

# Effect of Drying Processes on the Texture of Silica Gels

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## ABSTRACT

Peculiar xerogels and aerogels constituted by a silica network, made of spherical fully dense silica particles having the same size, are investigated by adsorption of nitrogen at 77.4 K. Comparison of sorption data between materials dried via different methods, gentle drying at room temperature, alcohol supercritical drying and CO<sub>2</sub> supercritical drying, shows that the specific surface area is associated to the particle sizes and necks established between them during drying and not to the sample density. The dissolution-redeposition of silica, which occurs in the alcohol supercritical drying process, induces a decrease of specific surface area and consequently an increase in the mechanical properties comparatively to CO<sub>2</sub> supercritical drying. Investigating pore volume measurements as a function of dwell time, which is the interval of time allowing a pressure change of 0.01%, we corroborate that for compliant materials the full volume can not be detected because of capillary stresses. So the time required to perform correct measurements of the pore volume decreases with sample bulk density increase and elastic properties increase. All these experiments qualitatively corroborate the theory proposed previously.

**Keywords:** Nitrogen Sorption; Pore Volume; Aerogel; Alcohol Supercritical Drying; CO<sub>2</sub> Supercritical Drying

## 1. Introduction

Silica xerogels and aerogels are materials exhibiting a high porous volume. They are characterized by pores having a size smaller than 100 nm. Moreover they are brittle and the mechanical properties values of some peculiar light aerogels can be considered as the lowest among the family of inorganic materials.

According to the small pore sizes, gas condensation easily occurs and induces capillary stresses. These capillary stresses do not have any effect on porous materials with acceptable mechanical properties. Conversely they induce significant strain in the case of aerogels whose elastic modulus is in the range of a few MPa. This strain is easily evidenced with lightweight aerogels having a porosity higher than 0.9. During a nitrogen adsorption-desorption isotherm experiment a length variation results from the compression of the sample which occurs as nitrogen molecules condense within the pores. This length change has been followed using an optical device [1] and more recently has been quantified using a linear variable differential transducer [2]. Thus the porous volume measured using adsorption technique is far smaller than the true porous volume of aerogel.

Previously other causes have been evoked to explain

the discrepancy between the true and measured porous volume. The first one concerns the range of pore size investigated using nitrogen adsorption technique. If the dried gel contains pores the size of which is higher than 50 nm, they will not be taken into account in the measurement. This possibility does not agree with permeability measurements which indicate that silica gels are mainly constituted by pores of very small size.

Another possible reason for such a discrepancy comes from the mean curvature of liquid nitrogen adsorbed on the material surface [3]. Condensation stops if the curvature reaches a value close to zero and consequently the true porous volume is not measured [4,5].

In this paper, we investigate the effect of capillary forces on the porous volume of peculiar gels constituted by a silica network made of spherical fully dense silica particles having the same size.

## 2. Experimental

### 2.1. Sample Preparation

Silica gels are obtained from a commercial colloidal silica solution called Ludox LS (Trade mark) consisting of spherical particles of about 14 nm size. Stabilization at pH equal to 8.2 is due to Na<sup>+</sup> ions which are located at the surface of dense silica particles. The calculated spe-

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cific surface area of powder is  $195 \text{ m}^2\cdot\text{g}^{-1}$ . Gelation is performed by adding hydrochloric acid aqueous solution. Different dilutions permit to synthesize two series of gels at controlled pH. The samples are labeled NX or AX (N for pH 7 and A for pH 5). X is related to the dilution and increases when the dilution of the starting gelling solution increases.

After gelation all the gels are soaked with ethanol. Three solvent exchanges are performed. The total solvent exchange requires one month to obtain a gel with pores mainly filled by ethanol. Traces of water are about 1% as measured with Karl Fischer method.

Gels are dried using three different processes. The first one consists in a gentle drying at room temperature. The resulting material is a conventional xerogel. The second one is dried in an autoclave by rising the temperature at a rate of  $100^\circ\text{C}/\text{h}$  up to  $300^\circ\text{C}$ . So the pressure increases up to 15 MPa. The duration of the depressurization step is four hours. Materials are called alcohol supercritically dried (SCD) aerogels. The last series of gels is dried using  $\text{CO}_2$  instead of alcohol in supercritical drying. This treatment consists to exchange alcohol with liquid  $\text{CO}_2$  at  $10^\circ\text{C}$  and 6 MPa for 2 h 30 min then increasing the autoclave temperature up to  $50^\circ\text{C}$  and the pressure up to 10 MPa. The time of depressurization is six hours.

## 2.2. Nitrogen Adsorption-Desorption Measurements

The bulk densities of samples  $\rho_a$  are evaluated from weight and linear dimensions. Due to the large shrinkage, the bulk density of xerogels is less accurate than that of aerogels. The theoretical total porous volume  $V_{\text{pth}}$  is calculated from the relation:

$$V_{\text{pth}} = \frac{1}{\rho_a} - \frac{1}{\rho_s}$$

where  $\rho_s$  is the skeletal density of silica which is  $2.2 \text{ g}\cdot\text{cm}^{-3}$  [6]. The porosity of this material is totally open. The specific surface area is obtained from nitrogen adsorption-desorption isotherm at 77 K using BET theory [7]. The accuracy is about 4%. Normally for rigid porous materials, when the nitrogen relative pressure  $P/P_0$  approaches 0.99, the volume of adsorbed nitrogen must correspond to the porous volume. We have chosen to estimate the mean pore size using BJH theory applied to desorption step [8]. Taking the same sample, different runs are performed by changing the dwell time. The equilibrium time which is imposed by the investigator, is the interval of time allowing a pressure change of 0.01%. It has been varied from 5 to 240 seconds.

According to previous reported recommendations [9] adsorption nitrogen experiments are performed on small pieces of monolithic samples. The sample weight varies between 0.12 to 0.24 g, the lowest weight corresponding

to the lowest density in order to characterize the same samples volumes. Samples are cut with a razor blade from a monolithic one to avoid crushing which can result in a partial densification of lightweight aerogels.

## 2.3. Young Modulus Measurements

The mechanical behaviors of samples are investigated by the nanoindentation technique. Indentation experiments are carried out on samples monoliths exhibiting flat surfaces using a home made instrumented microindenter [10]. Typical force versus penetration depth curves are obtained. The standard way to determine the elastic modulus is by using the initial slope of the unloading curve [11]. Because of the aerogels brittleness difficulties are encountered to obtain an adjusted surface for indentation, so only a few samples have been characterized. The bulk modulus  $K$  is then calculated making use of the relation  $K = E/3(1-2\nu)$  with the Poisson's ratio taken to be 0.2 [12].

## 3. Results

The density of samples dried under conventional conditions (xerogels) varies from 1.15 to 1.3. The bulk density of aerogels is within the range  $0.19 - 0.48 \text{ g}/\text{cm}^3$  depending on the dilution in aqueous solution of the starting silica sol and on the supercritical drying technique. The shrinkage of xerogels is of great extent even though the gels analysed here are constituted by an assembly of silica spherical particles with size and shape not modified during the drying step. Moreover, since both supercritical drying procedures are performed on the same gel samples, it is possible to compare the densities of obtained aerogels (Table 1). Aerogels obtained from alcohol supercritical drying show a slightly lower density than those issued from  $\text{CO}_2$  supercritical drying whatever the dilution of the starting solution allowing to prepare the gel. This feature is not presently well understood since  $\text{CO}_2$  is relatively inert and is expected unreactive versus silica. We hypothesis that largest pores shrink during the

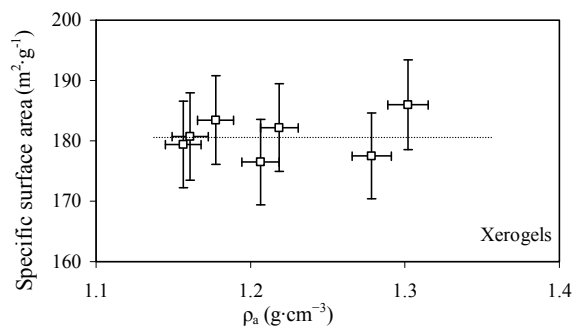
**Table 1. Bulk density in  $\text{g}/\text{cm}^3$  for xerogels and alcohol or  $\text{CO}_2$  SCD aerogels. Density values are depending on dilution and pH of the gelling solution (accuracy on the density 1%).**

	Alcohol SCD	$\text{CO}_2$ SCD	Xerogels
N1	0.432	0.437	1.16
N2	0.404	0.426	1.15
A1	0.475	0.475	1.30
A2	0.364	0.381	1.28
A3	0.285	0.295	1.21
A4	0.241	0.235	1.22
A5	0.193	0.213	1.18

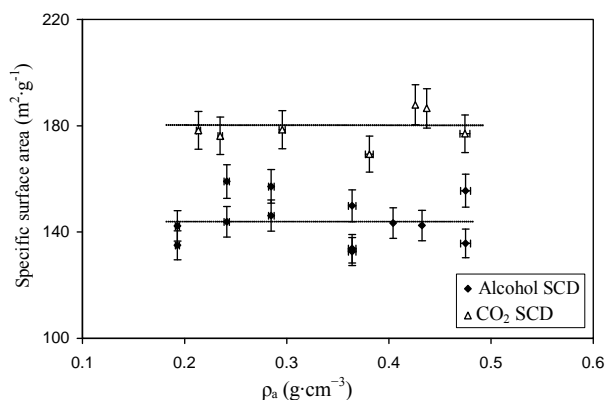
stage of depressurisation because of the previous solvent exchange stage, between liquid alcohol and liquid CO<sub>2</sub>, which is not complete.

The specific surface area of xerogels is nearly constant (180 m<sup>2</sup>·g<sup>-1</sup>) as a function of bulk density (**Figure 1**). This value, smaller than that of isolated particles (195 m<sup>2</sup>·g<sup>-1</sup>), obviously corresponds to the formation of the network which is constituted by linked particles. Concerning aerogels, the evolution of specific surface area with bulk density exhibits two families (**Figure 2**). Surface area values of aerogels obtained from CO<sub>2</sub> supercritical drying are close to those obtained for xerogels. Contrarily aerogels issued from an alcoholic supercritical drying show a smaller specific surface area (145 m<sup>2</sup>·g<sup>-1</sup>). The surface area lost associated to this last supercritical drying process is about 40 m<sup>2</sup>·g<sup>-1</sup>. It is worth noting that for all the investigated series of samples the specific surface area does not depend on the density. This feature also indicates that the surface is related to the size of particles while the density mainly acts on the porous volume.

The pore size distribution of silica gel spans over the entire range of pores measured using nitrogen adsorption measurements. So the pore volume corresponds to pores sizes smaller than 50 nm (mesoporosity) and its mea-



**Figure 1.** Xerogels specific surface area as a function of bulk density.

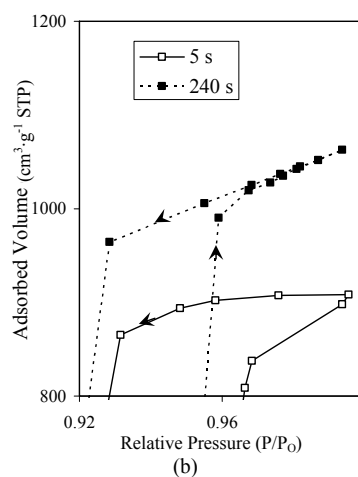
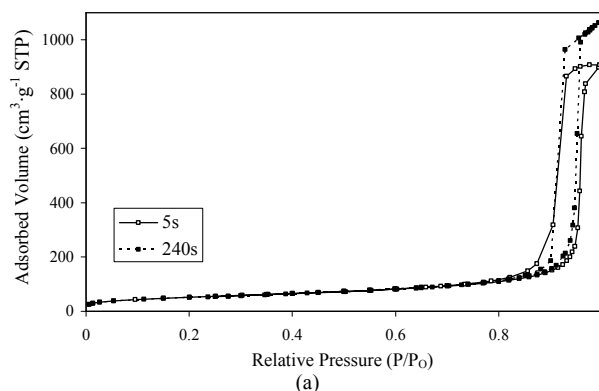


**Figure 2.** Aerogels specific surface area as a function of bulk density: effect of drying process.

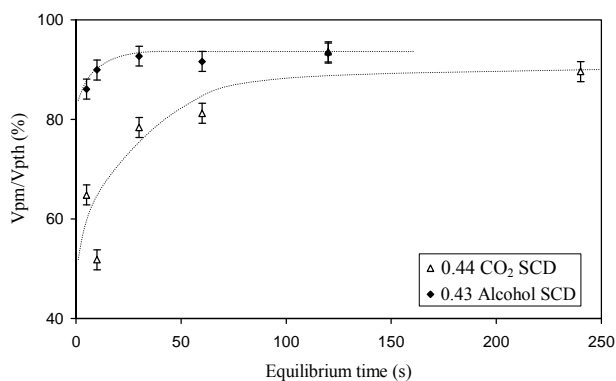
surement needs to choose adjusted adsorption-desorption parameters.

**Figure 3** exhibits the difference between two runs performed on a same sample by changing the dwell time (5 s and 240 s) between a pressure change of 10<sup>-4</sup>. The two curves superimpose up to a relative pressure of 0.95. Beyond this P/P<sub>0</sub> value, the curve characterized by a dwell time of 240 s, give higher adsorbed volumes and the hysteresis have different shape close to saturation. Whereas the adsorbed volumes are different between adsorption and desorption for the 5 s dwell time, for the 240 s dwell time, volumes are slightly identical (**Figure 3(b)**).

Two kinds of aerogels have been investigated changing dwell time (**Figure 4**). The value of the ratio V<sub>pm</sub>/V<sub>Pth</sub> (where V<sub>pm</sub> is the measured porous volume) becomes constant for alcohol 0.43 sample and for a dwell time of 30 seconds. For CO<sub>2</sub> 0.44 sample the ratio increases continuously as a function of dwell time. It seems possible to assert that equilibrium can be reached with a dwell time about 120 s.



**Figure 3.** Nitrogen adsorption-desorption isotherm of a SCD CO<sub>2</sub> aerogel. (a) Complete isotherm; (b) Enlargement of the isotherm ends. Empty symbols are related to a dwell time of 5 s after a pressure change of 0.01% and full symbols to a dwell time of 240 s.



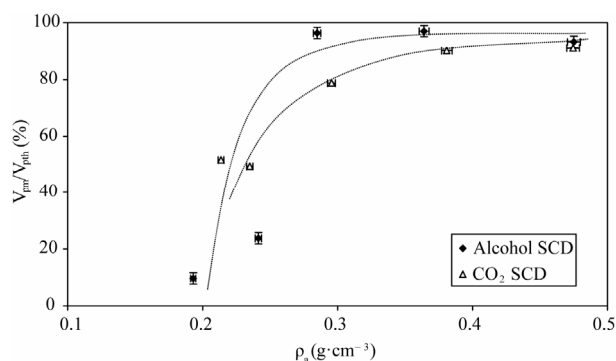
**Figure 4. Relaxation effects versus bulk density (dwell time 120 s). Empty symbols for CO<sub>2</sub> SCD-Full symbols for alcohol SCD.**

In **Figure 5**,  $V_{pm}/V_{pth}$  is plotted as a function of bulk density for aerogels issued from the two kinds of supercritical drying and for a dwell time of 120 s. This figure displays that these measurements are valid only for highest densities and express a relaxation phenomenon which takes place as a function of time. In order to corroborate this effect, **Table 2** gives bulk modulus measured for the two kinds of aerogels. We note that, for a given density, CO<sub>2</sub> SCD samples are less stiff.

#### 4. Discussion

The xerogels dried at room temperature and under air atmosphere are obtained in the shape of lumps. The specific surface area is about constant ( $180 \text{ m}^2 \cdot \text{g}^{-1}$ ). It does not depend on the pH (5 or 7) at which the gelation is carried out. CO<sub>2</sub> aerogels issued from the same gels display a surface value in the same order of magnitude. This fact indicates that the CO<sub>2</sub> supercritical drying does not induce a deep change in surface area. Consequently the surface can be mainly associated to the size of the particle keeping in mind that an area is lost between particles at the location of necks. Moreover nitrogen molecules cannot reach the entire surface located between linked particles [6]. This value crudely corresponds to that estimated from simple geometrical arguments [13]. Thus we can say that the specific surface area of these silica xerogels and CO<sub>2</sub> SCD aerogels is mainly associated to the particle size.

The surface area of alcohol SCD is about  $146 \text{ m}^2/\text{g}$ . The comparison with xerogels or CO<sub>2</sub> SCD aerogels indicates that a surface is lost during the alcohol supercritical stage. The surface decrease is related to the solubility of silica at high temperature ( $300^\circ\text{C}$ ) and high pressure (20 MPa) [14]. The dissolution-redeposition of silica induces a redeposition of silica at the necks between particles and consequently an increase in the mechanical properties as shown in our mechanical results. Moreover it was previously demonstrated [12] that the



**Figure 5. Relaxation effects versus dwell time for two kinds of aerogels with same bulk density. Empty symbols for CO<sub>2</sub> SCD-Full symbols for alcohol SCD.**

**Table 2. Properties of silica aerogels.**

	Bulk density ( $\text{g}\cdot\text{cm}^{-3}$ )	E (MPa)	K (MPa)
A1: Alcohol SCD	0.475	$233 \pm 5$	$129 \pm 3$
A3: Alcohol SCD	0.285	$22 \pm 1$	$12.2 \pm 0.5$
A5: Alcohol SCD	0.193	$19 \pm 1$	$10.6 \pm 0.5$
A1: CO <sub>2</sub> SCD	0.475	$74 \pm 4$	$41 \pm 2$
A2: CO <sub>2</sub> SCD	0.381	$33 \pm 2$	$18 \pm 1$

microporosity, *i.e.* porosity due to pores having size smaller than 2 nm, disappears

The effect of capillary forces arising during the last instants of nitrogen adsorption measurements are now better understood [9]. The whole porous volume measured at a relative pressure  $P/P_0$  close to 1 should theoretically correspond to real one. However due to capillary forces associated to nitrogen condensation inside the pores, the gel shrinks at the beginning of condensation [8]. Additionally Reichenauer and Scherer have demonstrated that when the relative partial pressure approaches 1 an expansion can be observed. It corresponds to the fact that the capillary stresses become of a smaller extent as the curvature radius of the interface liquid-vapour increases. If the experiment is performed under usual conditions, the expansion of gel cannot establish and consequently the measured pore volume  $V_{pm}$  is much smaller than theoretical pore volume  $V_{pth}$  calculated from relation (1).

The difference between the measured porous volume  $V_{pm}$  and the theoretical porous volume  $V_{pth}$  depends on the aerogel geometrical dimensions, on its elastic modulus and on the selected time for experiment. This difference, which is unequivocally related to a macroscopic shrinkage of the aerogels, is for a given data acquisition time obviously higher for aerogels having low density and consequently displaying the lowest elastic properties. We observe that for a given equilibrium time the  $V_{pm}/V_{pth}$  ratio is lower for aerogels issued from CO<sub>2</sub> than from alcohol. This implies that the shrinkage induced by

capillary condensation is higher for CO<sub>2</sub> aerogels for which the network is more connected. Reichenauer and Scherer have demonstrated that the capillary stresses operated on the silica backbone can reach 0.1 to 0.8 MPa. This value is high enough, comparatively to the bulk modulus of some samples, to induce contraction upon sorption in mesopores. However, our experiments can not allow correcting the isotherm according to the uniform contraction model.

In all cases, equilibrium times must be sufficiently long to assume that the samples are enough equilibrated. So, the time required to perform correct measurements of the pore volume decreases with sample bulk density increase and elastic properties increase. All these experiments qualitatively corroborate the theory proposed previously [9].

## 5. Conclusions

The gel shrinkage associated to the drying steps is demonstrated dependant on the kind of drying and on chemical reaction occurring during syneresis and dissolution-redeposition of silica. The specific surface area is mainly constant and does not depend on the bulk density of gels. It is associated to the particle sizes and necks establishing between them.

We corroborate that the pore volume can not be easily obtained by nitrogen adsorption-desorption. Because of capillary stresses induced during measurement, a divergence between the measured porous volume and the expected one is observed. This divergence is linked to the mechanical properties of material and on the selected time to estimate the adsorbed volume.

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