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# Preparation of Porous $ZrO_2$-$SiO_2$ Glasses by the Sol-Gel Method

## ——Effect of Hydrolysis-Condensation Conditions on Pore Characteristics——

Kanichi KAMIYA, Shigeto MABE, Toshinobu YOKO† and Katsuhisa TANAKA

(Department of Industrial Chemistry, Faculty of Engineering, Mie University, Kamihama-cho, Tsu-shi, Mie 514)

# ゾルゲル法による多孔性 $ZrO_2$-$SiO_2$ ガラスの調製

## ——細孔特性に及ぼす加水分解・縮重合反応条件の影響——

神谷寛一・間部重人・横尾俊信†・田中勝久

(三重大学工学部工業化学科, 514 津市上浜町)

*The effect of parameters involved in the sol-gel preparation of the monolithic $ZrO_2$-$SiO_2$ glasses from Zr- and Si-alkoxide/ $H_2O$/ alcohol/ HCl solutions on their pore characteristics was investigated. As a result, a hydrolysis temperature as high as 80°C, the HCl content as high as 0. 5 in molar ratio to alkoxides and heating at a temperature as low as 600°C were found to be favored for making the glasses porous. Specific surface area ranging from 450 to 550 $m^2 \cdot g^{-1}$, pore volume from 0. 4 to 0. 7 $ml \cdot g^{-1}$, mean pore diameter from 40 to 60 A and high alkaline-resistivity have been attained in the resultant monolithic $ZrO_2$-$SiO_2$ glasses containing $ZrO_2$ up to 14 mol%.* [*Received October 13, 1988 ; Accepted December 15, 1988*]

***Key-words*** : *Porous $ZrO_2$-$SiO_2$ glasses, Sol-gel method, Metal alkoxide, Hydrolysis-condensation*

## 1. Introduction

The porous materials have been widely used in the field of science and technology as absorbents, filters, separation membranes, carriers for catalysts and enzyme, etc. As one of those materials, the porous $SiO_2$ glass has been fabricated from the $Na_2O$-$B_2O_3$-$SiO_2$ glasses by phase-separating them and leaching out the acid-soluble $Na_2O$-$B_2O_3$ phase. Its pore characteristics can be varied in a wide range by controlling the phase-separation condition. However, the $SiO_2$ porous glass has merely the low alkaline resistance, limitting its application.

So far, attempts to improve the alkaline resistance of the porous glasses have been made. Eguchi et al.[1] have prepared the alkaline-resistant porous $ZrO_2$-$SiO_2$ glasses from the $Na_2O$-$B_2O_3$-$ZrO_2$-$SiO_2$ glasses by a similar process to the Vycor-method, i. e., the phase-separation of the mother glasses into phases rich in $ZrO_2$-$SiO_2$ and in $Na_2O$-$B_2O_3$, followed by leaching out of the latter in the acidic solution.

The sol-gel method using metal alkoxides as raw materials can also provide the $ZrO_2$-$SiO_2$ glasses which are not obtainable by melting technique because of high tendency toward crystallization during cooling. The $ZrO_2$-$SiO_2$ glasses have been successfully made by this method in the form of fibers[2] or coated films[3] as well as a monolithic form.[4),5)] The monolithic glasses were apt to be porous if the heating temperature for glassification was not so high, suggesting its usefulness for the alkaline-resistant porous glasses. The mean pore size in those glasses, however, was as small as about 20 A in diameter.[4),5)] From a viewpoint of the practical use, the porous $ZrO_2$-$SiO_2$ glasses with a variety of pore characteristics are required.

In the present study, as an extention of previous works, the monolithic $ZrO_2$-$SiO_2$ glasses were prepared by the sol-gel method under different conditions, and the effect of parameters involved in the process on their pore characteristics was investigated.

## 2. Experimental

$Zr(O \cdot nC_3H_7)_4$ and $Si(OC_2H_5)_4$ were used as raw materials without any further purification. Absolute $C_2H_5OH$ or $i$-$C_3H_7OH$ was used as a solvent and HCl as a catalyst. Amounts of materials except HCl used in the experiments are listed in **Table 1**. The molar ratio of HCl to

† Present adress : Institute for Chemical Research, Kyoto University, Gokasho, Uji-shi, Kyoto-fu 611
現在:京都大学化学研究所窯業化学部門, 611 宇治市五ケ庄

**Table 1.** Amounts of starting chemicals for the calculated compositions and analyzed content of $ZrO_2$ in the $ZrO_2$-$SiO_2$ system.

| Calculated Composition / mol% | $Zr(O{\cdot}nC_3H_7)_4$ / g | $Si(OC_2H_5)_4$ / g | $H_2O$ / ml | $C_2H_5OH$ or $i$-$C_3H_7OH$ / ml * | Analyzed content of $ZrO_2$ / mol% Method 1 | Method 2 |
|---|---|---|---|---|---|---|
| $5ZrO_2{\cdot}95SiO_2$ | 1.64 | 19.79 | 90.0 | 87.6(76.6) | 4.9 | 4.8 |
| $10ZrO_2{\cdot}90SiO_2$ | 3.27 | 18.74 | 90.0 | 87.6(76.6) | 6.6 | 6.9 |
| $15ZrO_2{\cdot}85SiO_2$ | 4.91 | 17.70 | 90.0 | 87.6(76.6) | 11.2 | 11.8 |
| $20ZrO_2{\cdot}80SiO_2$ | 6.55 | 16.66 | 90.0 | 87.6(76.6) | 14.4 | 14.4 |

* numbers in ( ) denote the amount of $i$-$C_3H_7OH$

alkoxides (h) was varied in the range from 0.005 to 0.5. The amount of water added for hydrolysis was as large as 50 in the molar ratio to alkoxides.

The mixing of starting materials was conducted in two different ways. In method 1, the mixture of $Zr(O{\cdot}nC_3H_7)_4$ and $Si(OC_2H_5)_4$ was first diluted with a half of the prescribed amount of alcohol, then water was added dropwise to the alkoxides/alcohol solution together with remaining alcohol and HCl under stirring at room temperature (r.t.). In method 2, less reactive $Si(OC_2H_5)_4$ was first partially hydrolyzed by adding equimolar water together with a half of the prescribed amount of HCl and alcohol, then, $Zr(O{\cdot}nC_3H_7)_4$ was mixed, followed by slow addition of remaining water, HCl and alcohol under stirring at r.t.

The mixed alkoxide solutions were kept standing at r.t., 40°, 60° and 80°C without any covers to undergo the hydrolysis-condensation reaction. The resultant gels were heated to 600°, 800° and 1000°C in air. A following heating schedule was adopted to avoid the crack formation in gels during heating. Namely, the gels were dried in the room for about a month, then further dried at 50°C for 2 days and at 100°C for one more day, followed by heating to desired temperatures with a heating rate of 0.1°C/min.

The chemical compositions of finally obtained glasses were determined with an X-ray fluorescence technique. The $ZrO_2$ content was determined from the intensity ratio of $ZrL\alpha$ line to $SiK\alpha$ line. The non-crystallinity of the heated gels was examined by the conventional X-ray diffraction technique, using Ni-filtered $CuK\alpha$ radiation.

The apparent and bulk densities were measured by Archimedes method using water as a displacement liquid. Pore characteristics of the heated gels were measured with Sorptmatic 1800 (Carlo Erba Co.) by the absorption and desorption of nitrogen gas.

The durability toward alkaline attack was evaluated from the weight loss of the glass in 2N NaOH solution at 30°C.

## 3. Results and discussion

### 3.1 Chemical compositions of heated gels

The analyzed $ZrO_2$ content of 600°C-treated gels are shown in Table 1. It is seen that in any compositions, some $ZrO_2$ was lost during processing. The $ZrO_2$ content for the gels obtained by method 2 was also less than that calculated, while Nogami[4] has reported little loss of $ZrO_2$ when this method was adopted. However, since the content of water added for hydrolysis is different from his, the reason for the difference in the $ZrO_2$ content between ours and Nogami's is still to be clarified.

### 3.2 Crystallization behavior of gels

The change of X-ray diffraction profile with heating temperature for the gels prepared using method 1 and 2 is shown in **Fig. 1**, All composi-

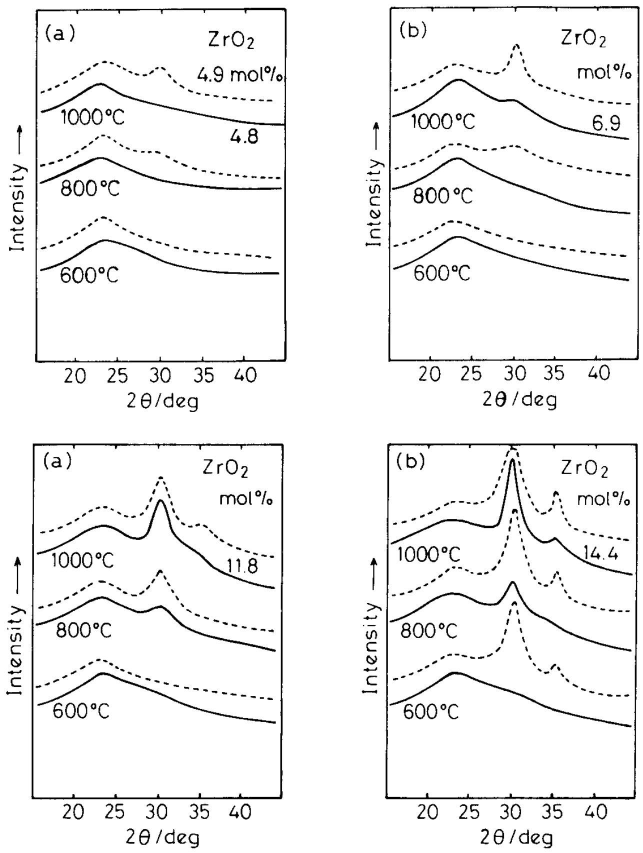


**Fig. 1.** X-ray diffraction profiles of the $ZrO_2$-$SiO_2$ glasses obtained from gels prepared by method 1 (···) and method 2 (—).

tions except one which was prepared by method 1 and has an analyzed $ZrO_2$ content of 14.4 mol% are amorphous at 600°C. Apparent densities of the gels at 600°C were almost identical with calculated ones, indicating that the glassification of gels is completed even at a temperature as low as 600°C. At higher temperature, crystalline $ZrO_2$ of tetragonal (or cubic) form precipitated in the glasses. The diffraction intensity of $ZrO_2$ is increased with heating temperature and the $ZrO_2$ content. Furthermore, it should be noted that the precipitation of $ZrO_2$ in the glasses prepared via method 1 occurs more intensively than that made by method 2. Such a difference in crystallization behavior between gels may be ascribed to the difference in the solution preparation. Higher hydrolysis rate of $Zr(O{\cdot}nC_3H_7)_4$ than $Si(OC_2H_5)_4$ may have led to the aggregation of $ZrO_2$ in the resultant gel in some extent when method 1 was applied. In such a sense, it seems that method 2 is superior to method 1 if the glass of a high $ZrO_2$ content is desired. However, it should be mentioned here, that, because partial hydrolysis of $Si(OC_2H_5)_4$ does not give monomeric products such as $Si(OC_2H_5)_{4-x}(OH)_x$ but siloxane oligomers[6] under the acidic condition, it is still unclear whether the resultant $ZrO_2$-$SiO_2$ glasses are homogeneous at an atomic level or not, even though method 2 is applied.

In spite of above results, in the followings, method 1 has been adopted for a composition with the $ZrO_2$ content of about 5 mol% in the case of investigating the effect of reaction parameters on the pore characteristics of the resultant glass, because of the convenience in solution preparation.

### 3.3 Effect of hydrolysis-condensation temperature on pore characteristics of the resultant glasses

The solution for the analyzed composition of 4.9 $ZrO_2$·95.1 $SiO_2$ (mol%) was prepared using method 1. The $h$-value, here, was kept at 0.05. The solution was subjected to hydrolysis-condensation at r.t., 40°, 60° or 80°C. The solution was gelled after 390, 240 and 150 min at 40°, 60° and 80°C, respectively.

The pore characteristics of the gels heated to 600°C are given in **Table 2**. Significant difference in specific surface area (SSA), pore volume (PV), mean pore radius (MPR) and porosity between glasses obtained from gels prepared at different hydrolysis temperatures is not seen. However, as can be seen in the pore size distribution curves of the glasses shown in **Fig. 2**, the PV due to large pores is increased with hydrolysis temperature, suggesting that high hydrolysis temperature is favored for making porous gels or glasses consisting of large micropores as reported for the $SiO_2$ gel made from $Si(OCH_3)_4$.[7]

### 3.4 Effect of HCl content

The gel for the composition of 4.9 mol% $ZrO_2$ was prepared using method 1 at different $h$-values. The hydrolysis was carried out at r.t., and the gel was converted to the glass at 600°C.

The pore characteristics of the glasses are listed in **Table 3**. The pore size distribution curves are shown in **Fig. 3**. As can be seen in Table 3 and Fig. 3, the effect of $h$-value on pore characteristics is drastic, that is, as HCl content becomes larger, larger micropores resulted. In order to explain such an effect of $h$-value, the gel

**Table 2.** Variation of the pore characteristics of the 4.9 $ZrO_2$·95.1 $SiO_2$ (mol%) glass with hydrolysis temperature (HCl/alk, molar ratio=0.05, heat treatment temper.=600°C).

| hydrolysis temper. /°C | S.S.A. /$m^2{\cdot}g^{-1}$ | P.V. /$ml{\cdot}g^{-1}$ | M.P.R. /Å | A.D. /$g{\cdot}cm^{-3}$ | B.D. /$g{\cdot}cm^{-3}$ | Porosity /% |
|---|---|---|---|---|---|---|
| 80 | 484.2 | 0.269 | 11.2 | 2.429 | 1.446 | 40.5 |
| 60 | 496.8 | 0.250 | 10.1 | 2.399 | 1.450 | 39.6 |
| 40 | 470.4 | 0.258 | 11.0 | 2.384 | 1.464 | 38.6 |
| room temper. | 467.5 | 0.258 | 11.1 | 2.364 | 1.439 | 39.1 |

S.S.A. = specific surface area, P.V. = pore volume,
M.P.R. = mean pore radius, A.D. = apparent density, B.D. = bulk density

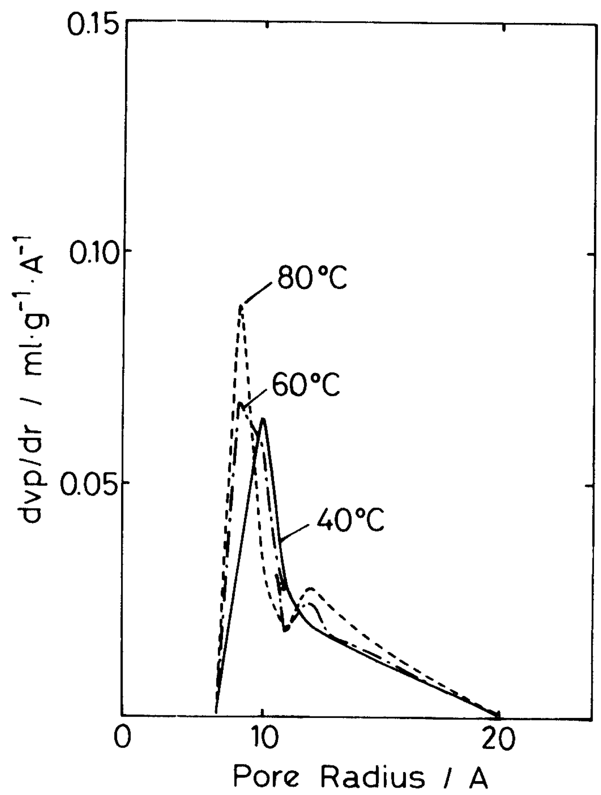


**Fig. 2.** Pore size distribution curves of the 4.9 $ZrO_2$·95.1 $SiO_2$ (mol%) glasses obtained from gels prepared at different hydrolysis temperatures (HCl/alkoxide molar ratio=0.05, heat-treatment temper.=600°C). ——; 40°C, —·—; 60°C, ----; 80°C

**Table 3.** Variation of the pore characteristics of 4.9 $ZrO_2$·95.1 $SiO_2$ (mol%) glass with the amount of HCl used as a catalyst (hydrolysis temperature=r, t., heat treatment temper. =600°C).

| HCl/alk. * | S.S.A. $/m^2 \cdot g^{-1}$ | P.V. $/ml \cdot g^{-1}$ | M.P.R. /Å | A.D. $/g \cdot cm^{-3}$ | B.D. $/g \cdot cm^{-3}$ | Porosity /% |
|---|---|---|---|---|---|---|
| 0.005 | 366.7 | 0.198 | 10.8 | 2.322 | 1.556 | 33.5 |
| 0.05 | 467.5 | 0.258 | 11.1 | 2.364 | 1.439 | 39.1 |
| 0.5 | 458.9 | 0.446 | 19.4 | 2.196 | 1.042 | 52.5 |

* molar ratio to alkoxides

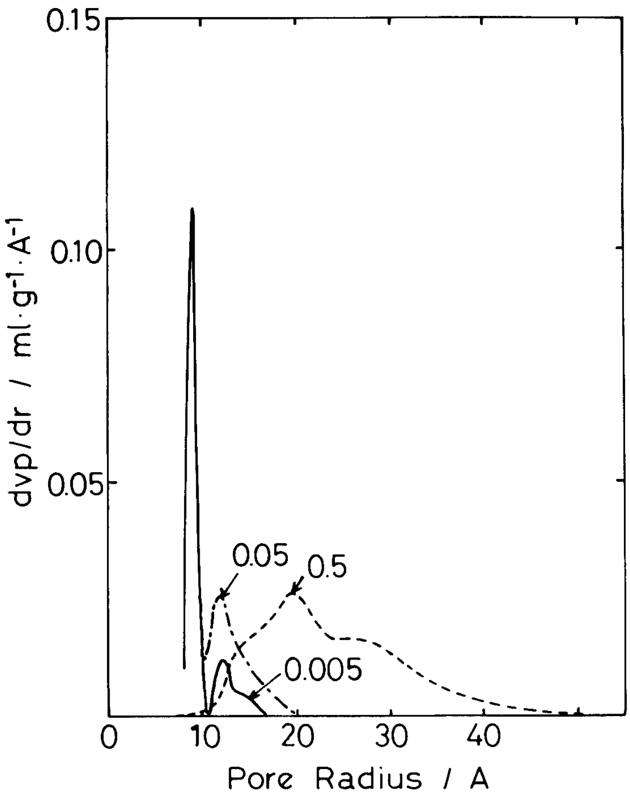


**Fig. 3.** Pore size distribution curves of the 4.9 $ZrO_2$·95.1 $SiO_2$ (mol%) glasses obtained from gels prepared using different HCl/alkoxide molar ratios (hydrolysis temper. =room temper., heat-treatment temper. = 600°C).
—— ; HCl/alkoxide ratio=0.005, —·— ; 0.05, ---- ; 0.5

volumes just at gelling was measured for three solutions with different $h$-values. The gel volume was increased with increasing $h$-value as shown in **Fig. 4**. This must be due to the fact that the solution with a larger $h$-value was gelled faster (although exact gelling time was not determined). Then, the solution with a large $h$ is set to gel before a considerable amount of volatile matters such as alcohols and water is lost by evaporation, providing a bulky dried gel. As mentioned above, the reaction rate was also increased with hydrolysis temperature. However, in that case, the increase of hydrolysis temperature accelerated the evaporation of the volatile matters as well as the reaction, which may not lead to meaningful difference in gel volume or pore characteristics.

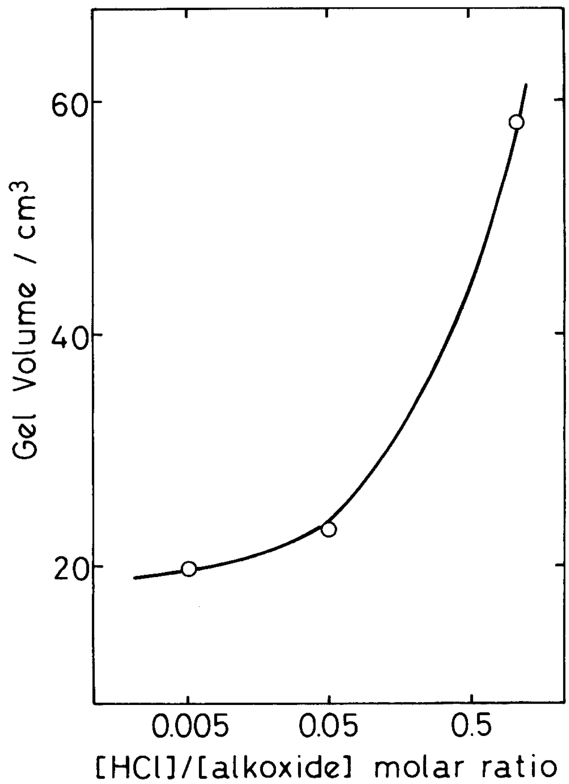


**Fig. 4.** Volumes of gels just at gelling for the 4.9 $ZrO_2$·95.1 $ZrO_2$ (mol%) composition prepared at room temperatures using different HCl/alkoxide molar ratios.

**Table 4** Pore characteristics of the 4.9 $ZrO_2$·95.1 $SiO_2$ (mol%) glass heat-treated at different temperatures (HCl/alk, molar ratio=0.5, hydrolysis temper, = r. t.).

| Temper. /°C | S.S.A. $/m^2 \cdot g^{-1}$ | P.V. $/ml \cdot g^{-1}$ | M.P.R. /Å | A.D. $/g \cdot cm^{-3}$ | B.D. $/g \cdot cm^{-3}$ | Porosity /% |
|---|---|---|---|---|---|---|
| 600 | 458.9 | 0.446 | 19.4 | 2.196 | 1.042 | 52.5 |
| 800 | 408.4 | 0.364 | 17.8 | 2.325 | 1.136 | 51.2 |
| 1000 | 210.3 | 0.225 | 21.4 | 2.302 | 1.431 | 37.9 |

### 3.5 Effect of heating temperature

The gel for the composition of 4.9 mol% $ZrO_2$ prepared at r.t. using $h$-value of 0.5 was heated to 600°, 800° or 1000°C. The pore characteristics data of the glasses are listed in **Table 4**. The SSA, PV are decreased with the increase of heating temperature, while the shape of pore size distribution curve and MPR remain almost unchanged, suggesting that pores collapsed in ones without coalescence. Thus it can be said that the raise of heating temperature does not lead to the improvement of pore characteristics of the glasses.

### 3.6 The porous $ZrO_2$-$SiO_2$ glasses with different amounts of $ZrO_2$ and relatively large micropores, and their alkaline-

In addition to reaction parameters discussed above, a type of alcohol used as a solvent is considered to play a certain role for controlling

Sol-gel derived porous $ZrO_2$-$SiO_2$ glasses

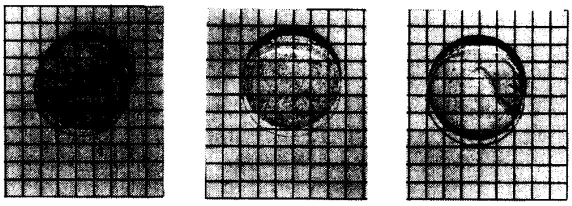


**Fig. 5.** Photographs of the porous $ZrO_2$-$SiO_2$ glasses.

**Table 5.** Pore characteristics of the $ZrO_2$-$SiO_2$ glasses prepared in the present study (HCl/alk, molar ratio= 0.5, hydrolysis temper. =80°C, heat treatment temper. =600°C).

| Sample /mol% | S.S.A. $/m^2 \cdot g^{-1}$ | P.V. $/ml \cdot g^{-1}$ | M.P.R. /Å | A.D. $/g \cdot cm^{-3}$ | B.D. $/g \cdot cm^{-3}$ | Porosity /% |
|---|---|---|---|---|---|---|
| $4.8ZrO_2 \cdot 95.2SiO_2$ | 542.3 | 0.667 | 24.6 | 2.239 | 0.843 | 62.4 |
| $6.9ZrO_2 \cdot 93.1SiO_2$ | 474.3 | 0.444 | 18.7 | 2.343 | 1.092 | 53.4 |
| $11.8ZrO_2 \cdot 88.2SiO_2$ | 309.4 | 0.261 | 16.9 | 2.256 | 1.130 | 52.0 |
| $14.4ZrO_2 \cdot 85.6SiO_2$ | 457.4 | 0.675 | 29.5 | 2.450 | 1.183 | 51.8 |

pore characteristics of gels and/or glasses. An alcohol with a large molecular size is expected to leave the gel a larger pore. This effect has been studied by Mackenzie[8] for $SiO_2$ composition to some extent.

The SSA, PV and MPR of the 4.9 $ZrO_2$·95.1 $SiO_2$(mol%) glass obtained using $i$-$C_3H_7OH$ as a solvent in the starting alkoxide solution were larger than that from $C_2H_5OH$ containing solution. This may be attributed to a larger size of $i$-$C_3H_7OH$ than $C_2H_5OH$.

Finally, porous $ZrO_2$-$SiO_2$ glasses of the compositions listed in Table 1 were made, taking the above results into consideration. Namely, the gels were prepared by method 2 using $i$-$C_3H_7OH$ as a solvent and $h$-value of 0.5 at 80°C. The gels were converted to glasses at 600°C. In **Fig. 5**, the sol-gel derived porous $ZrO_2$-$SiO_2$ glasses thus obtained are shown. These glasses are 1-2 mm in thickness and mechanically strong enough for cutting and polishing.

Pore characteristics of the glasses are shown in **Table 5**. The MPR of the glasses ranges from 20 to 30 Å, which is comparable to that of the Corning #7930 porous glass (MPR=20-30 Å), while SSA and PV are larger.

In **Fig. 6**, the weight loss of the glasses in 2N NaOH solution at 30°C is plotted against immersion time. It is clearly seen that the resistance toward alkaline attack is increased with the $ZrO_2$ content.

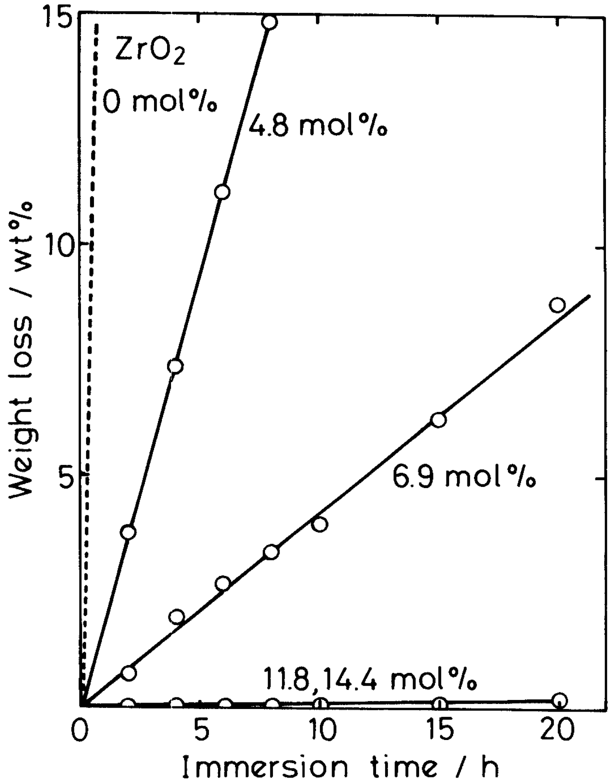


**Fig. 6.** Weight loss of the $ZrO_2$-$SiO_2$ glasses in 2N NaOH solution at 30°C plotted against immersion time.

## 4. Summary

The effect of parameters involved in the sol-gel preparation of the monolithic porous $ZrO_2$-$SiO_2$ glasses on the pore characteristics has been investigated. Followings have been obtained.

(1) A high hydrolysis temperature seemed to be favored to form large micropores in the resultant glasses.

(2) The surface area (SSA), pore volume (PV) are decreased by increasing heating temperature, while mean pore radius (MPR) remained almost unchanged.

(3) The influence of the content of HCl used as a catalyst was most remarkable. As the HCl content becomes higher, the larger MPR resulted.

On the basis of above results, the porous monolithic $ZrO_2$-$SiO_2$ glasses containing $ZrO_2$ up to 14.4 mol% have been made via sol-gel reaction at 80°C using $h$-value as high as 0.5, $i$-$C_3H_7OH$ as a solvent. The pore size as large as 40-60 Å in diameter, SSA and PV ranging from 450 to 550 $m^2g^{-1}$ and 0.4 to 0.7 $ml \cdot g^{-1}$, respectively, have been attained. Those glasses are highly alkaline-resistant compared to the porous $SiO_2$ glass.

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