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Amorphous Oxides Prepared from Organometallic Compounds Part2. Structure Evolution in Sodium Borosilicate Gels

Akiyoshi OSAKA*, Motokazu YUASA**, and Yoshinari MIURA*
and
Katsuaki TAKAHASHI*

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SYNOPSIS

Sodium borosilicate gels of compositions similar to that of Vycor^R glass like $80SiO_2.15B_2O_3.5Na_2O$ (wt%) were prepared from hydrolysis and polycondensation of metal alkoxides under the HCl catalysis. Variation of specific surface area and porosity with temperature indicated that closed pores were opened below 400°C, and collapsed above 450°C after the porosity reached a maximum value around 450°C. The structural evolution was examined due to IR spectra and a phase separation in the gels was observed. The solubility of the gels into 1N-HCl was studied as a function of the treatment temperature.

1. INTRODUCTION

In the previous paper(1) we dealt with gelation time and thermal behavior of the sodium borosilicate gels of compositions similar to Vycor^R glass. In this paper, we will examine the variation of specific surface area and porosity as well as their IR spectra as a function of the heat treatment, based on which the structure evolution will be discussed of the gels under treatment. The solubility of the gels after various stages of the treatment is examined and interpreted with respect to phase separation in the gels.

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* Department of Applied Chemistry

** Now at Sekisui Chemical Industry, Ltd.

2. EXPERIMENTAL

2.1. Preparation

The compositions of the gels were

i) $80SiO_2.(20-x)B_2O_3.xNa_2O$ [wt%] $(0<x<20)$

ii) $75SiO_2.(25-x)B_2O_3.xNa_2O$ [wt%] $(0<x<20)$

The starting materials were the use of tetraethyl orthosilicate (TEOS), trimethyl borate and sodium methylate. HCl was employed as the catalyst. Among several values of the mixing molar ratios H_2O/TEOS and HCl/TEOS adopted previously(1), the fixed ratios H_2O/TEOS=1 and HCl/TEOS=1/100 have been taken for preparing the gels (method I). Although the gels have also prepared from the mixtures of the alkoxides and acetylacetone without water (method II), discussion in the present paper will be focused on the gels through method I, unless otherwise noticed. Full hydrolysis and polymerization of the starting solutions need much water than added, hence the deficient amount for that is supplied from the air. The detail of the preparation procedure is described in the previous paper(1).

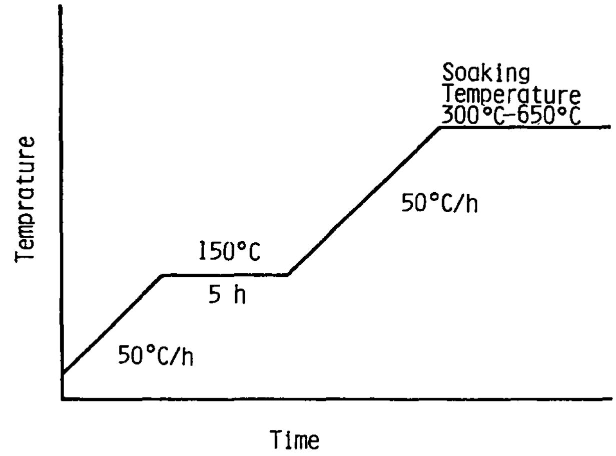


Fig. 1.
The heat-treatment schedule for the sodium borosilicate gels.

Figure 1 shows the heat-treatment schedule. After the heating at a rate of 50°C/h up to 150°C, the dried samples were kept for 5h at 150°C in order to drive off water and solvents adsorbed on the gel surface. The temperature was subsequently raised at a rate of 50°C/h to the soaking temperature, ranging from 300° to 650°C at which temperature the samples were soaked for varied duration of time. After those treatments, the gels were let cooled in the furnace by cutting off the furnace power.

2.2. Porosity and thermal shrinkage

Apparent density of as-prepared and heat-treated gels was measured by the Archimedes method using EtOH as the immersing liquid and a silica glass block as the reference. Apparent porosity represents the volume fraction of open pores in a bulk porous solid. The gels were dried for a day at 120°C in an oven. Before the weighing in EtOH the pieces of the gel were immersed in EtOH for 10 to 20 min. After the immersion in EtOH the gels were quickly taken out, and excess EtOH on the gel surface was wiped off. The apparent porosity then was obtained by weighing the gels whose open pores were filled with EtOH. Specific surface area was measured for the pulverized gels by means of the BET method with using N_2 gas.

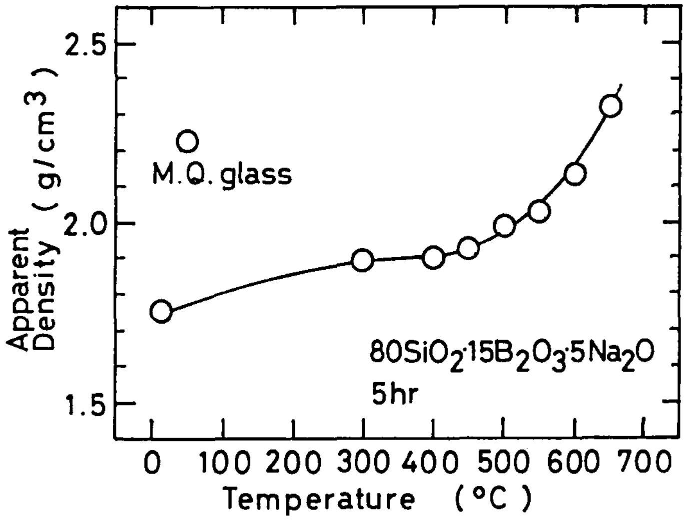


Fig. 2.
Apparent density of 80S-15B-5N gel as a function of the soaking temperature. Density of a melt-quenched borosilicate of the same composition is also plotted.

3. RESULTS AND DISCUSSION

3.1. Porosity and specific surface area

Figure 2 shows the variation of the apparent density of a gel of composition $80SiO_2.15B_2O_3.5Na_2O$ (80S-15B-5N) plotted as a function of the soaking temperature. The density of the gels little changes below

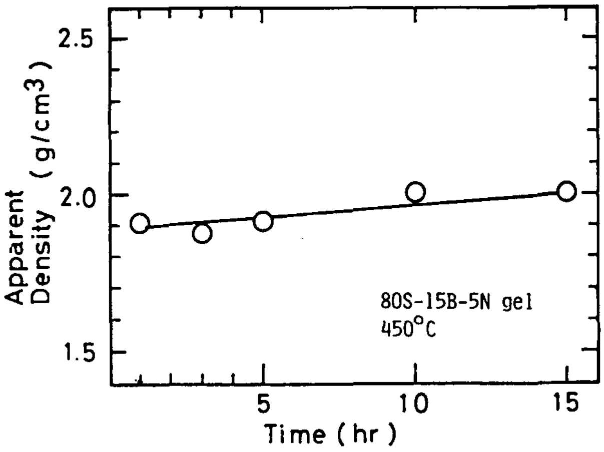


Fig. 3. Apparent density of 80S-15B-5N gel soaked at 450°C as a function of the soaking time.

400°C and is about 3/4 times as dense as that of the melt-quenched glass of the same composition, indicating the presence of isolated closed pores as much as 20% in volume in the 80S-15B-5N gel. The density of the gels slowly increases above 400°C and is almost equal to that of melt-quenched glass after they are heated at 620°C for 5 h. The apparent density, however, shows little dependence on the time of soaking as indicated in Fig. 3. Figs. 4 (a) and (b) indicate the apparent density for the gels of compositions i) $80SiO_2.(20-x)B_2O_3.$-

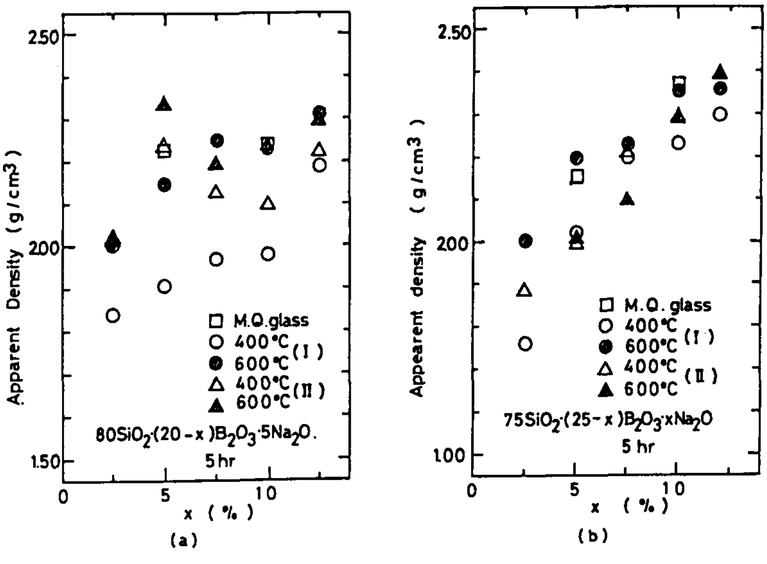
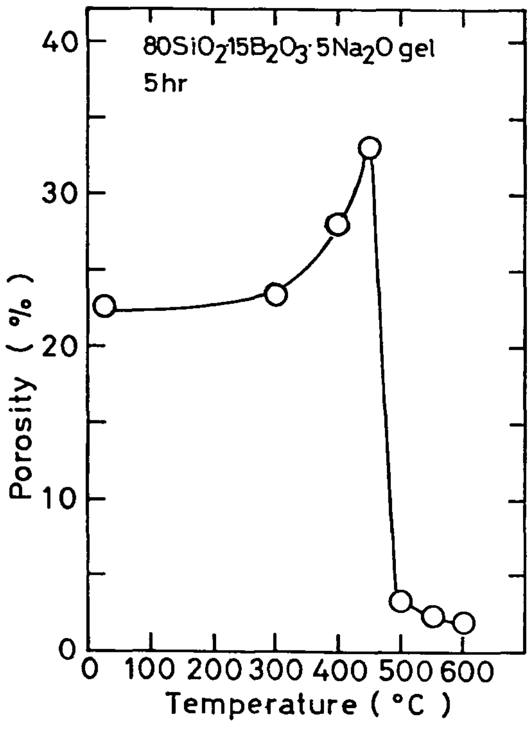


Fig. 4. Apparent density of gels of composition (a) $80SiO_2.(20-x)B_2O_3.xNa_2O$ and (b) $75SiO_2.(25-x)B_2O_3.xN_2O$ prepared through methods I and II and treated at various temperatures.

xNa_2O and ii) $75SiO_2.(25-x)B_2O_3.xNa_2O$ (0<x<10wt%), respectively. They were heated for 5 h at temperatures from 400°C to 600°C. The triangles indicate the plots for the gels through method II. The trend that apparent density for method II is larger than that for method I shows porous solids of less porosity is obtained by the slower gelation reaction caused by retarded supply of water only from the air. The apparent density increases with increase in the soaking temperature and approaches that of the melt-quenched glass represented by the open squares.

Figure 5 shows the porosity of the gel of composition 80S-15B-5N as a function of the soaking temperature. Porosity of the gels starts increasing with the soaking at 450°C. It is therefore suggested that a part of the closed pores in the gels are opened due to the heat-treatment. After reaching a maximum, porosity suddenly decreases after the soaking above 450°C. The specific surface area of the gel has been plotted in Fig. 6 as a function of the soaking temperature,



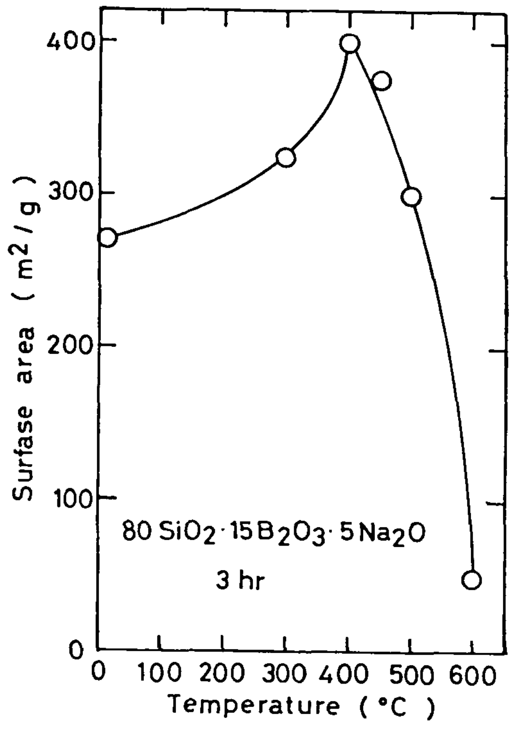


Fig. 5(left). Porosity of 80S-15B-5N gels as a function of the temperature of soaking for 5h.

Fig. 6(right). Specific surface area of the gels as a function of the soaking temperature.

indicating a temperature dependence similar to that for the porosity. The specific surface area increases up to 450°C and then decreases rapidly with the soaking temperature. It has already been indicated(1) that the gel shrinks gradually in the soaking treatment below about 450°C and that an appreciable amount water is driven off below 150°C. Since only a little loss of the surface area is found around 450°C the volume fraction of the pores is not significantly reduced during the initial stages of the pore collapse. The fact that the surface area becomes maximum after the treatment at 400°C is probably related to opening of the closed pores. The small shrinkage has been found(1) with loss of water on heating the gels between 120°C and 450°C, which fact is an indirect evidence for condensation among adjacent Si-OH and B-OH groups on the pore walls, as shown later on the basis of IR spectra in Fig. 8. The condensation of these groups on one wall with those on an opposite wall of the micropore causes the pore collapse. This may occur locally to a limited degree at lower temperature, which explains the small amount of shrinkage that is observed below 4500°C.

The pore size distribution has been measured by the Hg method. Although the heated gels have the surface area as large as 250-350 m^2/g, the volume fraction of the pores from 100A to 10^4A in diameter is not so large as to explain the large surface area. On this basis, it is suggested that a considerable fraction of the pores is below 40A

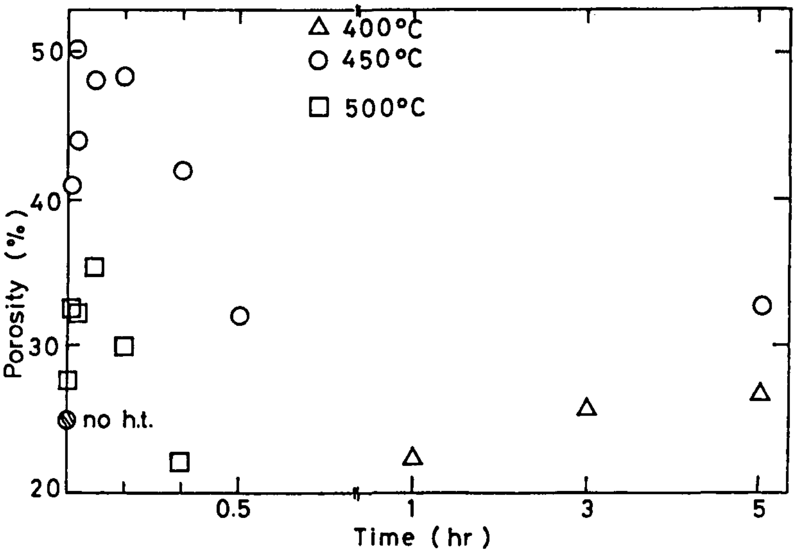


Fig. 7. Variation of porosity for 80S-15B-5N gels soaked at 400, 450 and 500°C is shown as a function of the soaking time. The value for the dried gel is represented as "no h.t."

in diameter and is not measurable by the Hg method. The mechanism of the pore collapse is not understood at this stage, but Tohge et al.(2) is against the viscous flow mechanism because of the low activation energy (about 5 kcal/mol) found for the borosilicate gel.

Figure 7 shows the effect of heat-treatment time on the apparent porosity of the 80S-15B-5N gel heated at 400, 450, 500°C. The porosity of the gels increases and reaches a maximum value after the soaking for about 10 min regardless of the temperature. After the maximum, the porosity for the gels heated below 450°C decreases and reaches a constant value, whereas that for the gels heated at 500°C decreases continuously to almost null (about 3% porosity). Such change can be interpreted as follows: At first the pore wall has a number of Si-OH and B-OH groups inside as well as outside for which the condensation takes place causing the closed pores to be opened. Then the pore wall shrinks itself due to further condensation among these active -OH groups inside the wall since they can easily find the counterpart in the vicinity. This causes the decrease in the porosity. The difference in the final porosity after the soaking as long as 5h depending on the treatment temperature may come from the difference in the size of the collapsed pores: that is, the larger pores are left without collapse at lower temperature but they are much less in number.

3.2. IR spectra of the borosilicate gels

Figure 8 shows the IR spectra for a sodium borosilicate gel of composition 80S-15B-5N heat-treated for 5h at various temperatures, together with that of the melt-quenched glass of the same composition which was heat-treated for 20 h at 700°C, the immiscibility temperature of the glass. The spectra of the gels before the heat-treatment have strong bands at 470, 810, 930, 1050 and 1400 cm^{-1}. The difference in the spectrum between the melt-quenched glass before and after the heat-treatment is characterized by the presence of a weak band around 930 cm^{-1} attributed to the deformation vibration of the Si-O-B bonds. This band becomes weak with increasing treatment temperature. A new band at about 680 cm^{-1}, due to the B-O-B bonds, appears for the gels treated above 450°C. The profile for these gels is very similar to that of the melt-quenched glass. Moreover, the intensity of the bands becomes well-defined with increasing the treatment temperature, indicating the structure evolution in the gel. Comparison of the spectra for the gels before and after the heat-treatment indicates that a band around 1600cm^{-1} due to the O-H groups is weak but still

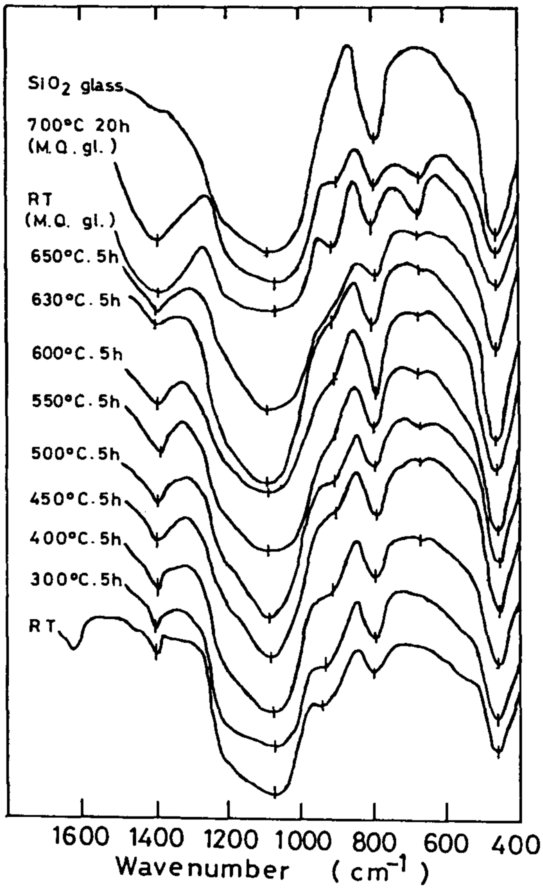


Fig. 8.
Infrared spectra of 80S-15B-5N gels treated at various temperatures. Those for silica glass and melt-quenched borosilicate glass of the same composition are also indicated.

found. It is suggested accordingly that the gel derived borosilicate glass experiences the phase separation when it is soaked at 650°C for 5h.

3.3. Solubility of the gels to acid

After dried at 120°C for 1 day in the oven and soaked at various temperatures for 5h, the gels were soaked in 10ml 1N-HCl solution for 1 day. Then the samples were washed with an excess amount of distilled water and dried at 120°C for 1 day. The weight of the gels before and after the acid-treatment was measured. Figure 9 shows the effect of heating temperature on the weight loss of the 80S-15B-5N gel due to leaching by 1N-HCl solution. The weight loss increases up to about 10 percent when the gels are heated below 400°C. The samples are cracked after the acid treatment due to capillary pressure of water immersed in the open pores of the gel. The loss decreases when the gels are treated above 400°C - 500°C, and reaches less than 1%. A slight increase is seen in the weight loss for the gel treated above 630°C. The dependence of the weight loss, shown in Fig. 9, is very similar to that of the apparent porosity and surface area. It is reasonable that the gels of larger specific surface area should suffer from the greater attack of acid than the gels of less surface area. Though the gels are phase separated after the soaking at higher temperatures, the leached loss is much smaller than that expected from the Na_2O and B_2O_3 content in the 80S-15B-5N gel, indicating that the phase-separated gels are resistant to acid. This suggests that an amorphous sodium borate phase is separated from the gel or gel-derived glass, whereas the phase separation is not an entangled type but a droplet type. The leaching hence takes place only at the surface of the glass. Such a possibility might be negligible as the structure is different between the melt-quenched glass and gel-derived glass, and the sodium borate phase separated from the gel is more alkali resistant than that separated from the melt-quenched borosilicate glass of the same composition.

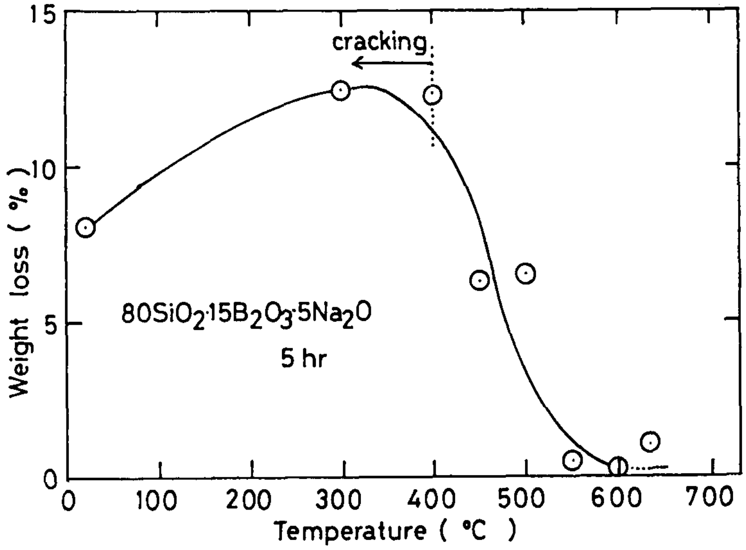


Fig. 9. Weight loss of 80S-15B-5N gel as a function of the temperature of the heat treatment for 5h after leaching in 1N-HCl for 5h.

4. CONCLUSION

Sodium borosilicate gels of compositions near the Vycor^R glass,

$80SiO_2.15B_2O_3.5Na_2O$ (wt%) have been prepared and their physical properties such as porosity, specific surface area, and IR spectra have been measured. The 80S-15B-5N gel has a maximum porosity (35%) when it is heated at 450°C. It becomes pore free and is phase-separated after the treatment at 500°C. Subsequent treatment causes precipitation of cristobalite. From the IR spectra it is concluded that the pore collapse begins with the formation of B-O-B bond from the condensation of B-OH bonds. The very small leaching loss of the phase separated gel-derived glass suggests the droplet-type phase separation but not the entangled-type one which is the usual case of the melt-quenched glass.

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