Journal of Non-Crystalline Solids 121 (1990) 84–89
North-Holland

EFFECT OF THE METHOD OF PREPARATION ON THE TEXTURE OF TiO_2–SiO_2 GELS

M. RAMÍREZ-DEL-SOLAR, N. de la ROSA-FOX and L. ESQUIVIAS
Department of Structure and Properties of Materials, University of Cádiz, Aptdo. 40, Puerto Real (Cádiz), Spain

J. ZARZYCKI
Laboratory of Science of Vitreous Materials (LA 1119), University of Montpellier II, 34060 Montpellier Cedex, France

The chemical reactivity of $Ti(OBu^n)_4$ was modified through the addition of acetic acid to obtain sonogels of the TiO_2–SiO_2 system by ultrasonic treatment of the alkoxide–water mixture. The characteristics of the resulting gels were compared with those of similar standard gels prepared in alcoholic solution. The influence of composition and method of preparation on the gels was studied. The results of density and BET measurements, thermal analysis and IR spectroscopy indicate that ultrasound drastically affects the texture.

1. Introduction

Glasses of the TiO_2–SiO_2 system show a high thermal stability, a very low thermal expansion and a high refractive index which make them suitable for the fabrication of devices such as telescope mirrors and thin coatings for spacecrafts. Nevertheless, the difficulties in their preparation (high melting temperatures, phase separation) and the limited range of compositions accessible by quenching methods have rendered interesting their preparation at low temperature by sol–gel techniques.

For preparation of homogeneous multicomponent gels, comparable hydrolysis and polycondensation rates of precursor alkoxides are required. Unfortunately, titanium alkoxides hydrolyse much more quickly than those of silicon which implies that a non-random number of Ti–O–Ti bonds will form to the detriment of Ti–O–Si bonds, giving rise to a microheterogeneous gel.

One of the methods proposed to favour the formation of a random network is based on the fact that acetic acid reacts chemically with tetrabutylorthotitanate (TBOT), leading to a new precursor with a lower functionality and therefore a lower gelation rate [1].

On the other hand, ultrasound can be applied to promote a faster hydrolysis of TEOS in a solventless mixture with water [2]. The combined effect of both actions allows for the preparation of homogeneous multicomponent gels with interesting properties characteristic of sonogels. It is the purpose of this work to evaluate the influence of ultrasounds on the texture on the gels.

2. Experimental

2.1. Preparation of samples

The hydrolysis of tetraethoxysilane (TEOS) was obtained by subjecting a mixture of TEOS and 4 mol H_2O/mol TEOS to ultrasonic radiation as described in ref. [3]. The pH of the hydrolysis water was adjusted to 2 by the addition of 12N HCl. The resulting solutions were cooled to 0 °C and then appropriate amounts of a mixture TBOT–AcOH–nBuOH were added under vigorous stirring to obtain sonogels of molar compositions $x TiO_2–(1-x)SiO_2$ $(x = 1,\ 5,\ 10)$, designated as Sx, with the following experimental conditions:

$$[Ti] \simeq 1.0\ \text{mol/l},\ [AcOH]/[Ti] \simeq 5.5,$$
$$[BuOH]/[Ti] \simeq 3.5.$$

The homogeneus liquids were kept in hermetic containers at 50 °C until gelation. The gelling times varied from 40 min for S10 to 90 min for S1.

The corresponding classic gels (Cx) were obtained in the presence of 50 vol.% ethanol. All gelling times for those preparations were several days.

Monolithic pieces of aerogel were obtained after autoclave treatment under hypercritical conditions ($p = 190$ bar and $T = 300$ °C).

2.2 Characterisation

The gels were chemically analysed for Ti and Si content.

The apparent density of aerogels was obtained by mercury volumetry, and their specific surfaces were estimated, using nitrogen adsorption, by the Brunauer–Emmett–Teller method (BET).

Systematic thermal analytical studies were made by differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and dilatometry and crystallisation in these heat treated samples was controlled using X-ray diffraction.

Infrared spectra are obtained from thin slices of hypercritically dried gels submitted to various heat treatments.

These results were compared to those of both classic-(C0) and sono- (S0) pure silica aerogels.

3. Results and discussion

3.1. Chemical analysis

The results shown in table 1 show that hypercritical drying does not modify the final TiO_2 amount in either of the samples.

Table 1
TiO_2 content (%) after hypercritical drying (error ±0.05)

Nominal x	Sonogels	Classic gels
1.00	0.75	0.90
5.00	5.11	5.60
10.00	10.00	10.10

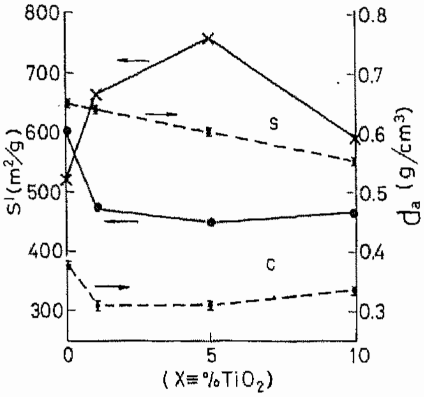

Fig. 1. (———) Specific surface $S' \pm 1$ m²/g and (— — —) apparent density d_a of both sono- (×) and classic (●) series; the lines serve as an eye guide only.

3.2. Density and specific surface

In fig. 1 one can observe the apparent densities d_a and specific surfaces S' of aerogels Sx and Cx.

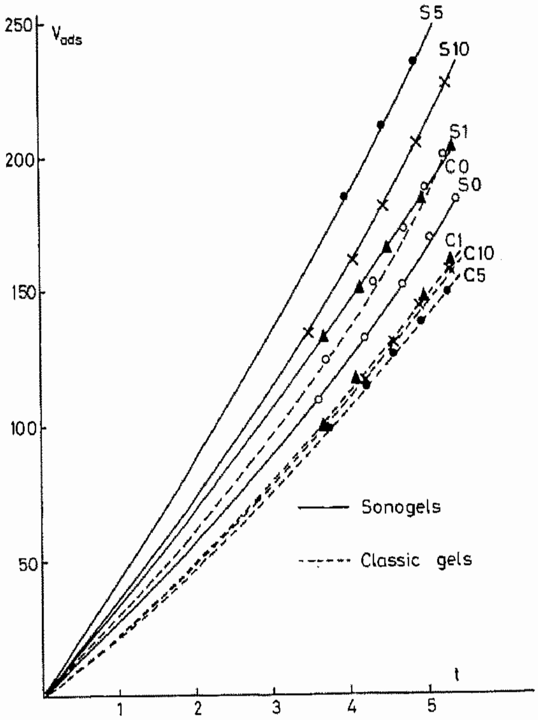

Fig. 2. Adsorption of N_2 on the Cx (— — —) and Sx(———) aerogels, expressed as the adsorbed volume versus the statistical thickness t of the film.

It can be seen that sonogels are approximately twice as dense as classic gels and have specific surfaces that are approximately 50% larger.

The inclusion of Ti in the SiO_2 network modifies the aerogel texture to an extent that depends on the mode of preparation and the amount of TiO_2. While the specific surface of each of the classic gels is almost 25% smaller than that of C0, the surfaces of Sx are greater than that of S0 and depend on x, reaching a maximum at $x = 5$. This result seems to indicate that the textural modification induced by the inclusion of Ti consists, in both cases, of an increase in the pore size. Thus, in sonogels, with small pores size (whether due to the solventless reaction or to a result of the action of ultrasounds) [4,5], S' increases up to a certain value so that an increase in the pore size implies a decrease in the number of pores. This situation is already present in C1 and so no noticeable variations in the specific surface are observed for a higher x.

The adsorption data analysis by the t-method [6] (fig. 2) reveals that no appreciable microporosity is present in these aerogels.

3.3. Thermal analysis

Figure 3 shows the DTA traces for both series of gels. The mass of the specimens used was 10.0 ± 0.2 mg and they were heated at a rate of 15 °C/min. The diagrams show an endothermic peak at about 70 °C, which broadens and increases with x, corresponding to desorption processes. An opposite evolution of the exothermic peak, appearing about 270 °C due to oxidation of organic groups, is observed for the Sx series but not for the Cx series.

The mass of the specimens used for TGA experiments was 20.0 ± 0.1 mg and the heating rate 5 °C/min. The results are presented in fig. 4 in differential form for easier comparison with DTA

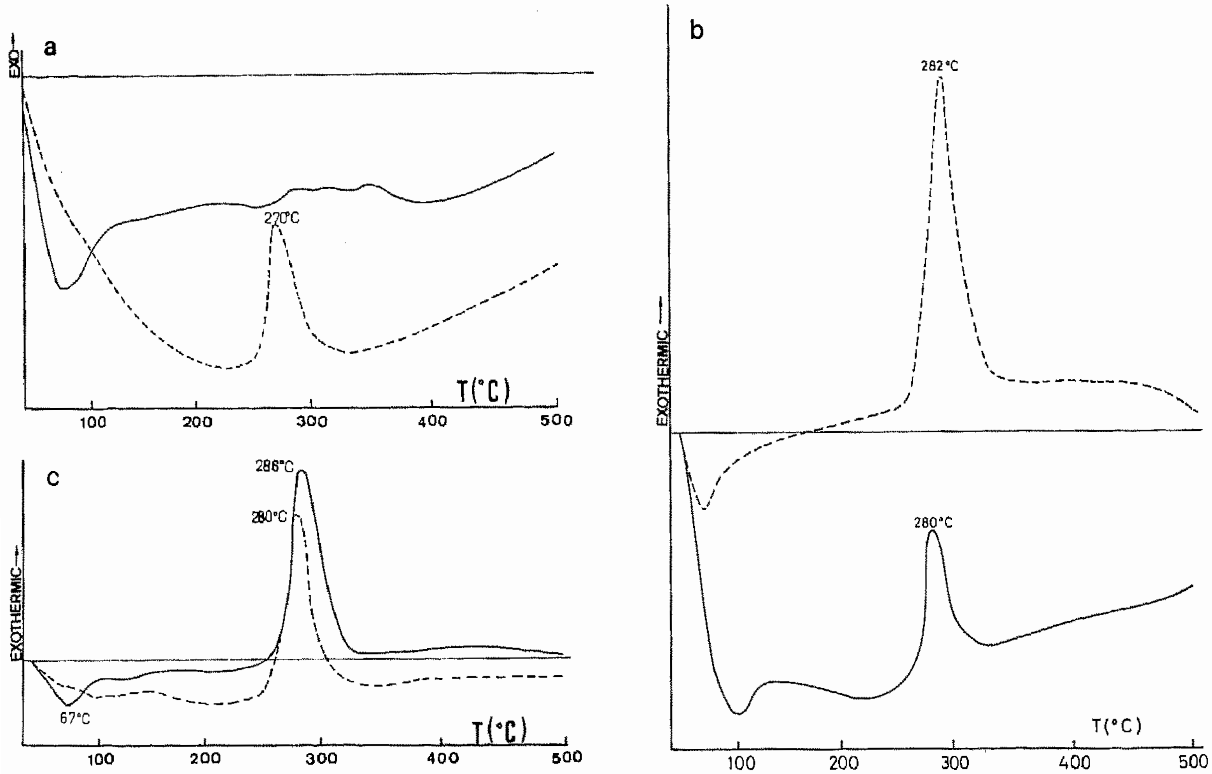

Fig. 3. DTA recordings for SiO_2–TiO_2 (———) sonogels and (— — —) classic gels; (a) $x = 10$, (b) $x = 5$, (c) $x = 1$.

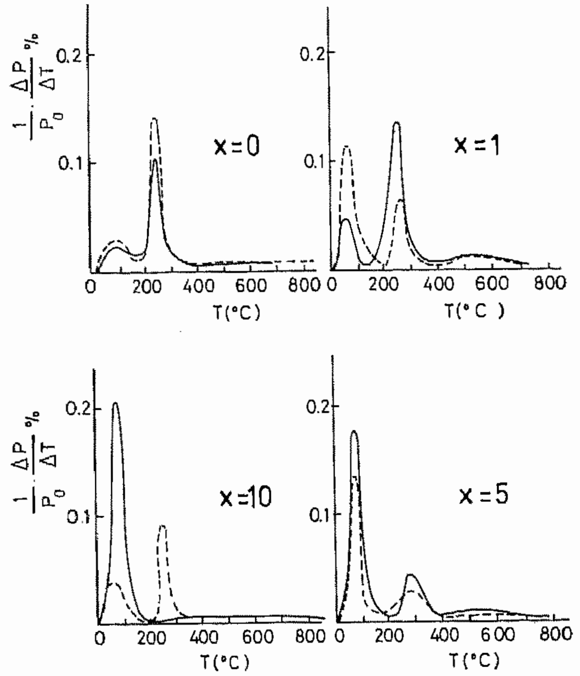

Fig. 4. Differential TGA curves for (— — —) classic gels and (———) sonogels.

curves. The relative weight losses can be assigned as follows.

(1) 50–220 °C evaporation of residual alcohol and water traces which remain adsorbed after drying.

(2) 220–300 °C oxidation of non-reacted –OR groups or those introduced by resterification.

(3) 300–1000 °C condensation of residual –OH groups.

In the sonogels the contribution of the adsorbed compounds becomes more important as the percentage of TiO_2 increases. In the case of Cx, $\Delta p/p_0$ values are strongly determined by the weight loss in the first interval because of large pores. These pores allow an important quantity of water to be adsorbed, except in the case of many organic radicals remaining inside, which is likely to be the case when $x = 10$.

Above 300 °C mixed gels have a behaviour similar to that of pure silica except that the slope rises slightly between 450 and 600 °C, with decreasing x.

The total weight loss of sonogels changes with x as S' changes. This behaviour is also observed in Cx for weight losses at temperatures above 220 °C as shown in fig. 5. When pores with 20–25 Å radius comprise most of the porous volume (as is the case for sonogels as shown by N_2-adsorption porosimetry [7]), this volume may be filled by the residue so that an increase in size allows for retention of a larger amount of residue. This retention does not occur in classic gels which have a wider pore size distribution [7].

Linear shrinkage measurements were carried out on monolithic specimens (9.5 ± 0.4 mm long) with an accuracy of $\pm 0.5 \times 10^{-7}$ mm. The shrinkages are represented in fig. 6 together with those of TGA. These indicate that weight losses due to

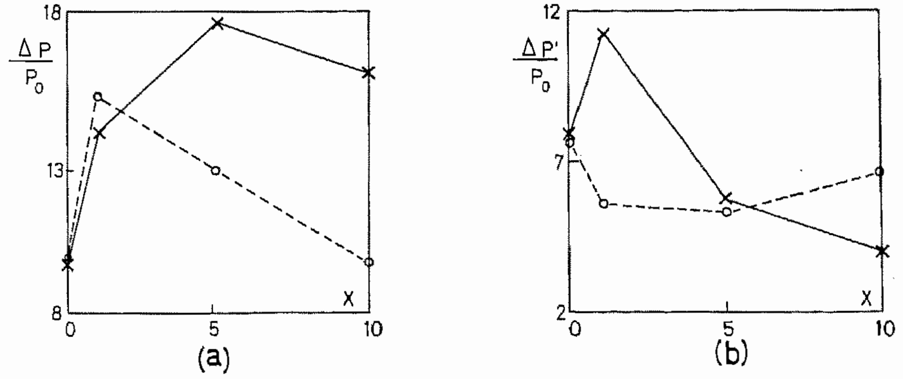

Fig. 5. Weight loss of sono- (×) and classic (o) gels versus the molar composition x; (a) 50–1000 °C, (b) 220–1000 °C (sensibility: 0.1 mg).

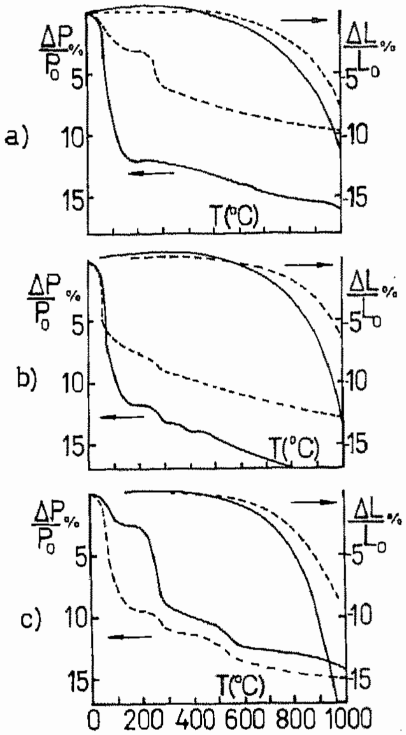

Fig. 6. Linear shrinkage and weight loss measured at 5 ° C/min for (———) sono- and (— — —) classic gels: (a) $x=10$, (b) $x=5$, (c) $x=1$.

structural changes only occur at temperatures above 500 ° C.

It can be noticed that there is a tendency (more pronounced for small values of x) for sonogels to densify at lower temperatures than classic ones. This result is in agreement with the above mentioned porous features, since gels with larger pores must be more difficult to densify. Sintering temperatures increase with the percentage of TiO_2.

The sonogels have a positive thermal expansion coefficient below 500 ° C which may be the result of the action exerted on small pores by trapped chemicals. In fact, this coefficient reaches its maximum for S5 which shows a large desorption and the highest surface/volume ratio.

X-ray diffraction analysis of these samples heated at 1000 ° C shows that crystallisation of small anatase particles occurs.

3.4. Infrared transmission

The IR spectra of C10 and S10 in the range 1400–4000 cm^{-1} were recorded with an IR spectrometer Perkin–Elmer 571 on thin slices of aproximately the same effective thickness, with an error of ± 0.1 mm.

Figure 7 shows the spectra of aerogels before and after different heat treatments at temperatures selected in correspondance with the prominent features of thermal analysis. The heating rate between these temperatures was 15 °/min. The main absorption peaks of interest in this region are attributed as follows:

(A) 3300–3760 cm^{-1}: molecular H_2O and –OH groups.
(B) 2840–3000 cm^{-1}: aliphatic $-CH_2-$ and $-CH_3$ groups.
(C) 1870 cm^{-1}: vibration of SiO_2 network.
(D) 1640 cm^{-1}: vibrations due to SiO_2 network and molecular water.

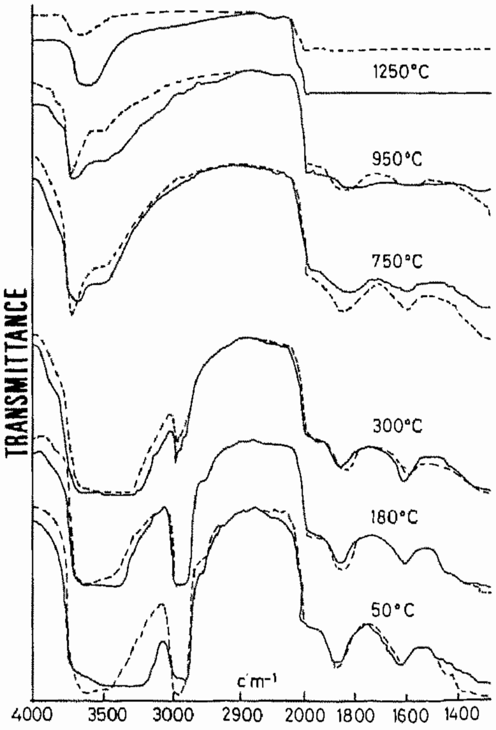

Fig. 7. Infrared spectra of C10 (— — —) and S10 (———) aerogels submitted to heat treatment at temperatures indicated.

The absence of characteristic bands of acetate ligands around 1500 cm^{-1} indicates that acetate is removed during hypercritical drying.

The more significant features of the evolution of bands with temperature can be summarized as follows.

(1) 50–180 °C: displacement of the first band (A) to lower wavelengths and the decrease of the peak intensity of the 1640 cm^{-1} band which indicates a reduction in hydrogen-bonded water content.

(2) 180–300 °C: decrease in the intensity of the peaks of the organic groups together with the widening of the A-band and sharpening of the B-band reveals that the combustion of –OR groups occurs in this range.

(3) At temperatures above 750 °C, there remains a significant amount of SiO–H bonded groups in sonogels which is greater than in classic ones as is indicated by the peak at 3750 cm^{-1} and its associated shoulder.

On the other hand, the SiO_2 bands decrease and disappear at lower temperatures for S10. This fact points to the possibility that the $x(TiO_2)$-$y(SiO_2)$ glass structure is formed at high temperatures and clearly differs from that of pure silica glass. Since the SiO_2 bands are present at low temperatures, it seems that at temperatures below 750 °C the structure, which is strongly conditioned by the surface effects [5], is similar to that of pure silica.

4. Conclusions

A comparison between mixed $xTiO_2$–$(1-x)SiO_2$ aerogels prepared by hydrolysis of alkoxides in alcoholic solution with the corresponding sonogels indicates that the silica gel texture is very much affected by the addition of TiO_2. This modification, which depends on the preparation mode and the amount of titanium, seems to lie in an enlargement of pores. Although neither sono- nor classic gels present microporosity, their textures behave in an opposite way with the TiO_2 content due to the important differences in their average pore sizes.

The sintering temperature increases with x, being always lower in Sx than in their classic counterparts, especially in case of a small Ti content.

Untreated gels have a structure similar to that of pure silica gels. The glass network begins to be formed at a lower temperature in Sx than in Cx, differing from that of pure silica glass.

The preparation mode does not influence the quantity of TiO_2 retained after drying.

This work has been supported in Spain by the project PB86/0225 of the CICYT.

References

[1] S. Doeuff, M. Henry, C. Sanchez and J. Livage, J. Non-Cryst. Solids 89 (1987) 206.

[2] M. Tarasevich, Am. Ceram. Bull. 63 (1984) 500.

[3] N. de la Rosa-Fox, L. Esquivias and Z. Zarzycki, Diffusion and Defect Data 53–54 (1987) 363.

[4] N. de la Rosa-Fox, L. Esquivias and Z. Zarzycki, in Proc. 2nd Int. Symp. on Aerogels, Montpellier, France, 21-23 Sept. 1988, Rev. Phys. Appl. Colloq. C4–24,(1989) C4–233.

[5] L. Esquivias, C. Barrera-Solano, N. de la Rosa-Fox, F.L. Cumbrera and Z. Zarzycki, in: Proc. 4th Int. Conf. on Ultrastructure Processing of Glasses and Composites, Tucson, AZ, 1989, eds. D.R. Uhlmann and D.R. Ulrich (Wiley, New York, 1990) in press.

[6] A.W. Adamson, Physical Chemistry of Surfaces, 4th Ed., (Wiley, New York 1982) p. 590.

[7] F.J. Botana, J.J. Calvino, G. Cifredo, J.M. Rodriguez-Izquerdo, L. Esquivias and M. Ramírez-del-Solar, to be presented at JUPAC-symp. on Characterization of Porous Solids (COPS-II), Alicante, Spain, May 6–9, 1990.