

Synthesis of monolithic silica gels by hypercritical solvent evacuation

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The method of obtaining monolithic dry gels by hypercritical solvent evacuation is presented. The influence of various parameters on the possibility of obtaining crack-free pieces is studied in some detail. The influence of these parameters on the final properties of the gel is also discussed.

1. Introduction

Gel powders of various chemical compositions have been successfully converted into "optically clear" glasses by melting or hot pressing [1-4].

Apart from the great advantage of a low processing temperature, it was recognized that homogeneous glasses could be prepared with high purity in this way [5, 6].

Cost considerations, however, show clearly that neither of the above processes could be advantageous as far as the conventional melting and forming technologies are concerned [7].

The most promising route to obtain glasses from gels is to prepare monolithic (without cracks) dried gels. An additional requirement to obtain monolithic glass is that this material has to be sintered without destroying its integrality.

Thus, glasses prepared from monolithic gels without hot pressing or melting conserve their purity, because of the absence of contamination from dies or containers.

The synthesis of monolithic silica gels has been reported by several investigators. So far only the use of colloidal silica solution led to monoliths which had at least one dimension higher than 10 cm [8, 9].

Some difficulties were encountered when metal alkoxides were used. In fact, drying times from two weeks for silica to a few months for more complicated systems are needed to avoid cracking [10]. Moreover, not much is known about the procedure to prepare gels of a size comparable to that previously mentioned.

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Even in this case, some cracks appear at high temperatures which are necessary to ensure the sintering of the gel.

Our purpose is to present a very simple, fast and reproducible process to obtain dry monolithic silica gels which have at least one dimension higher than 15 cm. The main characteristic of our process is that the evacuation of the solvent within the pores of the gel is carried out under hypercritical conditions.

The parameters affecting the monolithicity of the gels will be presented. The textural and structural features of this kind of gel have also been studied.

2. Gel synthesis and the problem of monolithicity

Two methods are generally used for the preparation of silica gels.

1. Destabilization of a colloidal silica sol.

2. Hydrolysis and polycondensation (dehydration) of silicon alkoxides. The different stages of each of these processes and the characteristic properties of the resulting material have recently been investigated [11].

Whatever the preparation technique, the freshly prepared silica gels contain an appreciable amount of solvent (usually 70 to 90 wt %) which must be eliminated.

A fast drying process either (i) under reduced pressure at room temperature; or (ii) by heating at atmospheric pressure, promotes the crumbling of the gel into grains of few mm³ volume. The

appearance of the cracks depends essentially on two factors: (a) rigidity of the silica network; and (b) compression forces inside the pores, when a liquid–gas curved interface is formed within the pores.

This second factor seems to prevail, in the first approximation, if stresses built up are considered to follow Laplace's law. Capillary stresses are proportional to the pore radius. The change of only the nature of the solvent, e.g. from methanol to water, the value of the stress given by Laplace's law changes by a factor of 3.

It is also clear that cracks appear easily when the freshly prepared gel has a low strength. So a low evaporation rate of the solvent helps to increase the strength of the material and therefore its resistance to capillary stresses.

The procedure of "low evaporation rate" has been used by several investigators for the synthesis of monolithic silica gels [10, 12, 13]. A more rigorous analysis of the parameters affecting the integrality of the gel during drying has been given in previous papers [13, 14]. Thus, several ways were suggested for increasing the possibility of obtaining monolithic gels [15]. A particularly efficient method consists in evacuating the solvent under hypercritical conditions; the surface tension is equal to zero due to the absence of a liquid–gas interface.

This very simple technique was the first used by Kistler in 1932 [16]. This author, in order to obtain gels with a high specific surface area, transformed the hydrogels into alcogels by successive flushes with alcohol, which was then eliminated under hypercritical conditions. The change of the solvent was necessary since water under high temperature and pressure has a high mineralizing effect which leads to the crystallization of the silica gel. The gels prepared by hypercritical evacuation of the solvent were called "aerogels".

Twenty five years later Nicolaon and Teichner [17] used a similar technique to prepare silica aerogels from silicon alkoxides. However no attempt was made in both cases to produce monoliths and to transform them into glasses.

3. Experimental procedure

3.1. Gel preparation

Tetramethoxysilane $\text{Si}(\text{OCH}_3)_4$ supplied by Fluka was used as the silica source. Hydrolysis (unless otherwise specified) was carried out with 4.65 mol of distilled water per mol of tetramethoxysilane

(TMS). Pure methanol was used as the solvent. In some cases, in order to avoid rapid gelation (e.g. with ammonia solution) the preparation was made at 0°C. To increase the miscibility range of the mixture the preparation of the gel was made at 40 to 60°C.

The TMS– CH_3OH – H_2O solution was vigorously stirred for 15 min and then poured into a cylindrical pyrex (R) tube (22 mm diameter, and 250 mm high) before hypercritical evacuation.

3.2. Hypercritical evacuation of the solvent

To evacuate the solvent under hypercritical conditions, the tube containing the mixture (TMS– CH_3OH – H_2O) was put inside an autoclave of 1 l capacity (Fig. 1). The methanol volume was then adjusted in order to attain critical conditions (for pure methanol $P_{\text{cr}} = 240^\circ\text{C}$, $P_{\text{cr}} = 79.7$ bars). The autoclave was hermetically closed and then put inside a vertical furnace. The rise in temperature was automatically programmed. Heating rates from 10 to 200°C h^{-1} were available.

As soon as the critical temperature was reached the vapours of the solvent were evacuated, keeping the temperature constant. When the pressure reached atmospheric pressure, the autoclave was flushed with dry argon for 15 min. The heating was then turned off and the gel was removed when the autoclave was cooled to room temperature. The whole operation (heating, evacuation, cooling) took less than 10 h.

3.3. Definition of some processing parameters

3.3.1. The specific volume

The specific volume (V_M) of the methanol is defined as

$$V_M(\text{cm}^3\text{g}^{-1}) = (V_1 - V_2)/(m_1 + m_2) \quad (1)$$

where V_1 corresponds to the effective volume capacity of the autoclave; V_2 corresponds to the gel volume (container included); m_1 corresponds to the weight of the additional amount of methanol; m_2 corresponds to the weight of methanol used to elaborate the starting solution or gel.

3.3.2. The hypercritical conditions

Since there is no pure methanol inside the autoclave, but a mixture of methanol–water (water provided by the polycondensation reaction + the excess from the stoichiometric hydrolysis) the

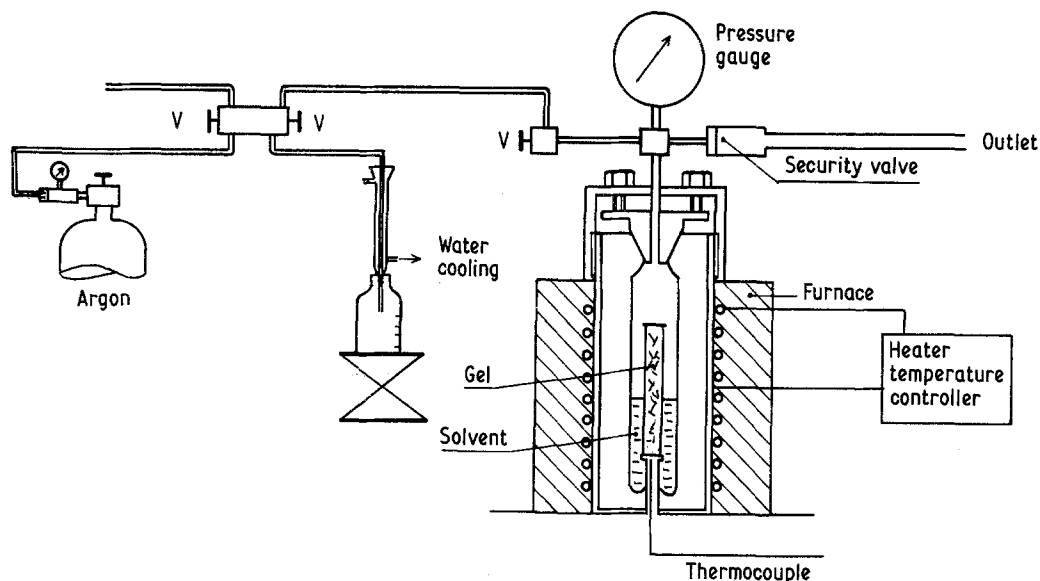


Figure 1 Autoclave equipment for the evacuation of the solvent under hypercritical conditions.

critical conditions were evaluated by using the following approximate relations:

$$T_{cr} = T_{cr}^{H_2O} + f_{CH_3OH}(T_{cr}^{CH_3OH} - T_{cr}^{H_2O}) \quad (2)$$

and

$$P_{cr} = P_{cr}^{H_2O} + f_{CH_3OH}(P_{cr}^{CH_3OH} - P_{cr}^{H_2O}) \quad (3)$$

where f_{CH_3OH} is the weight fraction of methanol in the whole solvent.

3.3.3. Gel code

All silica aerogels will be designated as ACS (which corresponds to the starting solution) where

$$C = \frac{10^2 \times \text{vol. of TMS}}{\text{vol. of TMS} + \text{vol. of "gel" methanol}} \quad (4)$$

The parameter C is related directly to the final porosity of the aerogels since the apparent volume of the aerogel is similar to that of the starting non-aged alcogel.

4. Results and discussions

4.1. Monolithicity

In this work, we are concerned mainly with gels which are formed only inside the autoclave during heating [20]. All aerogels have been characterized by the number of the cracks and the locality where they appear. Some of the parameters which have been dealt with in this study are classified in three categories.

1. Parameters governing the starting solution:

(a) the TMS concentration; (b) the molar ratio H_2O/TMS ; (c) the ammonia concentration of the water.

2. Parameters linked to the cell of the autoclave: (a) amount of the additional solvent; (b) the gel size.

3. Parameters in relation to the furnace: (a) heating rate.

The typical results obtained are shown in Tables I to V. As can be seen from Table I, monolithic aerogels have been prepared with 100% certainty when V_M has a value lower than 5.5. Cracks appear for higher values and their number increases when the evaluation is not well controlled.

The role played by the additional solvent can be explained, if we look at Fig. 2, which shows the liquid-gas equilibrium in a $T-V$ diagram (Fig. 2).

In fact if it is assumed that the specific volume of the methanol used $V_M = V_a$ is higher than the

TABLE I Influence of additional solvent on the monolithicity of a A60S gel. The diameter of the container is 22 mm. M denotes monolithic and C denotes cracked.

$V_m(\text{cm}^3 \text{g}^{-1})$	Special remarks
3.2	M
3.45	M
3.93	M
4.11	M
5.52	C
5.52	C Numerous cracks due to an irregular evacuation
6.50	C

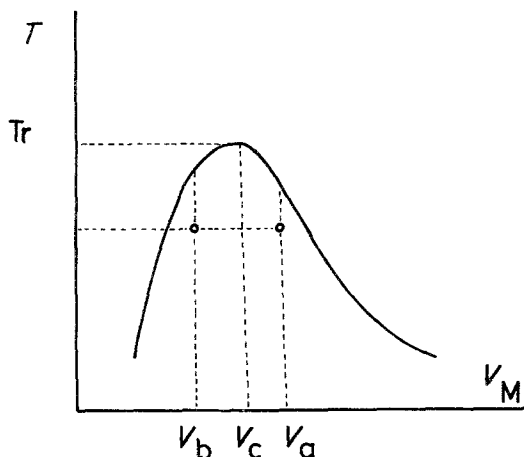


Figure 2 Temperature–volume diagram.

critical one ($V_M = V_{cr}^{CH_3OH} \sim 3.67 \text{ cm}^3 \text{ g}^{-1}$) during the heating of the autoclave, the proportion of the vapour phase is increased and the amount of the liquid decreased (Fig. 2, V_a).

At the temperature T , the whole liquid is transformed into a vapour phase. In such a configuration it is obvious that the solvent is removed from the gel, at least for the upper part of the gel, before the critical conditions are reached.

However, as the value of the surface tension of the liquid decreases when the temperature rises, the possibility of obtaining monoliths even in this case is not excluded.

This fact was supported by our experimental

TABLE II Influence of TMS content on the monolithicity. The diameter of the container is 22 mm

Gel code	Special remarks
A20S	C High shrinkage
A30S	C few number of cracks
A40S	M
A50S	M
A60S	M
A70S	C
A80S	C
	} Heterogeneous gels

TABLE III Influence of ammonia solution on monolithicity for a A60S gel (42 mm in diameter)

Normality of ammonia solution	$\frac{dT}{dt}$ ($^{\circ} \text{C h}^{-1}$)	Special remarks
0	216	M
0.1 N	216	C Two pieces with cracks. The concentration of cracks varies depending on the location of the sample
0.01 N	12	C Same remarks
0.001 N	216	M

results (see Table I). On the other hand, if the specific volume of the methanol ($V_M = V_b$) is less than the critical one, the amount of the vapour phase decreases and at a temperature $T < T_{cr}$ the autoclave may be quite filled up by a liquid (Fig. 2, V_b).

Evacuation of the solvent can in this case be conducted under hypercritical conditions. All aerogels produced in such a way are monolithic. However, since pressure increases very rapidly in this case (liquid compression), we have taken a V_M value in the range 3.5 to 4.5 $\text{cm}^3 \text{ g}^{-1}$ for the following experiments.

Conforming to the above conditions, we obtained monolithic aerogels from 40 to 60% of TMS (Table II).

Due to the inhomogeneity of the solutions, when TMS concentration is higher than 65%, gelation occurs in a heterogeneous way and gives rise to cracked gels. This can be avoided by pre-heating the solution before gelation at 40 $^{\circ}$ C or by using ammonia solution, the molarity of which is 0.005 N for the hydrolysis reaction (Table III).

For the low concentration (A20S, A30S), monolithicity of the gels, for unknown reasons, was more difficult to achieve. Monolithic aerogels from A60S solution with a diameter of 6 to 35 mm were obtained easily, whereas the 42 mm samples cracked systematically into two pieces.

A temperature gradient with increasing size of the gel was assumed to be the cause of this fracture. But experimental results show that this is not the case, because aerogels, prepared with a lower heating rate than the standard one previously used, show the same fracture and in addition a considerable number of small superficial cracks (Table IV).

TABLE IV Monolithicity of A60S gel as a function of the heating rate (42 mm in diameter)

$\frac{dT}{dt}$ ($^{\circ}\text{C h}^{-1}$)	Special remarks
12	C In two pieces with a small number of cracks
96	C In two pieces free of cracks
216	M
216 and then 96	M The change of the heating rate was made at 130 $^{\circ}$ C

Moreover the high heating rate was more favourable for the successful production of monoliths. This behaviour suggests that the temperature of gelation is the critical parameter. In fact, a low heating rate led to a gelation at low temperature. Therefore, the solvent starts to move out of the gel at the early stage of the heating, thus implying probable cracking. If gelation occurs at a higher temperature (rapid heating rate) monolithicity can be achieved with higher probability because the surface tension decreases with increasing temperature (as mentioned above). We have verified this by using two different heating rates (360 $^{\circ}$ C h $^{-1}$ up to 130 $^{\circ}$ C and 96 $^{\circ}$ C h $^{-1}$ above 130 $^{\circ}$ C). Cracks appeared at a low temperature (Table IV). Another test, which confirms the above assumption, is that when hydrolysis is made with ammonia solution (see Table III) aerogels are completely cracked. In fact, in this case, gelation occurs at room temperature from a few minutes to 1 h depending on the concentration of NH $_4$ OH. The higher the concentration of NH $_4$ OH, the more

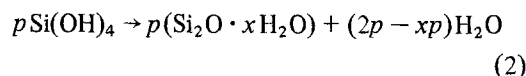
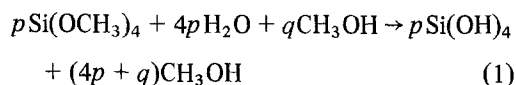
rapid will be the gelation, and therefore the probability of cracking is higher.

Finally, another parameter, which plays a role in the gelation process and consequently in the monolithicity of the aerogels, is the molar ratio of H $_2$ O/TMS. Some of the results concerning this parameter are shown in Table V.

An optimization of the gelation and processing parameters presented previously enables us to obtain monolithic silica aerogels in the wide range of concentration of TMS (20 to 70%). Fig. 3 shows typical silica aerogels of various sizes and shapes.

4.2. Chemical composition

Both reactions (shown below) give an approximate description of the gelation process



where p and q are the moles of TMS and CH $_3$ OH respectively used to prepare the solution and x the number of moles of H $_2$ O which remain on the silica framework. A chemical analysis from the solvent evacuated and condensed during the autoclaving operation shows, however, a proportion of methanol less than that predicted by Equations 1 and 2.

It is clear that a considerable amount of methoxy groups remain in the aerogel structure. It

TABLE V Influence of ratio $r = (\text{mol H}_2\text{O})/(\text{mol TMS})$ on the monolithicity of silica aerogels

Gel	Concentration of catalyst, ammonia aqueous solution (N)	r	Remarks
A70S	0	3	C Small number of cracks.
	0.005	3	M
	0.005	4	M
	0	4.65	C Small number.
	0	4.65	M Aged 1 h at 40 $^{\circ}$ C before autoclaving process.
A60S	0	2.5–4.65	M
		5	C
		5	M Aged 1 h at 40 $^{\circ}$ C before autoclaving process
A50S	0	4–6	M
A40S	0	4–6	M
A30S	0	4	M
		6	C Small number.
A20S	0	4	M
		6	C

was also shown that these organic groups are chemically linked to the silica framework and may be oxidized by heat treatment around 270 to 350°C [11].

It is assumed that, during the autoclaving operation, an exchange reaction between silanol groups and methanol takes place.

The value of the rate of this reaction has been studied in the case of silica gels [18].

Taking into account the above considerations, we can describe the gelation process by the following reactions.

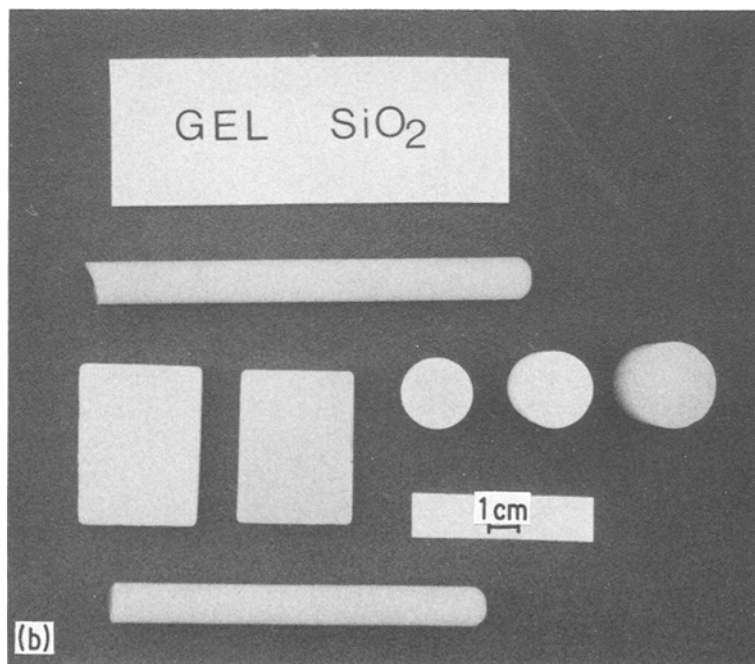
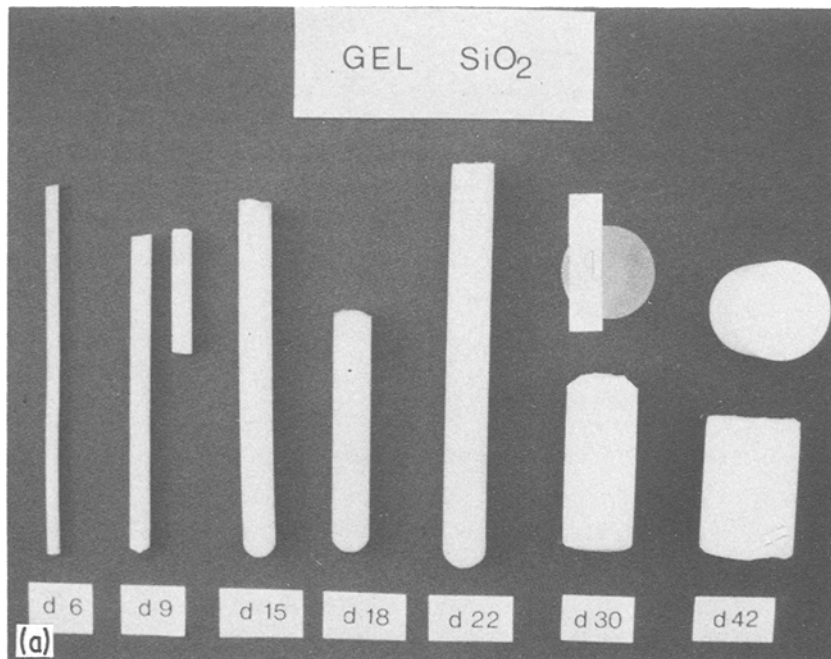
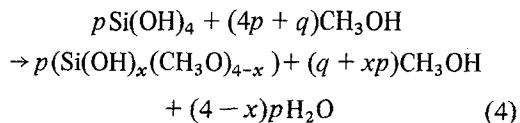
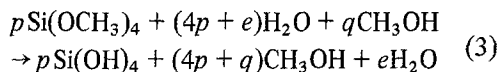


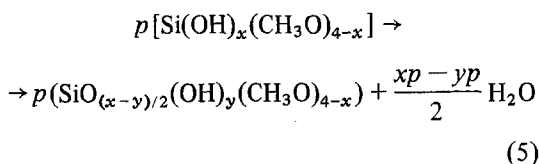
Figure 3 A60S gels of various sizes and shapes. (a) Gelation occurs in autoclave. (b) gelation and ageing are made at room temperature before the autoclave treatment.

TABLE VI Chemical composition of A60S aerogel

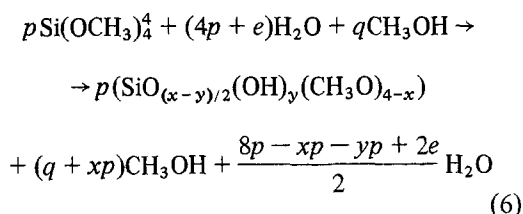
Time (h)	Chemical composition	Ratio (C/H in weight)
5	SiO _{1.67} (OH) _{0.4} (CH ₃ O) _{0.24}	2.55
8	SiO _{1.79} (OH) _{0.1} (CH ₃ O) _{0.31}	3.60

TABLE VII Textural properties of aerogels as a function of the Si(OCH₃)₄ content in the starting solution

Aerogel	Density	Specific surface area (BET) (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Porosity (%)	Average pore radius (nm)	Average particle radius (nm)
A50S	0.19	358	4.7	91.3	26.2	3.8
A60S	0.25	369	3.4	88.5	18.4	3.7
A70S	0.28	384	3.1	87.4	16.1	3.5



Thus the balance of the above reactions leads to



where e is the excess of water molecule used to hydrolysis reaction. The reaction [6] allows, in the case of the aerogels, the estimation of their chemical composition. In fact p , q and e are known and can be measured with a very high degree of accuracy (10^{-4}). Therefore x and y can be estimated by using the following equations:

$$x = \frac{m_{\text{CH}_3\text{OH}}}{32p} - \frac{q}{p} \quad (7)$$

$$y = 8\frac{q}{p} + \frac{2e}{p} - \frac{m_{\text{H}_2\text{O}}}{9p} - \frac{m_{\text{CH}_3\text{OH}}}{32p}$$

where $m_{\text{CH}_3\text{OH}}$ and $m_{\text{H}_2\text{O}}$ represent the weights of methanol and water, respectively, condensed during evacuation of the solvent.

Table VI shows that the carbon content of the aerogel increases with the length of heat treatment. The aerogels which have been left for a long time in the autoclave before evacuation of the solvent showed highly hydrophobic characteristics, whereas gels left for less than 2 h were more hydrophilic.

4.3. Textural and structural properties of silica aerogels

During this study, we have observed that exact reproducibility of the specific surface area of a given chemical composition of a gel was very difficult. As an example, A60S aerogels prepared during different times of the year (change in room temperature from 5 to 10°C) results in different specific surface areas. The standard deviation from the average is as high as $\pm 150 \text{ m}^2 \text{ g}^{-1}$ which is five times higher than the standard errors of the BET measurements.

Parameters such as room temperature, stirring time of the solution and also ageing time outside the autoclave, were expected to be the reasons for such a discrepancy.

In fact, we have verified that, if the preparation procedure is perfectly reproduced and the temperature is controlled within $\pm 2^\circ \text{C}$, the value of the specific surface area of a given gel is within the standard error of the measurement (10%).

Fig. 4 shows the evolution of the specific sur-

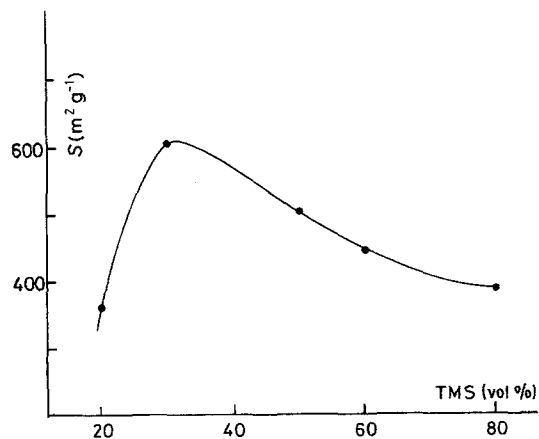


Figure 4 Specific surface area of aerogels as a function on their TMS content.

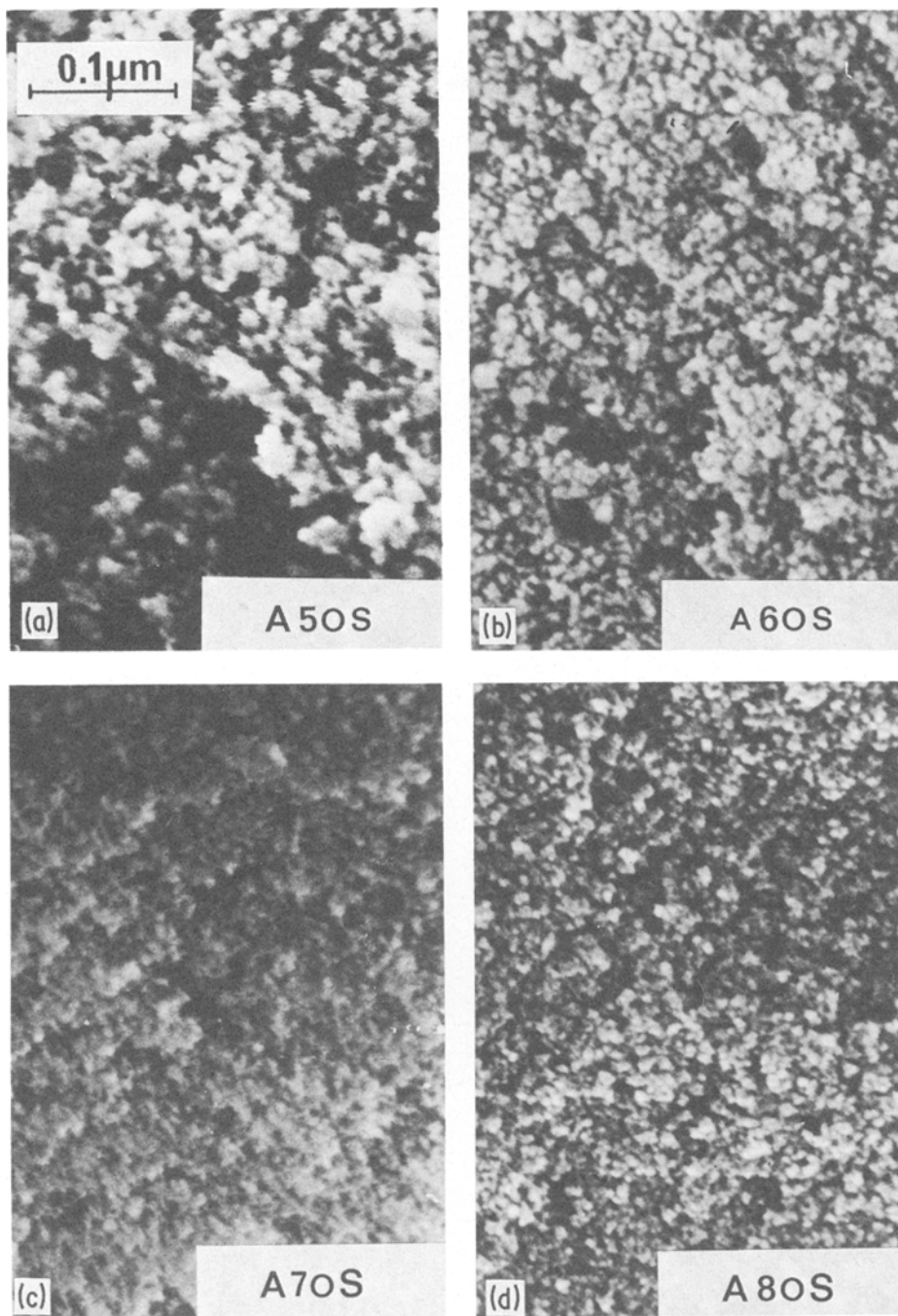


Figure 5 Scanning electron micrographs of various gels.

face area of various silica aerogels prepared in strictly the same conditions. As can be seen, the specific surface area passes through a maximum for aerogels having between 30 to 35 vol% of TMS.

For concentrations lower than 30%, there are not enough particles to give a high reticulate silica

network. Therefore, when concentration is lower than this value, there is a growth of particles. For concentrations higher than 30 vol% of TMS, we believe that the decreasing specific surface area is due to an increase of the connectivity of the polymeric chain rather than to a growth of the particles. This is probably true, since SEM (Fig. 5)

TABLE VIII Influence of the temperature of gelation on the textural properties of A50S aerogels

Temperature of gelation	Density	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Porosity (%)	Average pore radius (nm)	Average particle radius (nm)
25° C	0.34	448	2.5	84.7	11.1	3.0
During the temperature rise of the autoclave	0.91	358	4.7	91.3	26.2	3.8

for highly concentrated aerogels do not show any appreciable difference in particle sizes.

Silica aerogels are constituted by spherical particles of 3 to 4 nm (primary particles). The porosity varies between 84 to 91%, indicating a very "open" structure. However great differences in texture may be seen between two aerogels if their temperature of gelation is different. Aerogel A50S prepared at room temperature and a similar aerogel for which the gelation occurred within the

autoclave during the rise in temperature show very different textural properties (Table VIII).

TEM of these two above mentioned aerogels are shown in Fig. 6.

The structure of aerogels was studied by IR transmission spectroscopy on bulk material, the thickness of which was about 1 mm. The absorption bands of silica and water are shown in Fig. 7. Some absorption bands due to the chemically linked methoxy groups indicate that the gel is

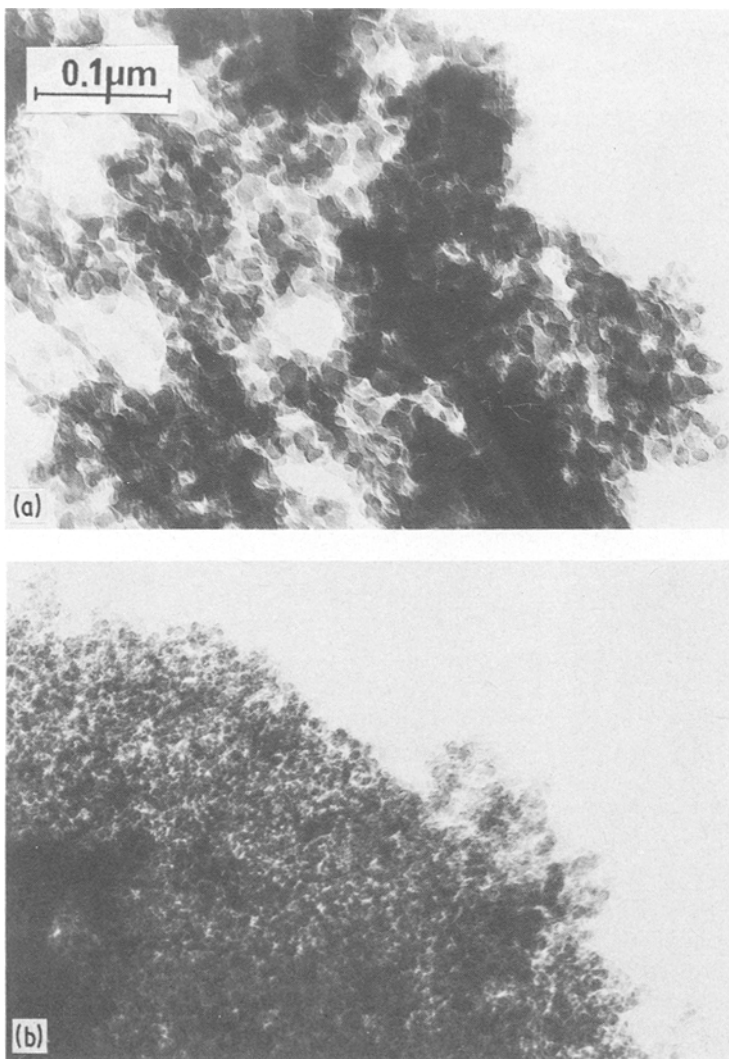


Figure 6 TEM of aerogels A50S. (a) Gelation occurs during the temperature rise of the autoclave. (b) gelation occurs at room temperature.

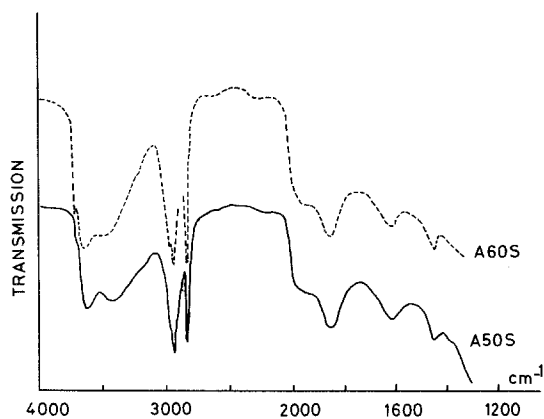


Figure 7 IR transmission spectra of aerogels.

strongly hydrophobic. The attribution of these bands and their evolution with the temperature have been described in a previous publication [19].

5. Conclusion

The hypercritical evacuation of the solvent within the pores of an alcogel leads to monolithic samples only under precise experimental conditions. Thus, TMS concentration, the molar ratio of water to TMS, the nature of the hydrolysis medium and also some processing factors such as the amount of additional methanol, heating rate and the size of gel were found to more or less affect the integrity of the resulting aerogels. Optimization of these parameters allows us to obtain monolithic silica aerogels which have diameters from 6 to 42 mm with the length of 250 mm in a autoclave of 1 l capacity. The whole operation from the solution preparation to the monolith obtention takes no more than 10 h.

Samples with different geometries also can be obtained if the initial solution is gelled and aged at 40 to 60°C before hypercritical evacuation. The autoclaving process gives to a aerogel, the formula of which is $\text{SiO}_x(\text{OH})_y(\text{OCH}_3)_z$. x , y , z may be known from condensed vapors which escape from the autoclave during evacuation.

Finally, it should be stressed that because of the absence of a liquid phase within the pores, monolithic silica aerogels were densified more rapidly and more easily than ordinary silica xerogels.

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