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Impact of depressurizing rate on the porosity of aerogels

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ABSTRACT

The effects of supercritical drying of diluted resorcinol–formaldehyde (RF) gels in CO_2 and in acetone are compared. We show that, for both processes, depressurizing rate of the autoclave after drying has a significant influence on the resultant shrinkage, and hence on resultant bulk density, surface area and pore volumes. At depressurizing rates below 2 MPa/min, acetone leads to much lower shrinkage than does CO_2, and is 1000 times cheaper. However, supercritical drying with CO_2 remains interesting because it is faster, easier to control, less sensitive to the experimental conditions and cleaner. We indeed show that acetone is degraded and leads to various compounds that might partly remain in the porosity of the dried RF gels. Supercritical CO_2 also clearly leads to the highest surface areas and micropore volumes, whereas supercritical acetone is in favour of higher mesopore volumes, especially at high depressurizing rates.

1. Introduction

Resorcinol–formaldehyde (RF) hydrogels are the most common precursors for preparing carbon aerogels, cryogels and xerogels [1]. Aerogels are usually dried by exchanging the solvent contained in the pores of their organic precursors with a supercritical fluid, whereas cryogels are obtained by solvent freezing followed by sublimation in vacuum. Xerogels are obtained by subcritical, either evaporative, convective or even microwave, drying. All other things being equal, each kind of material has its own porosity and pore structure, but aerogels are the most sought after. They indeed combine low density, mechanical resistance, and very narrow pores. Applications as thermal isolators, electrodes for supercapacitors, adsorbents, catalyst supports, or filling materials for HPLC columns have thus been suggested for carbon aerogels [2–7].

Supercritical drying may be achieved through the use of various solvents, provided that their critical temperature T_c and critical pressure P_c are not too high. Carbon dioxide ($T_c = 31$ °C; $P_c = 7.4$ MPa) is thus a good candidate and is indeed used in many laboratory and industrial processes. Applying CO_2 is known to induce very low shrinkage, leading to dry solids having the same morphology and approximately the same size as their elastic and fragile wet precursors. However, liquid CO_2 is an expensive fluid, and a number of cheaper supercritical fluids have been suggested such as acetone [8,9], ethanol [10,11], methanol [12], isopropanol [13] and petroleum ether [14]. For all these alternatives, successful tests and low resultant bulk densities have been reported, thus supporting the possibility of replacing expensive CO_2 by cheaper fluids.

However, the impact of the exact experimental conditions has not been much investigated. In particular, the possible role of the depressurizing rate has been reported only once in a letter by Qin and Guo [8], as far as the authors know. In their letter, only two depressurizing rates were studied which showed that shrinkage may be dramatically affected by the way acetone was released from the autoclave after supercritical exchange. Surprisingly, this work seemed to have a limited impact whereas its conclusions are very important and might be transferred to supercritical drying with CO_2. In the present paper, identical RF samples have been dried in either acetone or CO_2 in the supercritical state, and the fluid was released from the autoclave at different rates. Shrinkages and resultant densities, as well as BET surface areas and pore volumes, have been compared and discussed.

2. Materials and methods

2.1. Synthesis of RF hydrogels

It is well known that dense materials are less sensitive to the drying mode and hence are less prone to shrinkage, compared to

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highly diluted samples. This is the reason why nice xerogels, i.e. monolithic, not cracked and presenting a low shrinkage, could be obtained by subcritical drying from already rather dense hydrogels (see [15] and references therein). In the present case, a material having a high dilution ratio *D* (see below) was selected, in order to observe the effects of the depressurizing rate. Strictly identical resorcinol–formaldehyde hydrogels were thus prepared as follows. Resorcinol (R, 98% pure, Dyno Kjemi Norge, Norway) was diluted in distilled water (W) according to an R/W mass ratio of 0.05. The solution was next mixed with 37% aqueous solution of formaldehyde (F, stabilised by 10.6% of methanol, VWR, France), in such a way that the ideal stoichiometry was reached, i.e. corresponding to an R/F molar ratio of 0.5. Potassium carbonate (K, 97% pure, Prolabo, France) was added in such a way that the R/K molar ratio was 100.

All the reactants were mixed and stirred during 15 min in order to obtain a homogeneous solution which was poured into tubes of inner diameter 1 cm which were sealed afterwards. Doing this, the dilution ratio *D*, defined as the water/(resorcinol + formaldehyde + carbonate) molar ratio as suggested in a previous work [16], was 40.6. Gelation and ageing of RF hydrogels were carried out as follows. The tubes were first kept 48 h at room temperature, then transferred into an oven heated at 50 °C for 24 h and finally at 85 °C for 4 days. Orange–red transparent hydrogels were obtained.

2.2. Supercritical drying of RF hydrogels

The materials were removed from their tubes and cut into parallelepiped pieces, whose sides were carefully measured with a Vernier calliper. Typical dimensions were 10 × 6 × 3 mm. Before drying, water and other by-products of sol–gel reaction filling the pores of the hydrogels were exchanged by pure, dry, solvent. For that purpose, ethanol and acetone were used for samples subsequently dried with supercritical CO_2 and with supercritical acetone, respectively. Such exchanging step took 4 days during which solvent was replaced every day by fresh one. After this time, samples were supposed to be completely filled by pure solvent.

Supercritical drying in CO_2 was carried out in an Autosamdri – 815 automatic critical point dryer apparatus (Tousimis, USA). Samples were placed in a stainless steel sample holder and immersed in the drying chamber partially filled with absolute ethanol. The chamber, whose volume is close to 25 cm^3, was next closed and cooled to −10 °C before being filled with pure liquid CO_2. During this step, the pressure in the chamber increased from 0.1 to 4.83 MPa, and ethanol was replaced by liquid CO_2 (purge step) during 5 min. The apparatus was then stopped for 15 min, in order to let the excess of CO_2 diffuse inside the porosity of the gel and replace ethanol still possibly remaining in the pores. Filling and purging steps were repeated 4 times, again with 15 min breaks for each, to be sure that ethanol was completely replaced by liquid CO_2. After these cycles, the temperature inside the chamber was around 0 °C and was increased to 40 °C. The pressure consequently rose to 10.2–10.4 MPa, i.e. above the critical point of CO_2, and was maintained for 10 min. Then, the chamber was slowly depressurized at a controlled rate using the “bleed” metre valve of the critical point dryer. Table 1 gives the correspondence between position of the valve, time for going from 10 MPa back to 0.1 MPa, and related average depressurizing time.

Table 1
Correspondence between position of the “bleed” metre valve of Tousimis Autosamdri-815 automatic critical point dryer, and depressurizing time and depressurizing rate after CO_2 supercritical drying.

Position of the “bleed” metre valve	Depressurizing time (min)	Depressurizing rate (MPa/min)
0.07	473.5	0.02
0.09	20.6	0.45
0.13	6.5	1.41
0.15	4.8	1.93
0.20	2.7	3.48

Supercritical drying in acetone was performed in a lab-made device, comprising a vertical cylindrical autoclave connected either to the atmosphere or to a nitrogen cylinder, and heated by a fluidized sand bath. The hydrogels, completely exchanged with dry acetone beforehand, were introduced in a glass tube partially filled with acetone of technical quality and installed in the autoclave. First, the pressure in the autoclave was increased to around 11 MPa at room temperature by introducing nitrogen inside, and the sand bath was allowed to heat at 2 °C min^{-1} up to 250 °C. During this step, the pressure increased and was adjusted to its final desired value, 14 MPa. These temperature and pressure values, chosen in order to largely go round the critical point of acetone ($T_c = 235$ °C; $P_c = 4.7$ MPa), were maintained constant during 1 h. Next, the supercritical solvent was slowly exchanged by nitrogen at the same pressure, through the careful and simultaneously opening of two valves: the first one connected to the nitrogen cylinder, the second one connected to the exterior. One hour later, the exchange was assumed to be complete, given the low volume of the autoclave (around 15 cm^3), and the pressure was allowed to decrease at a controlled rate ranging from 0.08 MPa/min to 14 MPa/min. Once the atmospheric pressure was reached, the heating of the sand bath was switched off.

2.3. Analysis of the supercritical fluid after drying

Supercritical drying in CO_2 was carried out near room temperature, so no chemical modification of the RF gel was expected. In contrast, acetone was used at rather high temperature, so possible degradation reactions were looked for. For that purpose, the solvent evacuated from the autoclave before exchange with nitrogen was condensed and analysed by GC–MS. We used a Clarus 500 GC gas chromatograph equipped with a fused-silica capillary column, and coupled to a Clarus 500 MS quadrupole mass spectrometer (Perkin-Elmer Inc., USA). Detection was carried out in scan mode: m/z 20 to m/z 450. Compounds were identified by comparison with spectra from the NIST (National Institute of Standards and Technology, USA) mass spectral library.

2.4. Determination of pore texture parameters

The bulk density, ρ_b, defined as the mass of material divided by the total volume it occupies, was estimated for all RF aerogels using a Geopyc 1360 Envelope Density Analyser (Micromeritics, USA). From these results and from the known skeletal density, ρ_s, of non porous RF resin: 1.5 g cm^{-3} [16], the specific, total pore volume, V_{sp} (cm^3 g^{-1}), was calculated as:

$$V_{sp} = \frac{1}{\rho_b} - \frac{1}{\rho_s} \tag{1}$$

Surface areas, S_{BET}, and micropore volumes, V_{DR}, were both determined from nitrogen adsorption at 77 K (ASAP 2020, Micromeritics, USA) using BET [17] and Dubinin–Radushkevich [18] calculation methods, respectively. The volumes of mesopores, V_m, were defined as the difference of the Gurvitch volume, $V_{0.99}$ (defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $P/P_0 = 0.99$ [19]) minus the micropore volumes. The macropore volume, V_M, was finally obtained as the difference of the total pore volume minus Gurvitch volume: $V_{sp} - V_{0.99}$.

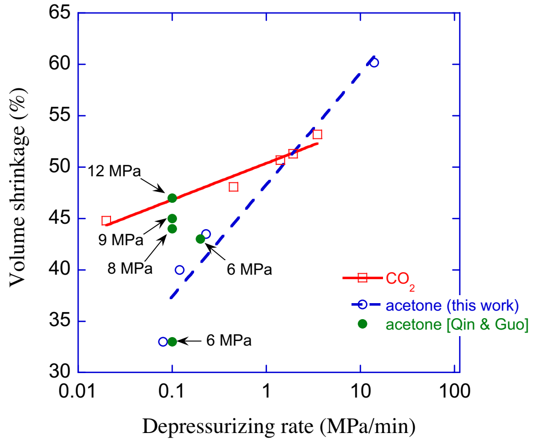


Fig. 1. Volume shrinkage of identical diluted RF gel samples submitted to supercritical drying in CO_2 and in acetone at 10 and 14 MPa, respectively. The lines are logarithmic fits to the experimental points. Data from Ref. [8] are given for comparison.

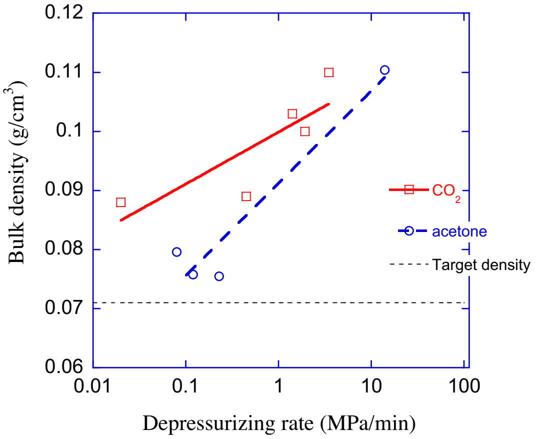


Fig. 2. Bulk density of diluted RF gel samples submitted to supercritical drying in CO_2 and in acetone at 10 and 14 MPa, respectively. The lines are logarithmic fits to the experimental points, and the dotted line is the density at zero shrinkage.

3. Results and discussion

3.1. Shrinkage

The samples dried with CO_2 were all monolithic, light brown, transparent and electrostatically stuck to fingers. Those dried with acetone were darker and, just like the previous ones, retained their initial shapes. They were also monolithic and crack-free as far as acetone was released at low rates. At high depressurizing rates, RF gels dried in supercritical acetone were black, sometimes cracked, and lost their initial rectangular shape. The effect of depressurizing rate on shrinkage is shown in Fig. 1. Volume shrinkage is reported here, which was calculated from the linear shrinkages measured along each direction of the parallelepiped samples. Using the digital calliper, linear shrinkages typically ranging from 12.5% to 26% could be measured with an accuracy of 0.01 mm, leading to volume shrinkages within the range 30–60%. Linear shrinkage α and volume shrinkage β are such that:

$$\beta = 3\alpha - 3\alpha^2 + \alpha^3 \qquad (2)$$

The uncertainty on volume shrinkage was always lower than 2.5%.

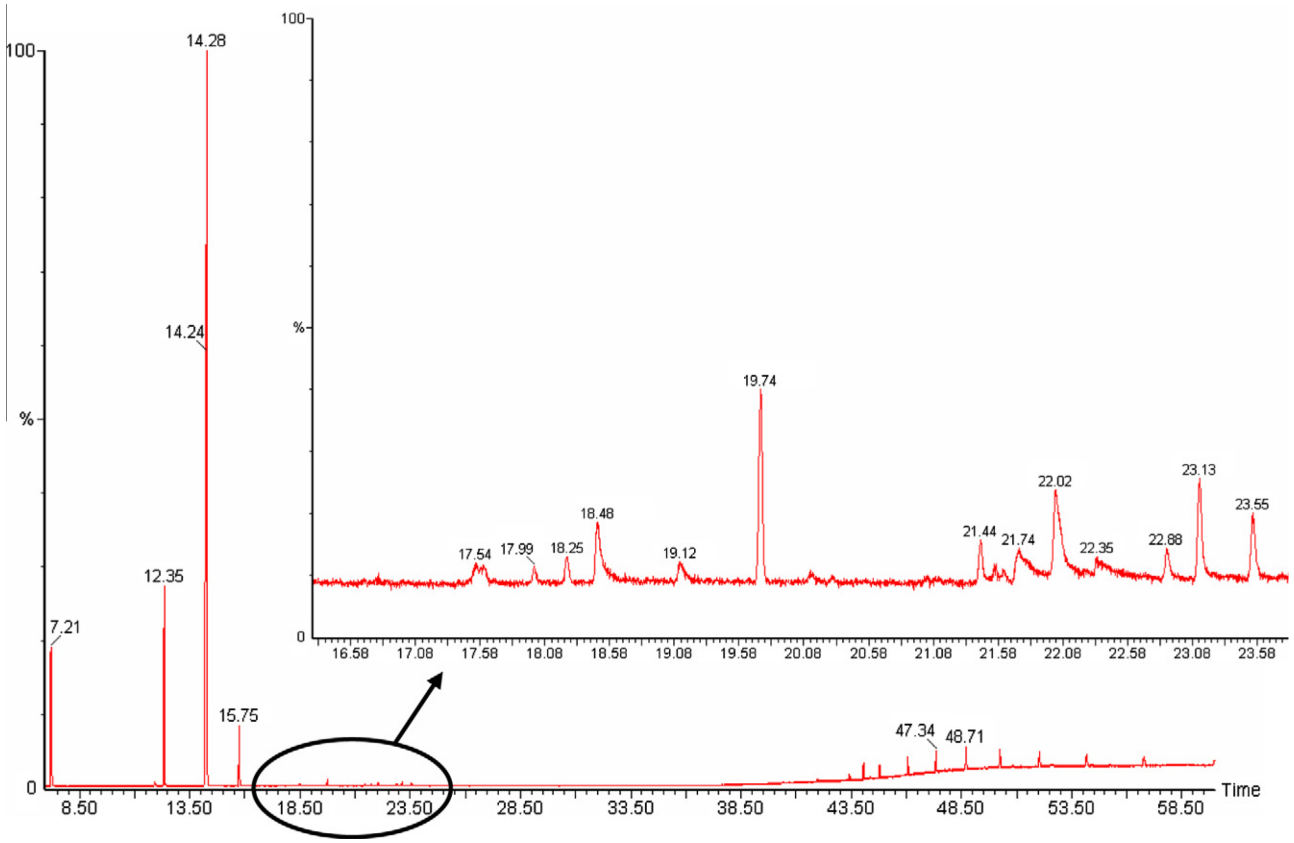


Fig. 3. GC–MS spectra of the solvent condensed at the outlet of the autoclave containing RF gels dried with supercritical acetone. The m/z region ranging from 16 to 24 has been magnified.

Shrinkage always increased with depressurizing rates, whatever the drying mode. Logarithmic fits have been drawn in Fig. 1, but there is no rigorous justification to this, and these lines should just be considered as a guide for the eye. Fig. 1 shows that, at low depressurizing rates, i.e. below 2 MPa/min, acetone leads to lower shrinkages than CO_2. It is interesting to recall that drying in supercritical CO_2 and in supercritical acetone was carried out at 10 and 14 MPa, respectively. Experimental data from Qin and Guo [8] have been added to Fig. 1 for comparison. Such data were obtained with supercritical acetone at the same temperature, 250 °C, but at different pressures ranging from 6 to 12 MPa. The results obtained at 6 MPa are in apparent agreement with ours, but straightforward comparison can not be made. The data of Qin and Guo were indeed obtained from a gel having a higher dilution, $D = 62.8$. According to their work, higher pressures lead to higher shrinkages. This finding suggests that even lower shrinkages might be obtained in our case, especially at low depressurizing rates, far below those obtained with CO_2.

3.2. Resultant density

The bulk density is reported for each sample in Fig. 2. These values were not compared to those formerly obtained by Qin and Guo because, as explained above, the dilution of their initial hydrogel was different. However, our results can be compared to the expected density at zero shrinkage, ρ_0. The latter reads $\rho_0 = m_d/(V_d + V_w)$, wherein m_d is the mass of dry matter, and V_d and V_w are the volumes of dry matter and water in the initial hydrogel, respectively. From the known composition of the hydrogel and from the known skeletal density of RF resin, the "target" density may be calculated as $\rho_0 \approx 0.071\ \mathrm{g\,cm^{-3}}$.

From Fig. 2, it is clear that supercritical acetone is a very valuable solvent for drying organic gels and converting them into lightweight aerogels. Using this fluid, higher densities than those obtained with CO_2 are achieved only at high depressurizing rates. Additionally, for performing the drying process, the amount of acetone was much lower, less than 4 g, compared to 2000 g in the case of CO_2. These amounts correspond to 0.004 € and 4 € per drying, respectively. In other words, drying in supercritical acetone is typically 1000 times cheaper than in supercritical CO_2, if all the other sources of cost, namely energy, manpower, facility costs, and equipment, are considered as constant. However, drying in supercritical CO_2 remains interesting from several other points of view. First, the process is faster than in acetone, allowing several dryings per day due to the narrow range of temperatures involved. On the contrary, acetone requires both heating and complete cooling of the autoclave, requiring several hours so that only one experiment per day is possible. Controlling the depressurizing rate is also much easier with CO_2, given that automatic critical point dryers working with liquid CO_2 are presently commercialised. It is then easy to fix the bleed metre valve at a given value. In contrast, drying with acetone requires the use of high-pressure valves, hardly controlled accurately, and throughout which the gas flow tends to decrease when the pressure in the autoclave decreases. A third argument in favour of CO_2 drying deals with the slopes of the lines given in Figs. 1 and 2, which are lower with CO_2 than with acetone. This finding suggests that the shrinkage and the resultant density are less affected by the depressurizing rate. The drying process based on CO_2 is thus not so sensitive to the experimental conditions, and therefore is more reliable.

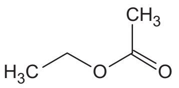
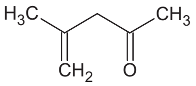
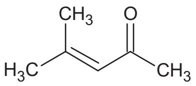
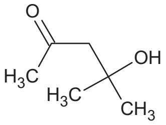
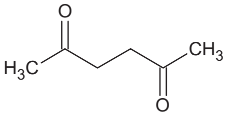
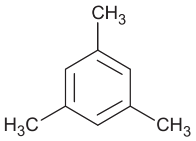
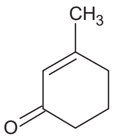
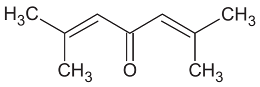
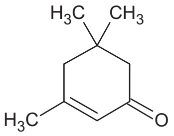
3.3. Purity of the dry gel

CO_2 is pure and should not react with the RF resin during drying, especially at temperatures as low as those used in the present study. On the contrary, at 250 °C, acetone reacted with itself and/or with the gel, and completely disappeared from the system. The GC–MS spectra presented in Fig. 3 and the corresponding list of compounds given in Table 2 prove this. We did a number of analyses with samples dried with different depressurizing rates, and all led to the same results. Only one aromatic compound, mesitylene, could be observed in very small amount, suggesting that the composition of RF gel was poorly modified during drying. However, the compounds derived from acetone might have polluted the gel and partly remain in the porosity, whereas CO_2 will always diffuse and be released at the end. Therefore, materials needing to remain very pure should not be dried in supercritical acetone, and CO_2 should be preferred.

3.4. Pore texture parameters

Finally, different surface areas and pore volumes were obtained, depending on both the nature of the supercritical fluid and the depressurizing rate. Nitrogen adsorption isotherms of RF aerogels dried in supercritical fluids at the highest depressurizing rates

Table 2
List of molecules detected by GS–MS at the outlet of the autoclave used for supercritical drying with acetone.

Peak (min)	Molecule	Formula	Structure
7.21	Ethyl acetate	$C_4H_8O_2$	
12.35	4-Methyl-4-penten-2-one (isomesityl oxide, isopropenyl acetone)	$C_6H_{10}O$	
14.28	4-Methyl-3-penten-2-one (mesityl oxide, isopropylidene acetone)	$C_6H_{10}O$	
15.75	Diacetone alcohol	$C_6H_{12}O_2$	
18.48	2,5-Hexandione (acetonyl acetone)	$C_6H_{10}O_2$	
19.74	1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	
22.02	3-Methyl-2-cyclohexen-1-one (methylocyclohexenone)	$C_7H_{10}O$	
23.13	2,6-Dimethyl-2,5-heptadien-4-one (diisopropylidene acetone)	$C_9H_{14}O$	
23.55	3,5,5-Trimethyl-2-cyclohexen-1-one	$C_9H_{14}O$	

available here: 14 MPa/min for acetone and 3.48 MPa/min for CO_2, are presented in Fig. 4(a). For the sake of clarity, only two complete adsorption–desorption isotherms are shown. A zoom of all adsorption isotherms plotted together on the same graph is given in the inset of Fig. 4(a). All isotherms presented the same type IV behaviour according to the IUPAC classification [20], characteristic of materials comprising mesopores in which capillary condensation occurs. Higher nitrogen amounts adsorbed at low relative pressure were always found for materials dried in CO_2, suggesting higher micropore volumes, whatever the depressurizing rate.

The BET surface areas of RF aerogels prepared in different conditions are shown in Fig. 4(b) and confirm this point. The impact of depressurizing rate is the lowest when the materials were dried in supercritical CO_2, as already observed for shrinkage and bulk density. The new features evidenced here are twofold: (i) the surface areas are rather different, depending on the supercritical fluid, and (ii) increasing the depressurizing rate has opposite effects. Indeed, materials dried with CO_2 presented slightly higher surface areas despite having higher bulk densities (see Fig. 2). Additionally, BET surface areas slightly increased with the depressurizing rate, whereas a strong drop was found for acetone. These results thus suggest that getting high surface areas is much easier through the use of supercritical CO_2, and especially when high depressurizing rates are used.

Micropore, V_{DR}, and mesopore, V_m, volumes are shown as a function of depressurizing rate in Fig. 5(a). As expected, the same trends are observed for V_{DR} and S_{BET}, since micropores majorly contribute to the value of the surface area. Nevertheless, the mesopore volumes of materials dried in supercritical CO_2 followed the same tendency and slightly increased with the depressurizing rate, though this effect is rather low. In contrast, the mesopore volumes of aerogels prepared in supercritical acetone strongly increased with depressurizing rate. This finding was rather unexpected, especially when macropore volumes, V_M, and total pore volumes, V_{sp}, are considered in Fig. 5(b). Both V_M and V_{sp} decreased when the depressurizing rate increased, and Fig. 5(b) is the "reverse" of Fig. 2. Therefore, the major part of the porosity of such aerogels corresponds to macropores, as also seen by the fact that V_M is typically, and only, 1 cm^3/g lower than V_{sp}.

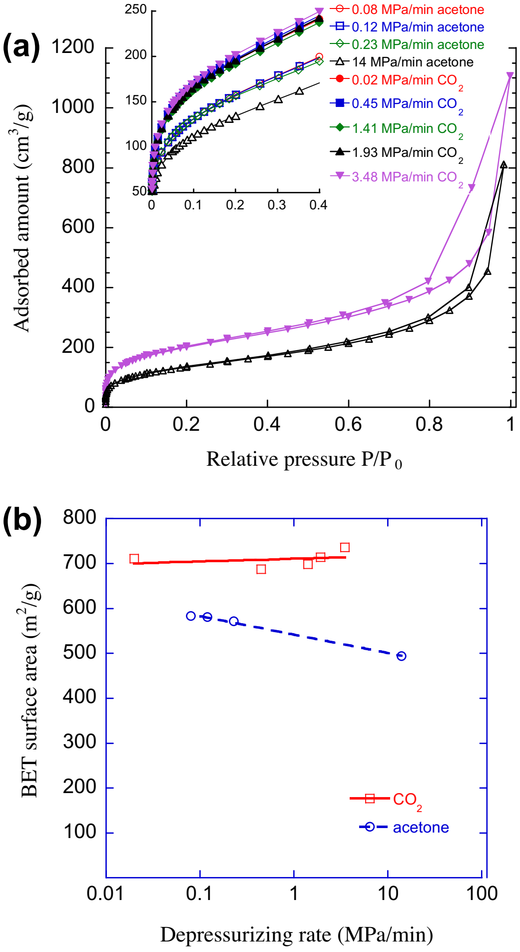


Fig. 4. (a) N_2 adsorption–desorption isotherms of RF aerogels dried in supercritical CO_2 and in supercritical acetone, using the highest depressurizing rate available here: 3.48 and 14 MPa/min, respectively. A zoom of all isotherms plotted together is given in the inset. (b) Corresponding BET surface areas for the complete range of depressurizing rate; the lines are logarithmic fits to the experimental points.

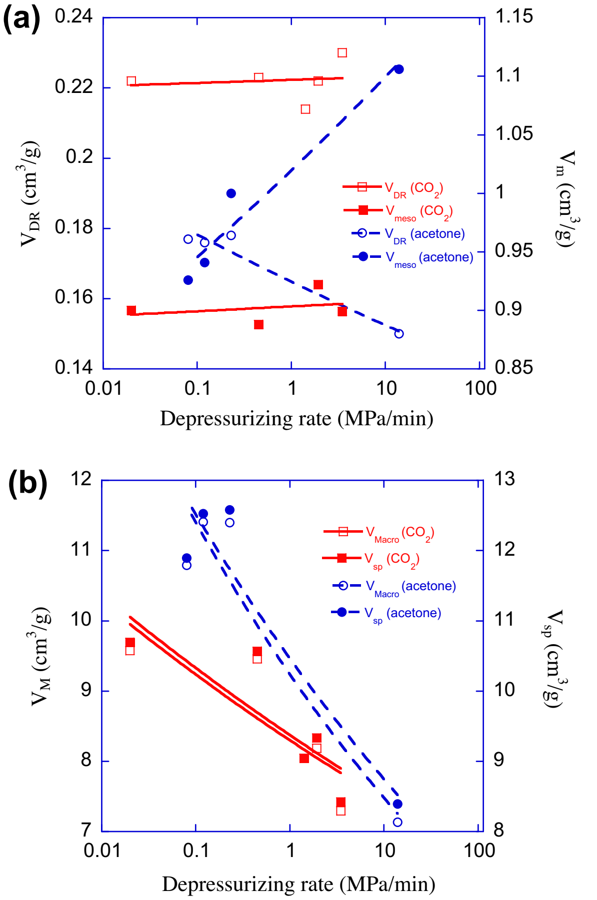


Fig. 5. Pore volumes of RF aerogels dried in supercritical CO_2 and in supercritical acetone at different depressurizing rates: (a) micro (V_{DR}) and mesopore (V_m) volumes, and (b) macro (V_M) and total pore (V_{sp}) volumes.

4. Conclusion

In this work, we have clearly confirmed the dramatic impact of the rate at which an autoclave used for drying a wet gel with supercritical acetone is depressurized. This conclusion has been extended to the case of CO_2 which is, however, less sensitive to such experimental parameter. Surprisingly, at depressurizing rates lower than 2 MPa/min, acetone was found to lead to the lowest shrinkages despite the much higher temperature involved. This finding seems to contradict the assumption of Qin and Guo [8] suggesting that further condensation of the RF gels occurs during acetone drying, a factor causing shrinkage.

Supercritical drying in acetone is thus an advantageous process and, moreover, is also 1000 times cheaper. Nevertheless, use of CO_2

in an automatic, commercial, critical point dryer is easier to control, faster, and should be preferred if purity is essential. In contrast, acetone decomposes in a number of chemicals that are prone to remain partly entrapped in the porosity of the dry material.

Other conclusions of the present works are that supercritical drying in CO_2 is in favour of high micropore volumes and high related surface area, but the impact of depressurizing rate on the corresponding values is rather low. In contrast, micropore and mesopore volumes of RF aerogels prepared with supercritical acetone are highly sensitive to the depressurizing rate. Lower micropore volumes and higher mesopore volumes are indeed obtained at higher depressurizing rate. Therefore, when results dealing with aerogels are reported in the literature, the value of the depressurizing rate should always be given in addition to the other experimental conditions, otherwise no reproducible materials can be obtained.

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