SILICA GLASS: PREPARATION AND CHARACTERIZATION

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Silica glass with good optical quality and low OH content has been prepared by a sol–gel process. The sols have been prepared by mixing TMOS, methanol and water in acid condition, and 0.15 µm SiO₂, Stöber microspheres or Cab-O-Sil M5 have been added to the sols in order to reinforce mechanically the gels and obtain monolithic samples. The gels were then dried at 60°C during 15 to 20 days. The gelation time and BET surface area have been determined as a function of the concentration of these additions and sol pH. The BET area shows an anomalous behavior with a narrow dip down to 300 m²/g for concentration of SiO₂ powder of the order of 1 wt%. The gelation time exhibits a maximum at a pH of 2.5 and a minimum at a pH of 4.5. Sintering into clear and bubble free amorphous silica has been obtained by heating under controlled atmospheres (CCl₄, O₂, and vacuum) up to 1070°C. The OH content was measured by IR spectroscopy and found to decrease with the chlorination time.

1. Introduction

The sol–gel method for glass preparation is a powerful and alternative technique to conventional glass melting. There are basically two ways to obtain silica glass using this process.

(1) Hydrolysis and polycondensation of silica alkoxides, followed by a densification process [1,2]. The xerogels prepared in this way can be densified at low temperature (~1100°C) but large monolithic pieces are difficult to obtain since cracks usually develop during the densification process. The aerogel route, involving hypercritical drying in an autoclave, allows an easier and safer densification [3]; however the drying technique is difficult to apply on an industrial basis.

(2) Gelation and sintering of colloidal silica powder [4,5]. The gels obtained by this method are usually denser (apparent density ~ 1.0 g/cm³) and mechanically stronger; they can be prepared in large pieces without the appearance of cracks and then densified into glassy components at relatively low temperature. However the microstructure of the gels is not very homogeneous and the method is not recommended for the preparation of multicomponent glasses.

In this paper, we present a study of the pre-

paration and characterization of silica glass using a combination of this two processes in order to take advantages of both methods and find a process which can be applied industrially.

2. Precursors, sol preparation and gel processing

Figure 1 summarizes the flow chart of our process. A first sol was prepared by mixing TMOS and methanol with a volume ratio 1 to 1. A second precursor sol was prepared by mixing Stöber microspheres having 0.15 µm mean diameter (fig. 2) or Cab-O-Sil M5 fumed silica powder with approximately 200 m²/g BET surface area in acidic water (pH = 4.5). The SiO₂ powders were dispersed by ultrasonic agitation for 6 min (Vibracell-Sonics and Materials Inc.). The SiO₂ Stöber particles were prepared by mixing 3 ml TMOS in a solution of 34.4 ml pure deionized water, 65 ml methanol and 22 ml NH₄OH (pH = 12.2).

Both precursor sols were then mixed by magnetic stirring and left to gel. The xerogels were aged for 5 days at 20°C and then slowly dried at 60°C for 15 to 20 days. If the dry gels exhibit cracks, they can be milled and re-used to prepare the second precursor sol.
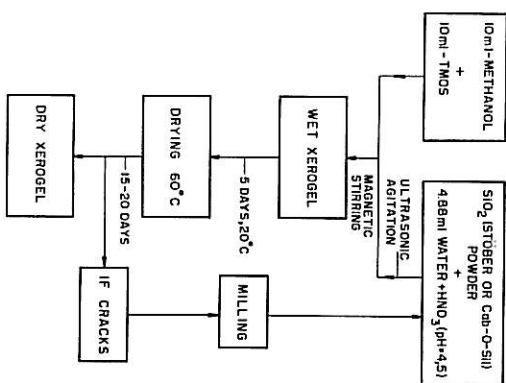
2.1. Influence of the powder concentration

In order to optimize the characteristics of the gel product, the concentration of silica powder used for the preparation of the second precursor sol was varied over a wide range and different properties such as gelation time, BET surface area, volume shrinkage, presence of cracks were measured. Figure 3 gives the variation of the gelation time observed for both types of sols plotted as a function of the ratio $N_S/(N_g + N_S)$, where N_S is the number of moles of Si atoms of the powder and N_g is the number of moles of Si atoms of the alkoxide (TMOS).

The introduction of the Stöber particles has a drastic influence and decreases the gelation time. On the other hand, no appreciable variation has been observed for sols prepared with Cab-O-Sil fumed silica. These variations have an important effect on the characteristics of the dry xerogel (see table 1).

Fig. 1. Block diagram of SiO₂ gel processing.
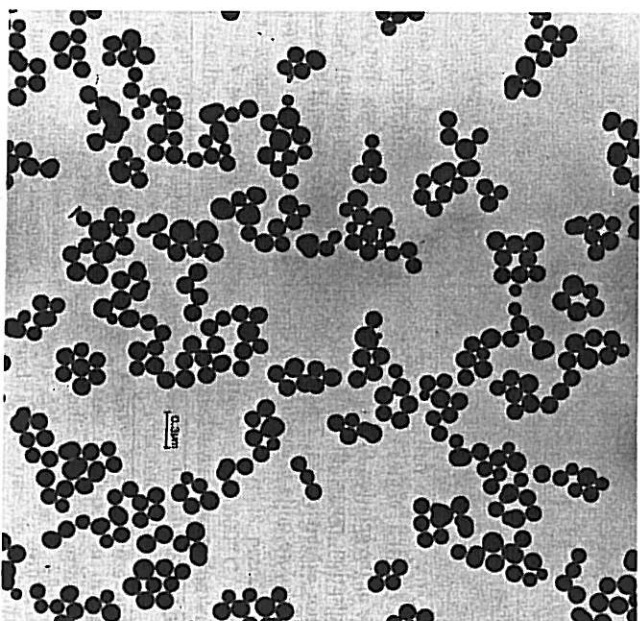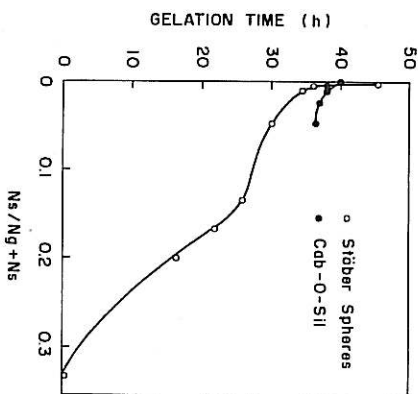

Fig. 2. TEM micrograph of SiO₂ Stöber microspheres.

Fig. 3. Dependence of the gelation time on the silica powder concentration (see text for the definition of N_s and N_g).

The change observed in BET surface area (Micromeritics-Accusorb 2100E) is shown in fig. 4 and some macroscopic characteristics of the dry xerogel are summarized in table 1.

Analyzing these results, we observe for increasing concentration of Cab-O-Sil powder (fig. 4) a continuous and monotonic decrease in BET area. The gels do not present crack but their visual aspect changes from transparent to white opaque. On the contrary, the gels prepared with the Stöber microspheres exhibit a sharp dip of the value of the surface area for $N_s/(N_g + N_s) = 0.01$. The initial sharp decrease in the BET values occurs together with a decrease of the gelation time (fig. 4). In this silica concentration range, the gels are transparent and do not exhibit cracks. This concentration region is therefore quite interesting for
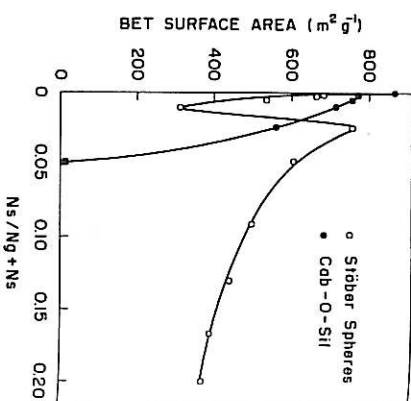
the polymerization process and leads to a strong reinforcement of the gels. For higher powder concentration the gels turn translucent and opaque and start to develop cracks.

Figure 5 shows a TEM micrograph of a dry xerogel with 0.01 Stöber powder concentration.

2.2. Influence of the pH value

The influence of the sol pH on the gelation time has been studied for sols prepared with the Stöber microspheres. For this purpose, we have kept a constant value $N_s/(N_g + N_s) = 0.01$ and have modified the pH between 2 to 6 adding nitric acid. Figure 6 shows the variation of the time of

Fig. 4. Dependence of the BET surface area on the silica powder concentration (see text for the definition of N_s and N_g).

Table 1
Visual aspect of the dried xerogel prepared with different SiO2 powder concentration

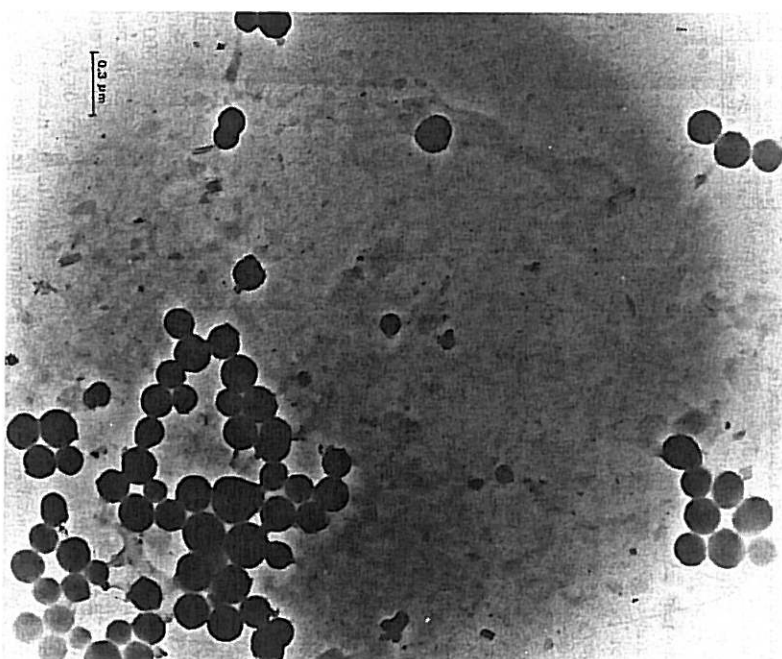| Powder	$N_s/(N_g + N_s)$	Cracks	Dried xerogel characteristics	Volume shrinkage
Stöber	0.001-0.005	No	transparent Gel	not measured
Stöber	0.01	No	translucent Gel	83%
Stöber	0.025	No	opaque Gel	not measured
Stöber	0.04-0.2	Yes	opaque Gel	not measured
Cab-O-Sil	0.001-0.005	No	transparent Gel	not measured
Cab-O-Sil	0.01	No	translucent Gel	83%
Cab-O-Sil	0.025	No	opaque Gel	not measured

Fig. 5. TEM micrograph of SiO2 dried xerogel prepared with a concentration of 0.01 Stöber microspheres.

gelation as a function of the pH values. The behavior is quite similar to that observed by Iler for silica gels [7]. It shows a minimum value of the gelation time for pH ~ 5 where the sol has a minimum stability and a fast gelling with a maximum value for pH ~ 2.5 where the sol has a maximum temporary stability. This behavior seems to be general whether polysilicic acid or relatively large colloidal silica particles are introduced into the sols.

3. Densification study

The densification process has been studied with both types of xerogel having $N_s/(N_g + N_s)$ values

ranging between 0.003 and 0.001 (gels having the lower BET surface area). Figure 7 shows a typical example of the BET surface area measured during a heat treatment, from room temperature to near 1000°C. There is practically no change in the BET value up to 600°C. Above this temperature sintering takes place, and at 1000°C the porous structure is essentially consolidated into a clear impervious silica glass.

Figure 8 shows the special heat treatment schedule developed in order to density the gels into pure dense amorphous silica. This program was established after various tentative attempts and allows one to remove the physically and chemically adsorbed water down to a concentration of 50 ppm; it also eliminates the organic
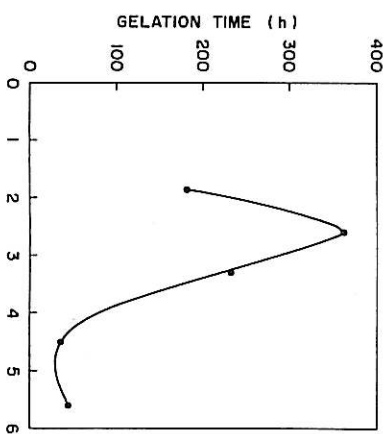
GELATION TIME (h)

Fig. 6. Dependence of the gelation time on the pH of the precursor sol. The sols were prepared using Stöber particles with $N_s/(N_s + N_l) = 0.01$.
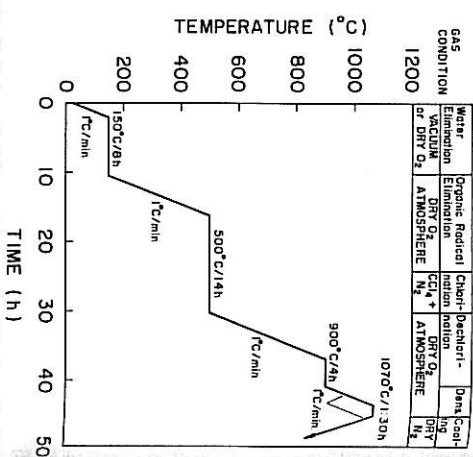
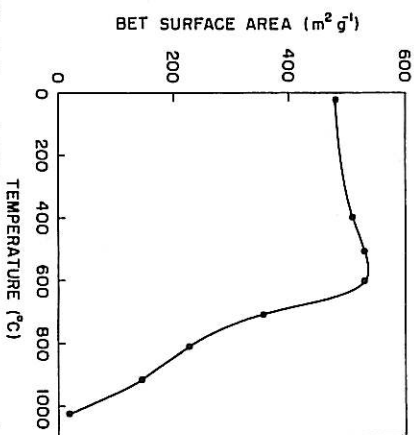BET SURFACE AREA ($m^2\ g^{-1}$)

TEMPERATURE (°C)

Fig. 7. Change in BET surface area with temperature during the densification process. The xerogels have been prepared with Stöber particles with $N_s/(N_s + N_l) = 0.005$.

radicals and avoids the appearance of foaming phenomena due to either OH^- or Cl_2 gases and any crystallization process. The first plateau at 150°C ensures that the physically adsorbed water on the micropore walls leaves the system. It is more efficient if the atmospheric pressure in the reaction tube is reduced or dry O_2 is passed through the reaction tube during the isothermal treatment.

The second plateau at 500°C allows the complete decomposition of the residual organic compounds before the micropore collapse begins. The introduction of dry oxygen at this temperature was found to be necessary. In order to further eliminate the residual OH^- radicals the process was completed by establishing a flow of CCl_4 and dry nitrogen for 5 h. During this process, chlorine radicals are introduced on the surface of the pores. When the OH^- radicals are not removed the samples undergo a foaming process at higher temperature. The chlorine elimination is performed in a pure dry O_2 atmosphere during the slow heating up to 900°C and followed by a 4 h isothermal treatment. At this temperature the samples are still porous but have a much lower BET surface area (fig. 7).

The final treatment performed under vacuum or dry helium atmosphere completes the densification process and allows the obtainment of bubble-free pure SiO_2 glass at temperature of the order of 1070°C.

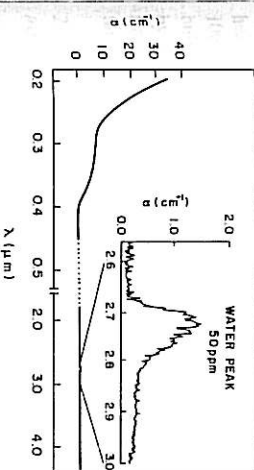Figure 9 shows the optical absorption spectrum measured from the UV region (190 nm) to the

TEMPERATURE (°C)

TIME (h)

GAS CONDITION				
Water Elimination	Organic Radical Elimination	Chlori-nation	Dechlori-nation	Dens Coal-ing
VACUUM or DRY O₂	DRY O₂ ATMOSPHERE	CCl₄ + N₂	DRY O₂ ATMOSPHERE	DRY N₂

150°C/6h   500°C/14h   900°C/4h   1070°C/1.30h

Fig. 8. Firing schedule used for the densification of gel into pure SiO_2 glass.

α (cm^{-1})

λ (μm)

WATER PEAK 50 ppm

Fig. 9. Optical absorption spectrum of dense silica glass. The inset is an amplification of the OH^- region between 2.6 and 3.0 μm.

near IR of a typical SiO_2 glass. This spectrum shows that the OH^- concentration has been reduced down to 50 ppm by weight, a value which is similar to commercial water-free fused silica such as Herasil (Heraeus Quarzschmelze). A small absorption band is observed in the UV region and is probably due to alkali metals present in the starting reagents.

No analysis was performed in order to measure the residual chlorine concentration of the glass samples.

4. Conclusions

Silica glasses of good optical quality and low OH^- content have been prepared by a sol–gel method. The gels were prepared by hydrolysis and polycondensation of TMOS in the presence of silica powder (Stöber particles or Cab–O–Sil M5). The influence of SiO_2 powder concentration on the gelation time, BET surface area, volume shrinkage and the presence of cracks was determined. Pure silica glasses are obtained by densification of gels following a special heat and gas treatment in order to remove almost completely the OH^- ions and avoid any foaming and crystallization phenomena. Spectroscopic analysis shows that the dense silica exhibit traces of alkali metals and an OH^- concentration of about 50 ppm weight. This process has been successfully tested with samples having a final thickness of 1.5 mm.

References

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