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Glasses from aerogels

Part 1 The synthesis of monolithic silica aerogels

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Experiments carried out to obtain monolithic silica aerogels are reported. The different ways to synthesize silica aerogels from alkoxides are investigated. The manner by which the critical point of the solvent can be reached is discussed as a function of the nature of the solvent. Physical parameters such as the amount of additional solvent or pressure, play a very important role in the direction of the liquid–vapour interface displacement during the heating of the autoclave. Some experiments performed using hypercritical drying with CO_2 liquid are also mentioned.

1. Introduction

A few years ago, research on the synthesis and characterization of aerogels underwent considerable development. Aerogels were initially studied for the catalytic properties expected from their large specific surface area [1–5]. However, recent works have shown their fascinating physical properties, such as extremely low thermal conductivity [6, 7], sound velocity as low as $100\,\mathrm{m\,sec^{-1}}$ [7, 9, 10] and fractal structure of the solid skeleton [11, 12]. Moreover, this solid exhibits a refractive index close to 1 and can be used as Cerenkov detectors [13, 14]. All these properties are adjustable by modifying the parameters used in the synthesization process.

Further interest in this material arises from the fact that Prassas and colleagues [15, 16] have sucessfully achieved the conversion of monolithic silica aerogel into bulk silica glass at a low temperature (1000° C).

The purpose of the present work was to develop the different processes leading to the synthesis of aerogels in the silica system as precursor for glass preparation. The results are reported here, and in Part 2 [17].

2. Principle of hypercritical drying

Hypercritical drying was initially developed by Kistler [1, 2] to obtain materials having large pore volume and specific surface area. He studied the conditions of drying for different kinds of gels such as oxide gels, cellulosic gels and gelatine. For the materials obtained, where the liquid within the porous structure was replaced by air, he proposed the term "aerogel". However, the gels were synthesized in an aqueous medium and due to the mineralizing effect of H_2O at high pressure and temperature, Kistler was contrained to exchange the water by alcohol, ether or other solvents. In more recent works scientists have used the ability of some gels to be synthesized in an alcoholic medium, so the solvent exchange was no longer necessary [3, 18]. Teichner and co-workers [3, 4] have enlarged this technique to cover a wide range of oxide gels. They determined the parameters which provide useful catalist aerogels having high specific surface areas.

2.1. Goal of the process

The goal of the process is to minimize the capillary stresses which appear during the drying of the gel. These stresses occur when the air–liquid interface is in contact with the solid part of the gel and are dependent on the interfacial energy, γ. For any liquid, γ decreases with temperature as presented below.

$$\gamma = A(T_c - T - T_x) \qquad (1)$$

This linear relationship applies up to $T = T_c - T_x$ where $T_x \simeq 6°\,C$, T_c is the critical temperature and A is a constant related to the liquid. The values of γ, A and T_c are given in Table I for some liquids.

Eötvös [19] has established that γ is related to the molecular mass, M, and the specific volume, V, of the liquid according to the relation

$$(MV)^{2/3}\gamma = K(T_c - T - T_x) \qquad (2)$$

Finally, it is possible to eliminate γ if the liquid is heated to T_c. Figures 1a and b show that above the critical point the liquid and the gas are not distinguishable and no interface exists. It should be noted that in

TABLE I Parameters allowing calculation of γ as a function of temperature

	γ (erg cm^{-2}) (20° C)	A (erg cm^{-2} °C^{-1})	T_c
H_2O	72.6	0.21	375
Heptane	20.26		27
Chloroform	25.3		54
Ethanol	22.3	0.10	240
Methanol	22.65	0.105	240
Acetone	23.3	0.111	235
Acetic acid	27.42		57
Benzene	28.88	0.11	48

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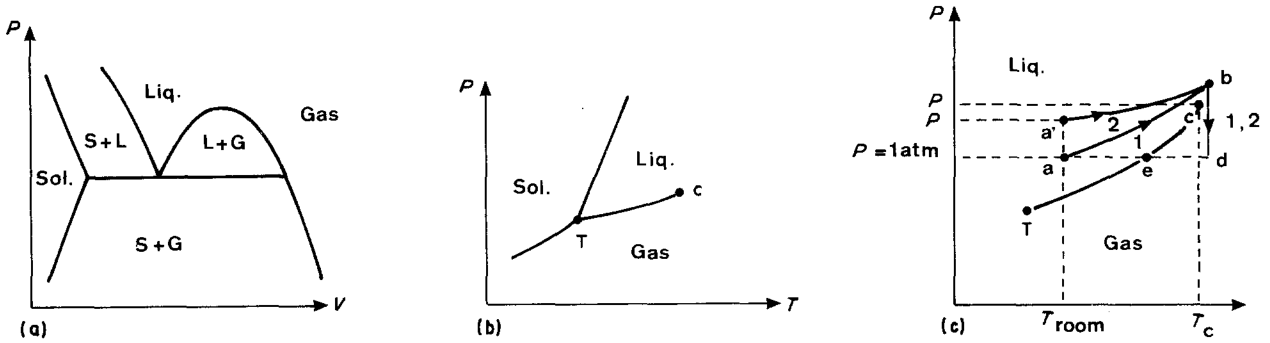

Figure 1 Phase diagram of liquid–gas equilibrium for a pure compound using different representations: (a) pressure–volume, (b) pressure–temperature, (c) ways to bypass the critical point.

the case of a heterogeneous medium (liquid–gel) the critical parameters of the liquid could be changed due to the reactivity between the solid and the liquid phase. This reactivity is revealed by the esterification reaction occurring in the autoclave between the silanol groups at the surface of the gel and the alcohol in the liquid phase [20]. This esterification is more extreme when the alcohol is of low molecular weight. Moreover, it is well known that while at room temperature the silica is insoluble in alcohol, at high temperature (500° C) the solubility is not negligible and thus the nature of the liquid is modified [21]. On the other hand, the silica dissolution–redeposition phenomenon may be significant in that instance.

2.2. Experimental process

Table II gives values of the critical parameters of the most common solvents used for the synthesis of inorganic gels. As a result of the temperature and pressure required, the experiments must be performed in an autoclave. Figure 1c shows two different methods allowing the aerogels to be obtained. In method 1, the gel and its liquid are heated together in the autoclave. Heating of the liquid induces an increase in pressure inside the autoclave. However, to reach point b (a pressure higher than P_c at temperature T_c) it is necessary to add an extra volume of liquid to the autoclave. In method 2, no extra volume is added, but a preliminary pressure, P_0, of an inert gas is applied from the beginning of heating. This procedure has been perfected in the laboratory with a prepressure of argon [22] and used recently with nitrogen gas [23]. Whichever route is used to reach point b, the pressure is then decreased isothermally to atmospheric pressure, by a gentle venting of the autoclave. Solvent vapours are allowed to condense outside the autoclave. When the whole volume of solvent is released (point d), the autoclave can be cooled to room temperature. However, to avoid condensation of solvent on the walls of the autoclave (point e) the autoclave must be flushed with an inert gas. No solvent droplets can thus come into contact with the gel and thereby destroy it.

TABLE II Critical parameters of common liquids

	P_c (MPa)	T_c (°C)
Methanol	7.9	240
Ethanol	6.3	240
1-propanol	5.1	265
1-butanol	4.3	290
Acetone	4.6	235
Ether	3.6	192.5
H_2O	22	375

2.3. Hypercritical drying of gel in the presence of two liquids

Up to this point we have only been concerned with a gel whose pores are saturated by a pure liquid. In the real case the solvent is a mixture of alcohol and water, and thus the hypercritical conditions will be completely modified compared to the pure solvent.

The curves $AC_{(CH_3OH)}$ and $BC_{(H_2O)}$ in Fig. 2a are the liquid–gas equilibrium curves for the pure liquid. They are, in fact, the boundaries of the volume corresponding to the two-phase equilibrium domain (gas–liquid) of the diagram. The pressure–composition and temperature–composition diagrams, shown in Figs 2b and c, respectively, are estimated from thermodynamic data. In the Fig. 2c the curve at $P = 1$ atm corresponds to the classical boiling diagram of the methanol–water mixture [24].

Fig. 3 shows the estimated P–T diagram constructed for methanol–water. The critical locus is calculated from both values given in Figs 2b and c. These values are estimated from an additivity formula expressed in weight per cent (see below). A P–T curve for a composition of about 50% is plotted. The border of this curve is sharp, indicating that there is no retrograde condensation. The critical locus shows no point at a higher temperature or pressure than that of water.

In the well-known ethanol–water system, the diagram shows an extremum for 95 wt % [25]. Similar behaviour is also observed for other systems, including the 1-propanol–water system [26] and 2-propanol–water [27] which are of interest in sol-gel processing. These last cases may be very useful because we can expect to surpass the critical point at a lower pressure and temperature, due to the presence of the azeotropic point which induces a plateau in the P–X curves at low temperatures and for composition rich in alcohol [27]. However, for temperatures higher than 250° C this plateau is usually absent. Cox [28] has shown how it is possible to evaluate this change graphically.

Usually silica aerogels are made from low molecular weight species of silicon alkoxides dissolved in low alcohol. If the synthesis is conducted with an alcoholic solvent different from the by-product alcohol of hydrolysis, the final liquid will be a three-component

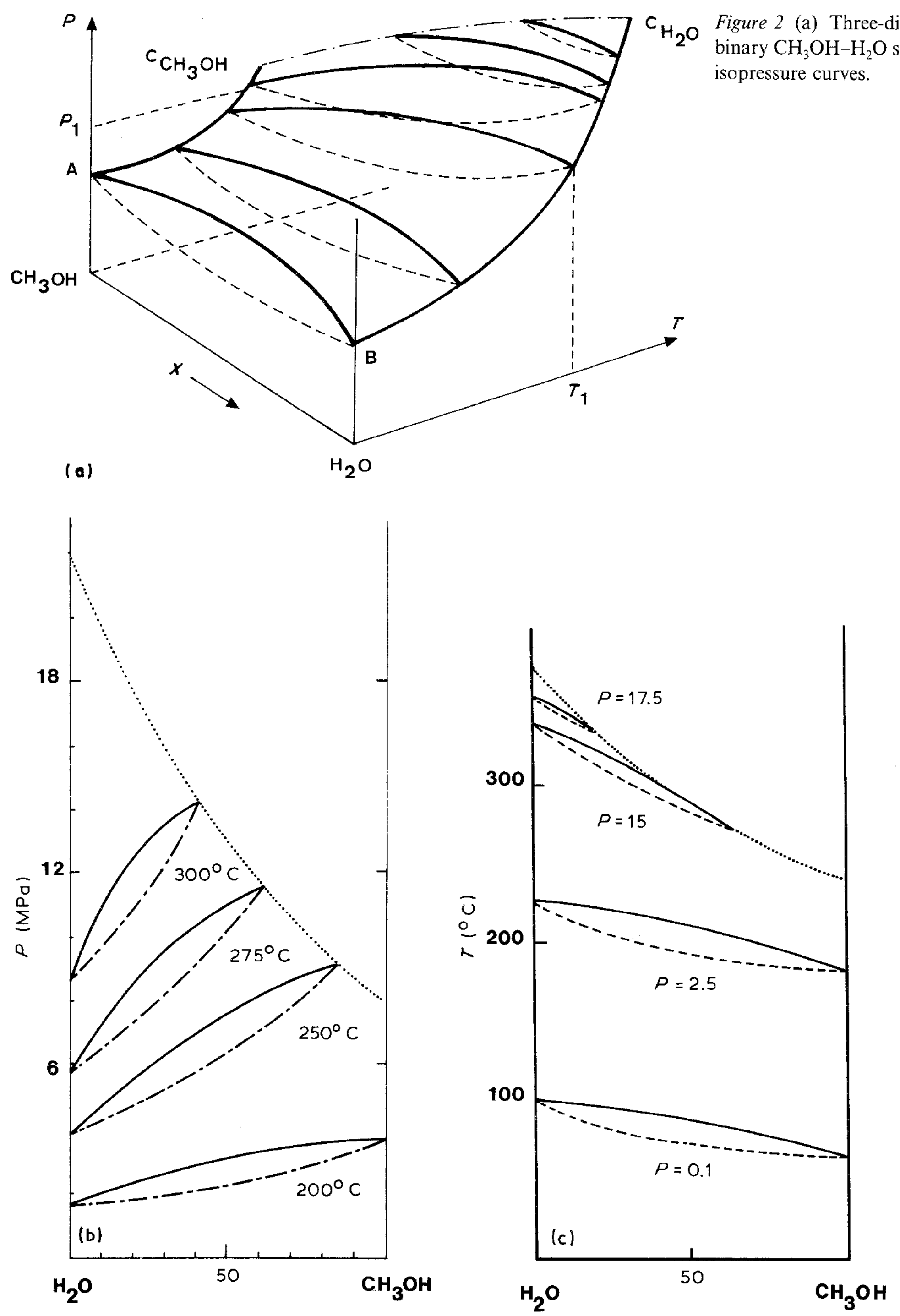

Figure 2 (a) Three-dimension representation of the binary CH_3OH-H_2O system. (b) Isothermal curves, (c) isopressure curves.

system. In silica aerogels, methanol-ethanol-H_2O [29] is the most common system. For alcohol with a higher molecular weight an immiscibility range occurs. The phase diagrams are then much more complex [30].

For a rough estimate of the critical parameters of the binary solution CH_3OH-H_2O, the following relations may be used

$$T_c = x_{(H_2O)}\, T_{c(H_2O)} + y_{(CH_3OH)}\, T_{c(CH_3OH)}$$

$$P_c = x_{(H_2O)}\, P_{c(H_2O)} + y_{(CH_3OH)}\, P_{c(CH_3OH)}$$

where $x_{(H_2O)}$ and $y_{(CH_3OH)}$ are the weight per cent of H_2O and CH_3OH. For a classical gel synthesized with a volumetric ratio TMOS/CH_3OH equal to 1.5 and hydrolysed with 4 mol water per mol TMOS, the liquid impregnating the pores of the alcogel would be a binary liquid containing between 15 and 35 wt % H_2O, depending on the completion of the hydrolysis

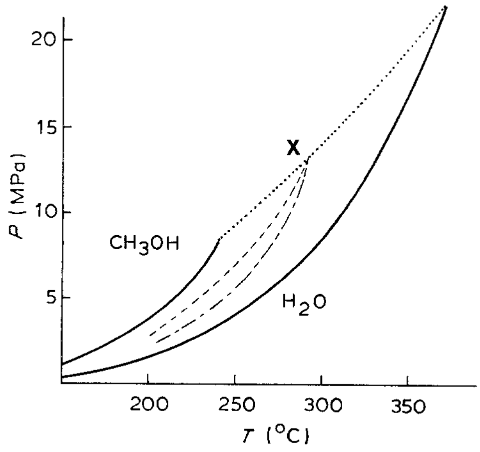

Figure 3 Planar representation of the critical locus curve in the binary CH_3OH-H_2O system. X represents the expected curve obtained for an equimolar composition. (— —) boiling curve, (–·–·–) dew point curve.

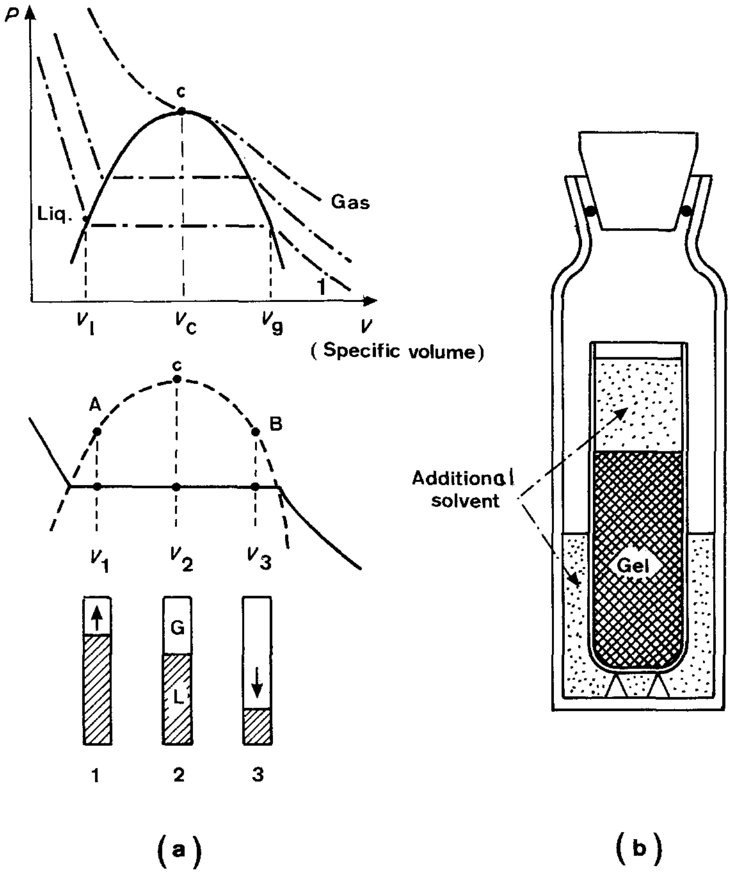

Figure 4 Role of the additional solvent in the evolution of the liquid-gas interface as the temperature increases.

and polycondensation reactions. Thus, the estimated critical parameters are $T_c = 260$ to 285° C, and $P_c = 10$ to 13 MPa. This calculation is done on the basis of results previously obtained in the C_2H_5OH–H_2O system for which the critical locus is approximately a straight line, as a function of composition expressed in weight per cent [31]. Refinements in calculations may be done using Gilliland's relation [32].

3. Hypercritical drying with an extra volume of solvent

Figure 4a shows the pressure–specific volume equilibrium diagram. The line corresponds to an isotherm for which the temperature is lower than the critical temperature (for example, room temperature). At this temperature, the specific volumes of the liquid and gas are, respectively, V_l and V_g. When $T = T_c$, V_l and V_g are identical and equal to the critical specific volume, V_c (see Table III for various liquids of interest).

Now let us consider the autoclave partially filled by the liquid at room temperature. Because the volume of the autoclave is constant, the specific volume is higher when the liquid volume in the autoclave is low. During the heating treatment the volume of the autoclave remains constant and as a consequence so does the specific volume. An increase in temperature can then be regarded as a vertical straight line on the equilibrium P–V diagram.

In case 1 (Fig. 4a) the liquid–gas system evolves from V_l to A which corresponds to the presence of the liquid alone; the liquid–gas meniscus rises. To be sure that this phenomenon will occur during autoclave heating, an extra amount of solvent must be added (Fig. 4b). A similar argument for case 3 shows that the liquid transforms into a gas at B and the liquid–gas meniscus falls. If the specific volume is equal to V_2 ($V_2 = V_c$), the meniscus does not move and disappears when $T = T_c$. Thus without additional solvent in the autoclave, a gel corresponds to case 3. During the increase in temperature, the liquid is transformed into gas and the skeleton of the gel will not always be totally immersed in the liquid. This phenomenon occurs at a temperature which depends on the preparation parameters of the gel (concentration of TMOS, H_2O, ageing, etc). Then, during heat treatment, only the upper part of the gel undergoes capillary stresses. The bottom part may remain wetted with the solvent when T reaches T_c. No textural evolution of the bottom part of the aerogel will therefore be detected. However, if this phenomenon appears at a high temperature, the γ value will be low and the possibility of obtaining monoliths even in this case is not excluded. With a low γ value the capillary stresses may have a low intensity and the solid part of the gel can resist without cracking. This fact was supported by our experimental results (Table IV) obtained with hypercritical drying of methanol. In such a case the critical volume is about $3.67\,cm^3\,g^{-1}$. As a consequence, shrinkage of the gel during the hypercritical drying step will be unusually high due to the effect of low capillary stresses.

TABLE III Critical specific volume of common liquids

Solvent	V_c ($cm^3\,g^{-1}$)
CH_3OH	3.67
C_2H_5OH	3.62
H_2O	3.1
CO_2	2.2

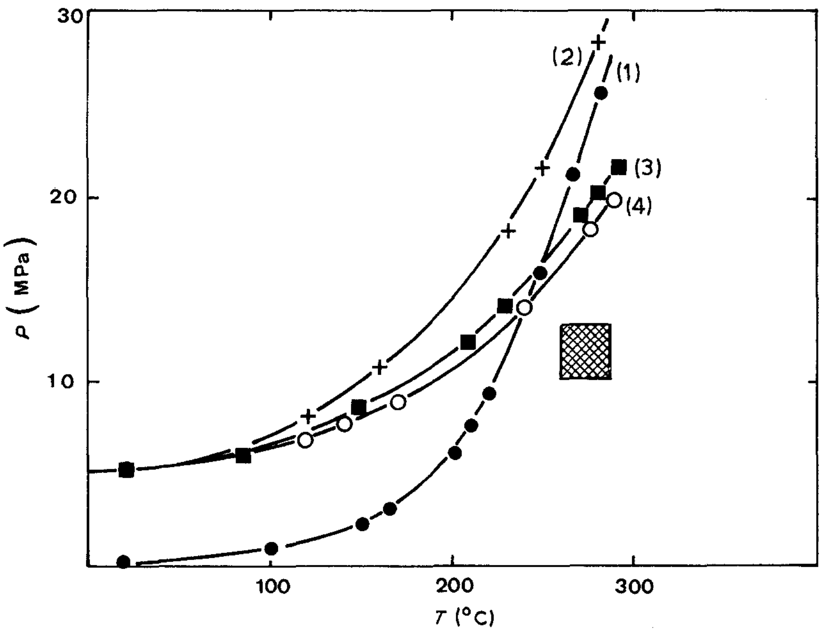

Figure 5 Experimental curves obtained with different amounts of additional solvent and with a prepressure (see text for details). Cross-hatched area: estimated value of the critical point of the liquid.

4. Hypercritical drying with a prepressure of inert gas

For a given temperature, the surface tension of a liquid decreases as the pressure increases [32]. Fig. 5 shows several experimental P–T curves obtained in a 1 l autoclave containing a gel whose volume is $130\,\mathrm{cm}^3$. Curve 1 corresponds to route 1 of Fig. 1c with an extra volume, V_0, of methanol of $250\,\mathrm{cm}^3$ ($V_\mathrm{m} = 3.7\,\mathrm{cm}^3\,\mathrm{g}^{-1}$).

Another way of reaching the hypercritical point is to apply a prepressure of an inert gas, for example nitrogen or argon. During heat treatment, the pressure increases due to expansion of the inert gas as well as to evaporation of the liquid. Curves 2, 3 and 4 correspond to the increase in pressure as a function of temperature for three different experiments: curve 2 for a prepressure of argon of 5 MPa and an extra volume of $150\,\mathrm{cm}^3$ CH_3OH; curve 3 for a prepressure of argon of 5 MPa and an extra volume of $50\,\mathrm{cm}^3$ CH_3OH; curve 4 for a prepressure of argon of 5 MPa and no extra volume of CH_3OH.

In all cases the pressure obtained at 300° C was higher than 14 MPa and all the aerogels were monolithic. Thus, application of an inert gas pressure extends the possibilities of hypercritical drying and the addition of an extra volume of solvent becomes unnecessary. However, the last case produces an aerogel whose shrinkage is greater than that of the others: it is thought that the solid part is not entirely wet by the liquid for the entire duration of the experiment. It is clearly apparent that this shrinkage is low when the extra pressure is high. No shrinkage is usually observed on base catalysed aerogels [33]. However, if the prepressure is not high enough, shrinkage occurs [34].

TABLE IV Monolithicity of the aerogel as a function of the experimental specific volume

V ($\mathrm{cm}^3\,\mathrm{g}^{-1}$)	Remarks
3.2	monolithic
3.45	monolithic
3.7	monolithic
3.93	monolithic
4.11	monolithic
5.52	cracked
6.5	cracked

5. Hypercritical drying after a solvent change

In the hypercritical drying of alcohol, the high critical parameters can induce reactions in the autoclave. As was mentioned above, esterification reactions take place between the OH groups at the surface of the gel and methanol. That phenomenon results in the formation of $SiOCH_3$ groups which are responsible for the "hydrophobic" property of the aerogel.

It has been shown [33] that for binary SiO_2–B_2O_3 and SiO_2–P_2O_5, an important loss in B_2O_3 and P_2O_5 happens during the hypercritical drying treatment. These losses are due to the corrosive nature of alcohol and water at elevated temperatures and pressures. The B–O–Si and P–O–Si bonds are no longer stable and a partial dissolution of the gel occurs. The effect is analogous to leaching which is very severe due to the high specific surface area of the material. With gels other than silica, another phenomenon may occur during the autoclaving heat-treatment. High pressure and temperature increase the tendency of the amorphous gels to crystallize. In order to avoid these phenomena, it is possible to perform the hypercritical drying with a less reactive solvent for which the critical parameters are lowered.

Table V summarizes the most common solvents which allow a gentle hypercritical drying. In this procedure it is necessary to extract the alcohol present in the gel and to exchange it with the chosen solvent. Then, the new solvent is released by hypercritical

TABLE V Solvents used for a gentle hypercritical drying

Solvent	P_c (MPa)	T_c (° C)
CO_2	7.3	31.1
Freon	3.8	28.9
N_2O	7.2	36.5
SO_2	7.8	157

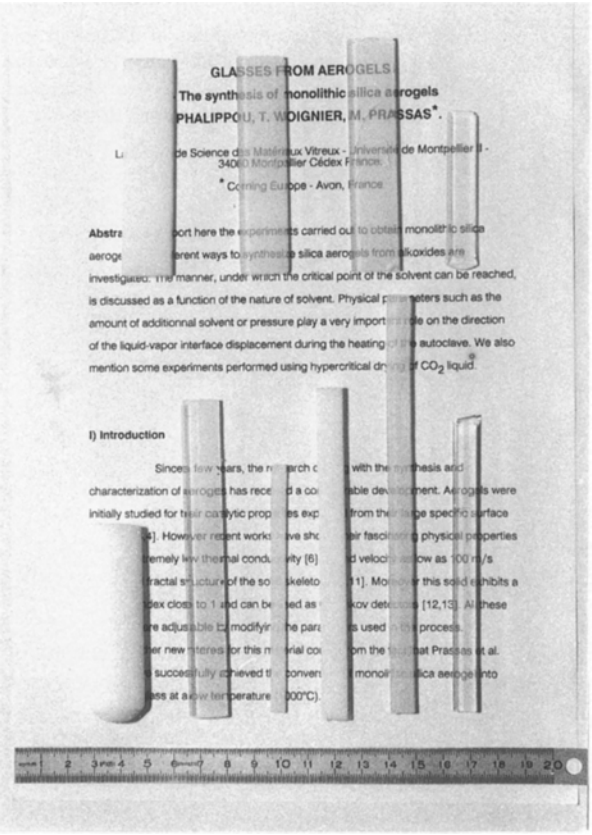

Figure 6 Monolithic silica aerogels with different shapes, sizes and transparencies.

drying. It is worth noting that the exchange must be done between two miscible solvents, otherwise the formation of an interface due to the immiscibility would again induce capillary stresses as previously pointed out by Kistler [1, 2].

Monolithic silica aerogels have thus been obtained by replacing the methanol (or ethanol) by CO_2 liquid. The experimental conditions for hypercritical drying are 50° C and 7.5 MPa [22–37]. This method has been successfully used to study the gel film formed at the surface of a leached glass [37] and also to the synthesis of alkali borate aerogels [39]. Silica aerogels of large dimensions are easily obtained using this method [40], but aerogel–glass conversion has not yet been reported.

To favour the solvent change (alcohol–CO_2), intermediate solvents may be useful such as acetone, diethylether or amyl acetate. Miscibility diagrams of more complex systems are given in the literature [41].

6. Conclusion

The problem of making monolithic gel as a precursor for the synthesis of glass may be solved by hypercritical drying. With this process, the capillary stresses responsible for cracking during the drying step are avoided, and large samples of monolithic materials are obtained (Fig. 6) in a few hours. Different methods are offered, allowing synthesis of silica aerogels with different characteristics and also multicomponent materials. However, in each case the effects of pressure, temperature and additional solvent on the solid part of the gel must be known to prevent great change in the gel structure. We have presented some ways with which to overcome the various difficulties encountered for silica aerogels. The objective is now to determine the best conditions for transforming these aerogels into dense silica glasses.

References

1. S. S. KISTLER, *Nature* **127** (1931) 741.
2. *Idem*, *J. Phys. Chem.* **36** (1932) 52.
3. G. A. NICOLAON and S. J. TEICHNER, *Bull. Soc. Fr. Chimie* **5** (1968) 1906.
4. S. J. TEICHNER, G. A. NICOLAON, M. A. VICARINI and M. E. E. GARDES, *Adv. Colloid. Interface Sci.* **5** (1976) 245.
5. J. B. PERI and R. B. HANNAN, *J. Phys. Chem.* **64** (1960) 1526.
6. J. FRICKE, in "Aerogels", Proceedings of the 1st International Symposium, Würzburg, edited by J. Fricke, (Springer, Berlin 1986) p. 94.
7. O. NILSSON, A. FRANSON and O. SANDBERG, *ibid.* p. 167.
8. R. CALEMCZUK, A. M. DE GOER, B. SALCE, R. MAYNARD and A. ZAREMBOWICH, *Europhys. Lett.* **3** (1987) 1205.
9. M. GRONAUER, A. KADUR and J. FRICKE, in "Aerogels", Proceedings of the 1st International Symposium, Würzburg, edited by J. Fricke (Springer, Berlin, 1986) p. 167.
10. T. WOIGNIER, J. PELOUS, J. PHALIPPOU and R. SEMPERE, *J. Physique* **49** (1988) 289.
11. D. W. SCHAEFER and K. D. KEEFER, *Phys. Rev. Lett.* **56** (1988) 2199.
12. R. VACHER, T. WOIGNIER, J. PELOUS and E. COURTENS, *Phys. Rev. B* **37** (1988) 6500.
13. M. CANTIN, M. CASSE, L. KOCH, R. JOUAN, P. MESTRAU, D. ROUSSEL, F. BONNIN, J. MOUTEL and S. J. TEICHNER, *Nucl. Instrum. Methods* **118** (1974) 177.
14. S. HENNING and L. S. SVENSON, *Phys. Scripta* **23** (1981) 63.
15. M. PRASSAS, Thesis, Montpellier (December 1981).
16. M. PRASSAS, J. PHALIPPOU and J. ZARZYCKI, *Glastechn. Ber.* **56** K (1983) 542.
17. T. WOIGNIER, J. PHALIPPOU and M. PRASSAS, *J. Mater. Sci.* **25** (1990) 3118–3126.
18. J. B. PERI, *J. Phys. Chem.* **70** (1966) 2937.
19. R. EÖTVÖS, *Wied Ann. Phys.* **27** (1886) 448.
20. S. KITAHARA, K. TAKADA, T. SAKATA and H. MURAISHI, *J. Colloid. Interface Sci.* **84** (1981) 519.
21. R. K. ILER, "The Chemistry of Silica" (Wiley, New York, 1979).
22. T. WOIGNIER, Thesis, Montpellier (January 1984).
23. C. A. M. MULDER and J. G. VAN LIEROP, in "Aerogels", Proceedings of the 1st International Symposium, Würzburg, edited by J. Fricke (Springer, Berlin, 1986).
24. D. F. OTHMER and R. F. BENENATI, *Ind. Eng. Chem.* **37** (1945) 299.
25. C. A. JONES, E. M. SCHOENBORN and A. P. COLBURN, *ibid.* **35** (1943) 666.
26. P. S. MURTI and M. VAN WINKLE, *J. Chem. Eng. Sci.* **3** (1958) 72.
27. F. BARR-DAVID and B. F. DODGE, *J. Chem. Eng. data* **4** (1959) 107.
28. D. J. COX, *Ind. Eng. Chem.* **15** (1923) 592.
29. A. O. DELZENNE, *J. Chem. Eng. Sci.* **3** (1958) 224.
30. G. M. SCHNEIDER, *Adv. Chem. Phys.* **17** (1970) 1.
31. J. GRISWOLD, J. D. HANEY and V. A. KLEIN, *Ind. Eng. Chem.* **35** (1943) 701.
32. E. R. GILLILAND, *ibid.* **28** (1936) 212.
33. T. WOIGNIER, J. PHALIPPOU and R. VACHER, in "Better Ceramics through Chemistry III", Vol. 21, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (Materials Research Society, Pittsburgh, 1988) p. 647.
34. J. C. VAN LIEROP, A. HUIZING, W. C. P. M. MEERMAN and C. A. M. MULDER, *J. Non-Cryst. Solids* **82** (1986) 363.

35. B. LEFRANCOIS, Y. BOURGEOIS, *Chim. Ind. Génie Physique* **105** (1972) 989.
36. T. WOIGNIER and J. PHALIPPOU in Proceedings of the 1st International Workshop on Non-Crystalline Solids, San Feliu de Guixols, edited by M. D. Baro, N. Clavaguera (World Scientific, Singapore, 1986) p. 415.
37. P. J. LEA and S. A. RAMJOHN, *Microsc. Acta.* **83** (1980) 291.
38. S. FILLET, J. PHALIPPOU, J. ZARZYCKI and J. L. NOGUES, *J. Non-Cryst. Solids* **82** (1986) 232.
39. C. J. BRINKER, K. J. WARD, K. D. KEEFER, E. HOLUPKA, P. J. BRAY and R. K. PEARSON, in "Aerogels", Proceedings of the 1st International Symposium, Würzburg, edited by J. Fricke (Springer, Berlin, 1986) p. 57.
40. P. H. TEWARI, A. J. HUNT and K. D. LOFFTUS, *Mater. Lett.* **3** (1985) 363.
41. A. W. FRANCIS, *J. Phys. Chem.* **58** (1954) 1099.

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