was proposed, since it is known that glass fibers of this system have excellent stability to alkaline solution and are used in the reinforcement of cement.³⁾⁻⁵⁾ However, porous glass containing ZrO_2 in vitreous skeletons cannot be obtained by a simple addition of ZrO_2 into mother glass compositions using the phase separation method, since ZrO_2 moves into a soluble phase, which results in the porous glass containing only a small amount of ZrO_2 . Recently Yazawa et al. reported that addition of a relatively large amount of alkaline earth oxide or zinc oxide into a $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ system was found to be effective in retaining ZrO_2 in porous glass skeletons.⁶⁾⁻⁹⁾ Thus, porous glasses of the $\text{SiO}_2\text{-ZrO}_2$ system were obtained by a phase-separation method. Pore size could be controlled in a range from 10 nm to 1 μm and the porous glasses were not dissolved even in a 0.1 mol·kg⁻¹ NaOH solution. However, the process was rather complicated, since a mother glass was at first prepared by melting starting oxides at about 1500°C, and the resultant glass was heated to induce a phase separation. Then acid treatment caused dissolution of the soluble phase, and an alkaline treatment removed silica gel from porous glass skeletons. Furthermore removal of zirconia gel using a strong acid was carried out.

On the other hand, Nogami reported on the preparation of $\text{SiO}_2\text{-ZrO}_2$ porous glasses using a sol-gel method.^{10),11)} The process was simple and the alkaline resistance of the porous glasses was high, since the ZrO_2 content could be easily controlled. The pore size of the resultant porous glass, however, was usually small, around 4 nm in radius at maximum.^{12),13)} Accordingly its practical use was rather limited. Thus two methods have already been investigated for the preparation of $\text{SiO}_2\text{-ZrO}_2$ porous glasses. One is based on the sol-gel method and the other is the conventional phase-separation method. However, a simple preparation process for alkaline-resistant $\text{SiO}_2\text{-ZrO}_2$ porous glasses with pore size larger than 10 nm has not yet been developed. Moreover, it has been difficult to prepare microspherical particles smaller than 100 μm using the phase-separation method.

We have reported that porous glass supports in the $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ system were prepared by heating the $\text{SiO}_2\text{-ZrO}_2$ gel impregnated with NaCl at temperatures between 730 and 800°C.^{14),15)} It is easy to prepare porous glass with a pore size larger than 10 nm, with microspherical particles smaller than 100 μm in size, and with a pore volume larger than 1.0 cm³/g, although the pore size distribution of porous glass was broad. The porous glass support was composed of 75 mass% SiO_2 ·16 mass% ZrO_2 ·8 mass% Na_2O , when the starting gel composed of 83 mass% SiO_2 ·17 mass% ZrO_2 was heated together with NaCl at 800°C and then the mixture was washed with water. The process is a new approach for preparation of porous glass supports. In the present paper, we report the mechanism of formation of the porous glass supports.

2. Experimental

2.1 Preparation of $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ porous glasses

A flow chart of the preparation of a mixed alkoxide solution is shown in Fig. 1(a). The mixed alkoxide solution and the dried gel were prepared on a scale double that previously reported.¹⁵⁾ A scheme for the synthesis of a dried gel, and a procedure for salt impregnation into the $\text{SiO}_2\text{-ZrO}_2$ gel and heat treatment, are shown in Fig. 1(b) and Fig. 1(c), respectively.

The following is a standard procedure for the salt impregnation and the subsequent heat treatment. A 15 mass%

Fig. 1. Preparation scheme of $\text{SiO}_2\text{-ZrO}_2$ porous glass supports.

amount of a sodium chloride aqueous solution was impregnated into the dried gel. The mixture was dried at 110°C for 5h, and was heated at 600°C for 3h in a quartz tube under a stream of air. The resultant mixture ("A" in Fig. 1(c)) was heated again in an alumina crucible at 760°C for 5h in a furnace. The calcined sample ("B" in Fig. 1(c)) was washed with water and hot water, collected by filtration, and then dried at 110°C for 5h.

2.2 Characterization of products

Scanning electron microscope (SEM) observations were performed on gold-coated surfaces using a Hitachi S-900. Particles during synthesis were observed without further treatment, such as washing with water. Element distributions were analyzed for samples embedded in epoxy resin using a Shimadzu EMX-SM electron probe microanalyser (EPMA). X-ray diffraction (XRD) measurements were made using $\text{Cu K}\alpha$ radiation and diffraction using a Philips PW 1700. Thermogravimetric-differential thermal analysis (TG-DTA) curves were measured using a Rigaku TG-DTA. The gel impregnated with NaCl in a Pt cell was heated at 600°C for 3h and cooled to room temperature. It was heated again to 800°C at a rate of $20^\circ\text{C}/\text{min}$ under an air stream and kept at 800°C for 5h.

2.3 Analysis of gas formed during heating

Heat treatment of the dried gel impregnated with NaCl was usually performed by first heating the mixture at 600°C for 3h under a stream of air and then calcining it in a furnace. For analysis of gas components, the mixture in a quartz tube was only heated at temperatures between 760

and 800°C for 5h under a stream of air or nitrogen, as shown with the dotted line in Fig. 1(c). The mixture was composed of weighed amounts of the dried gel (about 2 g) and NaCl. The heating rate from 100°C to a designated temperature was $3^\circ\text{C}/\text{min}$. Components in a gas were caught in two traps of a $0.1\text{ mol}\cdot\text{kg}^{-1}$ KOH solution (200 cm^3) connected in series. The amounts of Si, Na and Zr in the alkaline solution were analyzed by inductively coupled plasma (ICP) using a Seiko Denshi Kogyo JY-38P. A quantitative analysis of H^+ was performed by a back titration of HCl using an excess of alkaline solution and that of Cl^- by a titration of silver ions.

2.4 Treatment of silane coupling agents

An appropriate amount of silane coupling agent dissolved in 20 cm^3 of toluene was added to porous supports dried in vacuo, together with a few droplets of an amine. Silane coupling agents used were 2.0 g of 3-glycidylpropyltrimethoxysilane and 2.94 g of dimethyloctadecylchlorosilane per 1.0 g of support. Then the resultant slurry was refluxed for 6h. The supports were collected by filtration, washed with methanol, and dried in vacuo.

3. Results and discussions

3.1 SEM observation

Particles at each synthetic step were observed by SEM, during preparation of porous $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ glasses, which were prepared by heating the mixture of the $\text{SiO}_2\text{-ZrO}_2$ dried gel with NaCl (0.46 g/1.0 g dried gel) at 760°C . A SEM photograph of a sample prepared by heating the $\text{SiO}_2\text{-ZrO}_2$ gel at 600°C for 3h is shown in Fig. 2(a). The surface texture of particles was similar to that of the dried gel, and crystallites adhered to the particles were observed, which were attributed to NaCl. Uniform texture was not identified on observation even at a high magnification and only a structure typical of a gel was observed. SEM photographs of particles after subsequent heat treatment at 760°C for 5h are shown in Figs. 2(b) and (c). A skeleton of porous-glass-like texture was obviously formed even before supports were washed with water, since skeletons were apparently observed on both figures. Therefore, formation of porous glass mainly occurred on the preparative step of heat treatment of 760°C in a muffle furnace.

Structural change of the support during heat treatment at 800°C in a muffle furnace was investigated subsequently by sampling particles, formed from starting materials of the $\text{SiO}_2\text{-ZrO}_2$ gel and NaCl (0.29 g/1.0 g dried gel). Preliminary results indicated that a skeleton of porous glass grew when the mixture of the $\text{SiO}_2\text{-ZrO}_2$ gel and NaCl was heat-

Fig. 2. SEM photographs of porous supports, (a) after heating with NaCl at 600°C for 3h, (b) and (c) after an additional heat treatment at 760°C for 5h.

Fig. 3. SEM photographs of porous supports, after heating with NaCl at 800°C for (a) 10 min, (b) 40 min and (c) 60 min.

ed for at least 1 h at 800°C, and a further heat-treatment induced growth of glass skeletons. Therefore, samples heated at 800°C within 1 h of the mixture were investigated in detail. SEM photographs of particles after calcining for 10 min, 40 min and 60 min are shown in Fig. 3. Few particles after heating for 10 min advanced to form porous glass skeletons as shown in Fig. 3(a). However, an embryo of glass skeletons was found in some particles. For the supports after heating for 40 and 60 min, Figs. 3(b) and (c) demonstrate that almost all particles had a similar shape to those of porous glass, particularly the flat surfaces of particles. Since these shapes were observed even before the supports were washed with water, the gel was converted to porous glass with partial maintenance of original porosity.

Analogous starting materials but a different preparative method from that of the present study was reported by Siebers et al.¹⁶⁾ Porous materials were obtained by first heating a mixture of finely milled glass particles and an inorganic salt, sintering the mixture, and washing the sintered body to remove the inorganic salt. Pores ranging from 5 to 350 μm in diameter were formed through a template effect of the inorganic salt. At first, it was thought that pore formation in the present study also originated from the template effect of NaCl. NaCl filled up pores of the gel, and pore size of the gel was assumed to turn uniform during heat treatment. However, the results described above indicated unambiguously that porous glass skeletons had already formed even before the washing of supports, and the gel was transformed to porous glass with maintenance of its porosity. Accordingly, a mechanism of pore equalization was attributed to a partial sintering of the porous gel through formation of a liquid phase by reaction of the gel with NaCl. This result was also supported by the fact that the porosity of porous glass supports of the present study was much larger than that calculated on the basis of the volume of NaCl added to the gel.¹⁵⁾ Thus, the mechanism of pore formation of the present method was quite different from that of the method of Siebers et al.

3.2 Element distribution in particles

To investigate element distribution in particles, electron probe microanalysis (EPMA) was performed on a cross section of particles filled with the epoxy resin, for each synthesis step. Distributions of Si and Zr in particles were nearly homogeneous. Mapped distributions of the concentrations of Na and Cl are shown in photographs in Fig. 4. The amount of each element is indicated by a color bar on the side of each photograph. After heating the mixture of the $\text{SiO}_2\text{-ZrO}_2$ gel and NaCl (0.46 g/1.0 g dried gel) for 3 h at 600°C, Na and Cl existed heterogeneously in particles, as

shown in Figs. 4(a) and (b), respectively. Both elements seemed to exist as NaCl, since they were distributed in the same areas of the particles. This result was in accord with the results of X-ray diffraction as shown in Fig. 5, where only intense peaks of NaCl were identified.

Sodium distribution in a sample heated at 760°C for 5 h and before washing with water is shown in Fig. 4(c). Sodium was present over wider areas of particles compared with those of particles after heating at 600°C for 3 h, although some local distribution of Na was observed. In contrast, Na was distributed homogeneously in particles after heating at 760°C for 5 h and subsequent washing with water, as shown in Fig. 4(d). The areas of high Na concentrations were disappeared. Homogeneous distribution of sodium corresponded to a TEM observation which indicated that the size of the glass skeleton was almost the same in the observed particle.¹⁵⁾ On the contrary, the Cl concentrations of samples heated at 760°C, both before and after washing with water, were almost below the detection limit and were not sufficiently high to determine Cl distribution. However, in some areas of particles, the Cl concentrations seemed to be higher than in others in the sample before washing. In contrast, these areas of high Cl concentration might not be present after washing of particles with water.

From the results of electron probe microanalysis described above, NaCl existed heterogeneously in the gel particles after heat treatment at 600°C for 3 h. Calcination at 760°C for 5 h induced diffusion of sodium cations, which resulted in homogeneous distribution of sodium in particles. Although there remained certain areas where the Na concentration was high and locally distributed, removal of NaCl with water, resulted in homogeneous Na distribution in particles. The crystalline peaks assigned to NaCl were observed for both samples after heating at 600°C for 3 h, and after heating at 760°C for 5 h before washing with water, as demonstrated in Fig. 5. This result was consistent with that of electron probe microanalysis. The mechanism of Na diffusion in particles was assumed to be as follows. First, sodium cations were exchanged with protons of surface hydroxyl groups which were abundantly present in the gel, and then sodium cations diffused in the gel through ionic conduction. Diffusion of Na cations was reported to occur in a sol-gel derived membrane of a $\text{SiO}_2\text{-TiO}_2$ system even at 70°C (in 90% relative humidity for 100 h).¹⁷⁾ The $\text{SiO}_2\text{-ZrO}_2$ mixed oxides presumably had a conduction character of Na cation, since the glass composition of $\text{Na}_2\text{O-ZrO}_2\text{-SiO}_2$ was reported as good Na ion conductors.¹⁸⁾ Thus diffusion of sodium cations in particles might have occurred during heat treatment at temperatures above 600°C.

Fig. 4

Fig. 5

Fig. 4. Element distribution in porous supports, measured using an electron probe microanalyser, (a) Na distribution in a sample after heating with NaCl at 600°C for 3h, (b) Cl distribution in the same sample with (a), (c) Na distribution in a sample after an additional heat treatment at 760°C for 5h, (d) Na distribution in a sample after washing the sample (c) with water.

Fig. 5. X-ray diffraction patterns for samples during the synthetic process, (a) after heating with NaCl at 600°C for 3h, (b) after an additional heat treatment at 760°C for 5h and (c) after washing the sample (b) with water.

3.3 Analysis of evolution gas

Reaction of NaCl and hydroxyl groups, and formation of HCl and/or Cl₂ is necessary in order to obtain SiO₂-ZrO₂-Na₂O from SiO₂-ZrO₂ gel and NaCl. TG-DTA curves were measured for the SiO₂-ZrO₂ gel alone and that impregnated with NaCl. Each gel was heated at 600°C for 3h, and once cooled to room temperature, it was reheated at 800°C for 5h. For the gel not impregnated with NaCl, about 12 mass% weight loss was observed during heat treatment at 600°C. However, weight loss on reheating at 800°C was very slight (2 mass%). In contrast, weight loss of the gel impregnated with NaCl (0.29 g/1.0 g dried gel) continued during heating at 800°C for about 5h, as shown in Fig. 6. A volatile compound other than water was assumed to be formed, since weight loss reached to 24.4 mass%, with weight loss beginning at 734°C. Endothermal peaks were observed at 743 and 795°C on the DTA curve. The peak at 795°C was probably related to melting of NaCl.

Reaction of SiO₂ and NaCl in air and steam at temperatures ranging from 700 to 1000°C was reported in Ref. 19), and it proceeded through the formation of HCl in the presence of steam. Its formation is represented by Eq. (1), and not Eq. (2).

In the present study, steam was not involved during heat

Fig. 6. TG-DTA patterns of the gel heated with NaCl.

treatment. We investigated evolution gas to determine whether a similar reaction to that shown above in Eq. (1) occurred during heating of the SiO₂-ZrO₂ gel and NaCl mixture. In addition, any loss of SiO₂ or ZrO₂ into the vapor phase, in a form such as SiCl₄ or ZrCl₄, was also examined. The outlet gas was analyzed by trapping it in an alkaline solution on the preparative step indicated with the dotted line in Fig. 1(c).

The amounts of Zr and Na in the alkaline trap were trace, with less than 0.01 mg Zr as ZrO₂ and less than 1.0 mg Na as NaCl. There seemed to be little possibility that excess NaCl was lost into the vapor phase. The maximum amount of SiO₂ was 11.0 mg, corresponding to less than 1 mass% based on the SiO₂ content of the dried gel. These results indicated little loss of Zr, Na and Si into the vapor phase from the SiO₂-ZrO₂ gel and NaCl mixture. Detected Si was probably due to dissolution of silicate ions from the glass trap, since it was in contact with the alkaline solution. The amounts of Zr, Na and Si were low in the washing solution of the silicon connection tube between the calcination tube and trap.

Then the concentrations of H⁺ and Cl⁻ in alkaline traps were determined. H⁺ and Cl⁻ originated from a volatile compound. The amounts of H⁺ and Cl⁻ formed during heating mixtures of the dried gel and NaCl (0.46 g per 1.0 g of the gel) at 760, 780 and 800°C are shown in Table 1. As the molar ratio of H⁺ to Cl⁻ was approximately 1.0, the vapor formed was not Cl₂, but HCl. This was supported by the result whereby the molar ratio of H⁺ to Cl⁻ during heat treatment of the mixture performed under a nitrogen atmosphere was the same as that under an air flow. Thus the reaction expressed by above Eq. (2) did not occur in this study, or at least it was not the main route of the formation of SiO₂-ZrO₂-Na₂O. In Fig. 7, the molar ratio of Cl⁻ to NaCl impregnated into the dried gel was plotted against heating temperature. The molar ratio of Cl⁻ detected to NaCl added increased as heat treatment temperature increased. The effect of NaCl added to the gel was studied by using various concentrations of NaCl and maintaining the heating temperature constant. Experimental numbers from 5 to 8 in Table 1 corresponded to 0.21, 0.30, 0.41 and 0.61 g of NaCl added per 1.0 g of the dried gel and the mixtures were heated at 800°C. The molar ratio of Cl⁻ formed to NaCl added did not change substantially, when the amount of NaCl added was more than 0.30 g per 1.0 g of the gel.

Table 1. Results of Analysis of the Gas Formed during Heat Treatment

Exp. No.	Preparation condition			Detected		Mole ratio			
	NaCl/gel	NaCl added	Calcined temp./°C	H ⁺ /mmol	Cl ⁻ /mmol	H ⁺ /Cl ⁻	H ⁺ /NaCl added	Cl ⁻ /NaCl added	
1	0.46	16.4	760	3.29	3.31	1.00	0.20	0.20	
2	0.46	16.6	780	5.98	5.54	1.08	0.36	0.33	
3	0.46	16.0	800	6.88	6.93	0.99	0.43	0.43	
4*)	0.46	17.7	800	8.15	8.09	1.01	0.46	0.46	
5	0.21	7.4	800	7.93	7.52	1.05	1.08	1.02	
6	0.30	10.3	800	5.96	5.90	1.01	0.58	0.57	
7	0.41	13.2	800	7.03	6.96	1.01	0.53	0.53	
8	0.61	19.3	800	8.50	7.99	1.06	0.44	0.41	

*) under N₂ flow.

Fig. 7. Relationship between heat treatment temperature and Cl⁻/NaCl molar ratio.

○ under air flow, ● under N₂ flow.

Table 2. Results of Elemental Analysis of Samples after Treatment with a Silane Coupling Agent

Exp. No.	Preparation condition			Results of analysis			
	Coupling reagent	Porous support	Acid treatment	C / mass%	H / mass%	Surface area m ² /g	Carbon content g/m ²
1	GPS ^{a)}	A3 ^{c)}	None	0.34	<0.3	37	9.2 × 10 ⁻⁵
2	GPS	A3	0.1N-HCl	0.43	<0.3	37	12 × 10 ⁻⁵
3	GPS	Z-15 ^{d)}	None	1.31	0.33	38	34 × 10 ⁻⁵
4	GPS	PG ^{e)}	None	8.03	1.88	85	94 × 10 ⁻⁵
5	ODS ^{b)}	A3	None	0.63	<0.3	37	17 × 10 ⁻⁵
6	ODS	A3	0.1N-HCl	0.67	0.33	37	18 × 10 ⁻⁵
7	ODS	Z-15	None	2.73	0.64	38	72 × 10 ⁻⁵
8	ODS	PG	None	5.63	1.89	85	66 × 10 ⁻⁵

a) GPS : 3-Glycidyloxypropyltrimethoxysilane.

b) ODS : Dimethyloctadecylchlorosilane.

c) A3 : porous glass supports prepared using the SiO₂-ZrO₂ gel and NaCl mixture.¹⁵⁾

d) Z-15 : porous supports prepared using the SiO₂ gel, ZrOCl₂, and NaCl mixture.²⁰⁾

e) PG : a conventional porous glass (IPG).

3.4 Surface properties of porous glass supports

Surface hydroxyl groups of the porous glass supports were assumed not to be abundant since weight loss was small as determined by TG-DTA measurements for products prepared by heating the dried SiO₂-ZrO₂ gel with NaCl at 800°C.¹⁵⁾ The number of surface hydroxyl groups was estimated by analyzing the amount of silane coupling agent bound to the supports, after treating porous supports in the SiO₂-ZrO₂-Na₂O system with two types of silane coupling agents. One was 3-glycidyloxypropyltrimethoxysilane, which is a general coupling agent for modifying silica supports for gel-permeation liquid chromatography. The other was dimethyloctadecylchlorosilane, which is a typical agent for modifying silica supports for reversed-phase liquid chromatography. Two types of silica supports were used as references; one was the conventional type of porous glass prepared by phase separation (PG), and the other was a porous support (Z-15) manufactured by heating SiO₂ gel together with ZrOCl₂ and NaCl, then washing it with water.²⁰⁾ The results of elemental analyses of modified supports are tabulated in Table 2. Carbon content indicated the amount of coupling agents bound to hydroxy groups on supports. Carbon content per 1 m² of surface area of the porous support was also calculated and is tabulated in Table 2. The amount of silane coupling agent bound to the porous support prepared by heating the mixture of the SiO₂-ZrO₂ gel and NaCl (0.46 g per 1.0 g of the gel) at 760°C (sample A3) was relatively low compared to that bound to the conventional type of porous glass or porous supports prepared by heating SiO₂ gel together with ZrOCl₂ and NaCl. Similar results were obtained for two types of coupling agents. In addition, we obtained an analogous result when we used the SiO₂-ZrO₂-Na₂O support after acid treatment with 0.1 mol·kg⁻¹ HCl for 24h at room temperature. The results described above indicated that the number of surface hydroxy groups on porous supports in the present study was relatively small. It corresponded to the TG-DTA measurement; weight loss of the porous support was very small even at high temperature. Taking the surface area of SiO₂-ZrO₂-Na₂O porous glass into consideration, the presence of a low number of surface hydroxy groups was attributed not only to the low number of pores smaller than 10 nm in size, but also to the surface property of the glass texture formed by liquid-phase sintering which resembled that of bulk glass.

3.5 Mechanism of formation of porous glass supports

The results described in previous parts are summarized as follows:

(1) SEM observations indicated that the porous-glass-

like texture similar to products was formed even before the supports were washed with water.

(2) Heat treatment at 760°C for 5h caused diffusion of Na⁺ cations and their homogeneous distribution in particles, as measured by an electron probe microanalyser.

(3) HCl was found to be mainly evolved in a stream of air as a result of gas analysis.

(4) The paucity of surface hydroxy groups on products, measured by the number of coupling agents bound to them, supported that porous glass was formed via viscous sintering.

These results indicated that a porous-glass-like texture was fabricated through a liquid phase in a SiO₂-ZrO₂-Na₂O system when a mixture of the SiO₂-ZrO₂ gel and NaCl was heated at a temperature between about 760°C to 800°C. Sodium cations of NaCl were exchanged with protons of -OH groups abundant in the gel, to form -ONa together with HCl. Sodium cations diffused in the SiO₂-ZrO₂ gel by means of ionic conduction. This mechanism enhanced the degree of homogeneous distribution of Na in the gel particles after heating, although NaCl crystals were present locally at first. H₂O was formed by sintering of hydroxyl groups in the gel, which might promote the reaction described by Eq. (1).

Although the preparative method used in the present study resembled the 'salt method',²¹⁾ the change occurring due to sintering was caused not by crystallization, but by vitreous formation. We reported that heating a mixture of the SiO₂ gel and NaCl at 760°C resulted in crystallization of the SiO₂ gel into α -cristobalite.²⁰⁾ The SiO₂ gel employed was prepared by a similar procedure to that used in this study using a sol-gel technique. In addition, heat treatment at 760°C of a mixture composed of the SiO₂-TiO₂ gel and NaCl caused phase separation and crystallization of anatase and α -cristobalite.¹⁵⁾ A glassy composition of the SiO₂-Na₂O system and HCl was believed to be scarcely formed by heating the mixture of the SiO₂ gel and NaCl. A trace amount of sodium in the silica gel was found to cause crystallization of silica when the gel was heated.²²⁾ In contrast, crystallization to zirconia and/or silica did not proceed even at 760°C in the case of the mixture of the SiO₂-ZrO₂ gel and NaCl. Since a mixed oxide in the SiO₂-ZrO₂ system was much stronger solid acid than a silica,²³⁾ a neutralization reaction of the SiO₂-ZrO₂ with Na₂O as a base presumably resulted in the facile formation of the SiO₂-ZrO₂-Na₂O glassy composition.

The synthetic procedure used in the present study was also different from that of porous supports prepared from pulverized glass particles and salts. Therefore the present method was believed to be an advanced procedure for the preparation of porous glass. In order to prepare porous glass supports using this method, the heat treatment temperature was required to be higher than that at which ionic conduction occurred and lower than that causing complete sintering of the mixture. The temperature range was from approximately 730 to 800°C in the present system.¹⁵⁾ Gel composition was crucial for determining whether a crystalline phase appeared at the temperature of Na cation's sufficient conduction. In the case of the silica and SiO₂-TiO₂, porous glass was not obtained because of crystallization of the oxides. In addition, porous glass was not formed in the case when the sintering temperature was too low. For example, when a mixture of the SiO₂-ZrO₂ gel and a nitric salt of Na instead of NaCl was heated at 700°C, the mixture turned nearly sintered. Therefore, application of the

present method to other systems might be rather limited considering the mechanism of the formation of porous glass.

4. Conclusion

A formation process of porous glass supports in the SiO₂-ZrO₂-Na₂O system was investigated by SEM, electron probe microanalysis and X-ray diffraction. The porous-glass-like texture similar to products was formed even before supports were washed with water. Heat treatment at 760°C for 5h caused diffusion of Na⁺ cations and their homogeneous distribution in particles. The outlet gas analysis demonstrated that mainly HCl evolved. The presence of a low number of surface hydroxy groups on products was indicated by the number of coupling agents bound to them, which suggested that porous glass was formed via viscous sintering. These results indicated a mechanism whereby the sponge-like texture was fabricated via a liquid phase in the SiO₂-ZrO₂-Na₂O system when a mixture of the SiO₂-ZrO₂ gel and NaCl was heated at temperatures between about 730 to 800°C. Sodium cations of NaCl were exchanged with protons of -OH groups abundant in the gel, to form -ONa together with HCl. Sodium cations diffused in the SiO₂-ZrO₂ gel particles by means of ionic conduction. This mechanism probably induced homogeneous sodium distribution in the gel particles after heat treatment, although NaCl crystals were first present locally.

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