CHEMISTRY LETTERS, pp. 665-668, 1991

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

Yasushi TSURITA and Keisuke WADA*
Research Center, Mitsubishi Kasei Corporation,
1000, Kamoshida-cho, Midori-ku, Yokohama 227

A new method of preparation of porous supports with SiO_2-ZrO_2-Na_2O composition was investigated by heating the sol-gel derived SiO_2 gel together with NaCl and $ZrOCl_2$ at 760 °C. In the presence of $ZrOCl_2$, crystallization of the SiO_2 gel was suppressed and incorporation of Na_2O into composition was identified. The microspherical porous supports, thus formed, possessed porous glass like texture and their pore size was about 500 Å in radius.

Porous glasses containing ZrO_2 are of technological interest since they have high resistant property to the alkaline solution. Two methods have been reported in recent years for preparation of these glasses. Nogami prepared SiO_2-ZrO_2 porous glasses through the sol-gel route, whose pore size was less than 50 Å in radius.$^{1)}$ Eguchi et al. reported preparation of SiO_2-ZrO_2 based porous glasses by the phase separation method.$^{2)}$ However, their process was rather complicated, because SiO_2 and ZrO_2 gel had to be removed after phase separation and acid leaching. Therefore, the more simple method is desired for manufacturing the SiO_2-ZrO_2 porous glasses, which had large pore size suited for separation of biopolymers. We reported recently the new method for preparation of the porous glasses with SiO_2-ZrO_2-Na_2O composition by means of heating SiO_2-ZrO_2 gel together with NaCl.$^{3)}$ In this communication, we report another new preparative method of SiO_2-ZrO_2-Na_2O porous supports from the SiO_2 gel.

The SiO_2 gel, a starting material in this study, was prepared from partially hydrolyzed tetraethoxysilane by the O/W method, similar to that originally reported by Unger.$^{4)}$ It was nearly spherical particles of about 5 to 20 microns in diameter. An amount of $ZrOCl_2 \cdot 8H_2O$ and 0.58 g of NaCl was dissolved in 10 ml of water. This solution was added to the dried SiO_2 gel 2.0 g and then dried at 100 °C for 5 h. The gel was porous enough to adsorb almost all of the salt solution. The impregnated gel was heated at

Table 1. Effect of ZrO_2 on pore characteristics of the porous supports

Sample	ZrO_2 /Gel g/g	Surface area m^2g^{-1}	Peak top of pore radius Å	Pore volume between 100-1000 Å cm^3g^{-1}
Z-15	0.15	38	451	1.31
Z-10	0.10	32	602	1.19
Z-5	0.05	22	643	1.26
Z-0	0	13	1481	0.11

Table 2. Composition of the porous supports based on weight %

Sample	SiO_2	ZrO_2	Na_2O	Total
Z-15	78.2	11.9	3.9	94.0
Z-10	83.8	8.0	3.3	95.9
Z-5	88.9	4.7	2.6	95.9
Z-0	99.3	0.1	0.2	99.5

600 °C for 3 h under stream of air and heated again at 760 °C for 5 h. The calcined sample was washed three times with water and collected by filtration.

Three different samples (Z-15, Z-10, and Z-5) were prepared by adding different amount of $ZrOCl_2 \cdot 8H_2O$ (0.15 g, 0.10 g, and 0.05 g of ZrO_2 per 1.0 g of the dried SiO_2 gel, respectively), but the same amount of NaCl, and heated at the same temperature. For reference, the sample Z-0, in which the SiO_2 gel was heated only with NaCl, was prepared additionally.

Table 1 shows pore characteristics of these products measured by the mercury penetration porosimetry and nitrogen adsorption. The surface area reduced gradually as the amount of ZrO_2 added to the SiO_2 gel reduced. The peak top position of pore radius was also shifted to the direction of the larger pore radius. In the samples Z-15, Z-10, and Z-5, their pore distribution was rather sharp and the peak top positions of pore radius were around 500 Å. Their pore volumes in the range of 100 to 1000 Å were more than 1.0 cm^3/g. On the contrary, the peak top position of pore radius of Z-0 was about 1500 Å, much larger than samples containing ZrO_2.

The SEM photographs of samples Z-10 and Z-5 are demonstrated in Fig. 1. Glassy skeletons similar to porous glasses were observed on surface of microsphere particles in the both figures. Size of the skeletons was increased as the amount of ZrO_2 added to the SiO_2 gel was reduced, which was in accord with the result of pore characteristics. These results demonstrated that as the amount of ZrO_2 added was reduced, the degree of the sintering of the products was advanced, in the order Z-15 $<$ Z-10 $<$ Z-5 $<$ Z-0.

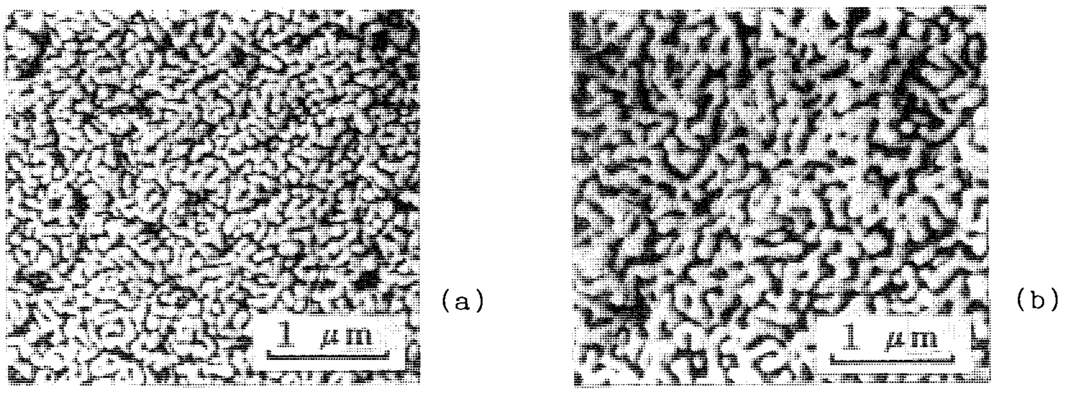

Fig. 1. SEM micrographs of the porous supports, (a) sample Z-10 and (b) sample Z-5.

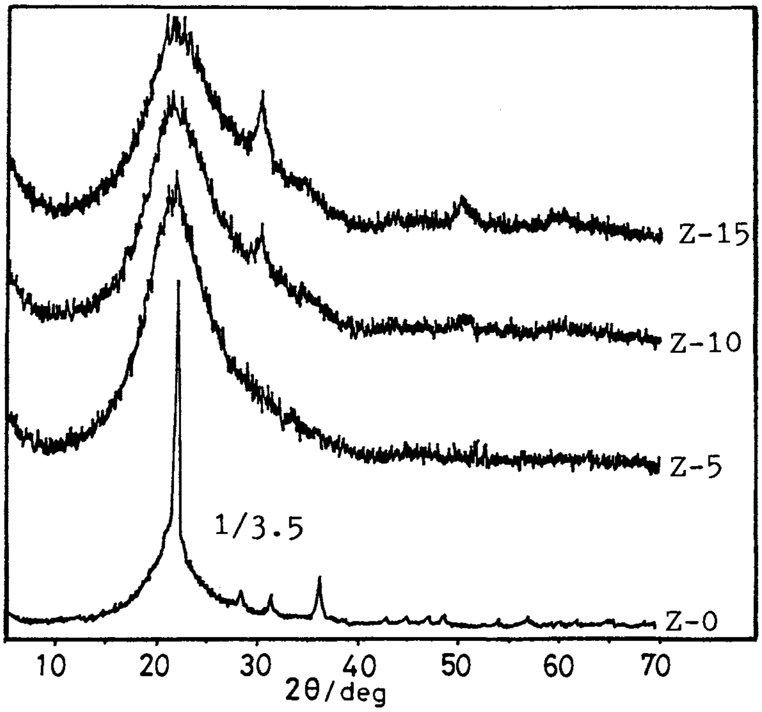

Fig. 2. X-Ray diffraction patterns of the porous supports.

In Fig. 2 are illustrated X-ray diffraction patterns of four samples. In the samples Z-15, Z-10, and Z-5, silica phase remained amorphous, although intensity of broad peak around $2\theta = 21°$ became stronger in the order Z-15 $<$ Z-10 $<$ Z-5. Peaks of tetragonal ZrO_2 were identified in Z-15 and Z-10, whose intensity became weaker as the amount of ZrO_2 added was reduced. On the contrary, in the absence of ZrO_2 (Z-0), peaks of α-cristobalite were clearly observed as the result of crystallization of the SiO_2 gel.

Oxide compositions of four samples determined by X-ray fluorescence are shown in Table 2. The amount of Na_2O in Z-0 was much less than those of other samples, which was consistent with the result of crystallization of the SiO_2 gel. On the other hand, an appreciable amount of Na_2O existed in Z-15, Z-10, and Z-5, and it increased gradually as the amount of ZrO_2 increased. The Cl contents, in contrast, were less than 0.2 wt% although they were qualitatively determined by X-ray fluorescence.

Pore size enlargement of SiO_2 gels was known as 'Salt impregnation of SiO_2 gel'5) or 'Salt method'4) when SiO_2 gels were heated with salts. This result has been attributed to sintering and crystallization of the SiO_2 gels. It was also reported that the SiO_2 gel containing even small amount of alkaline ions or other impurities had a strong tendency to crystallize during firing.6) This interpretation was in accord with the result obtained in the case of Z-0 in this study. In contrast, in the presence of ZrO_2 (Z-15, Z-10, and Z-5), a part of NaCl turned to Na_2O, which was incorporated into the SiO_2 gel, together with ZrO_2 dispersed on SiO_2, during heat treatment of the impregnated gel. Thus, the glassy phase of the mixed oxides in the SiO_2-ZrO_2-Na_2O system was formed, which suppressed the sintering of the SiO_2 gel by crystallization.

In the samples Z-15, Z-10, and Z-5, some heterogenity of ZrO_2 distribution remained since the crystalline peak of ZrO_2 in the X-ray diffraction patterns was observed in the samples Z-10 and Z-15. However, their morphology of the glassy skeletons and narrow pore size distribution was similar to that of the SiO_2-ZrO_2 based porous glasses obtained by the phase separation method.2) Therefore, the present method can be regarded as alternative one for manufacturing the porous glasses of SiO_2-ZrO_2 based composition whose pore size is larger than 50 Å in radius. Moreover, this method was quite simple as compared to the conventional procedure, especially in the preparation of microspherical particles.

In conclusion, the porous SiO_2-ZrO_2-Na_2O mixed oxides were formed when the SiO_2 gel was impregnated and heated together with NaCl and $ZrOCl_2$. In the presence of ZrO_2, sintering and crystallization of the SiO_2 gel was suppressed.

References

1) M. Nogami, Yogyo Kyokai Shi, 93, 195 (1985).
2) K. Eguchi, H. Tanaka, T. Yazawa, and T. Yamaguro, 1986 National Meeting of the Ceramic Society of Japan, Tokyo, May 1986, Abstr.(I),p.493.
3) Y. Tsurita and K. Wada, Chem. Lett., 1991, 255.
4) K. Unger, J. Schick-Karb, and K. Krebs, J. Chromatogr., 83, 5 (1973).
5) K. Krebs and H. Heinz, D.E.Patent 2042910 (1972).
6) M. Prassas, J. Phalippou, and L. L. Hench, J. Non-Crystal. Solids, 63, 375 (1984).

(Received December 27, 1990)