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New families of carbon gels based on natural resources

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Abstract. Carbon gels are versatile materials which can be used for many applications. They are extremely expensive, because generally prepared from resorcinol – formaldehyde (RF) resins first gelled and next dried with supercritical carbon dioxide. In the present work, resorcinol has been substituted partly or completely by tannins, a family of molecules extracted from mimosa tree barks. Tannins are natural, non-toxic products, typically thirty times cheaper than resorcinol. Their chemical resemblance with the latter makes them be often called natural resorcinol. Using tannins not only substantially decreases the cost but also allows preparing materials in a much wider range of pHs than that usually employed for RF gels. Consequently the main pore size and the fraction of given families of pores, controlling the carbon gels' properties, are tuned in an easier way, and a much wider range of pore structures is obtained. Finally, two alternative ways of drying are suggested for further decreasing the cost: freeze-drying and supercritical drying in acetone. Both are shown to lead, in some conditions described below, to materials having similar characteristics to those of expensive RF carbon aerogels previously dried in supercritical CO₂.

1. Introduction

Carbon gels are porous materials which have been suggested as adsorbents, porous electrodes for electric double-layer supercapacitors, filling material for HPLC columns, catalyst supports and heat insulators at high temperature. These solids indeed present both a suitable mesoporosity (i.e. pores whose width ranges from 2 to 50 nm) for all these applications and a high chemical resistance. Usually, such materials are prepared by pyrolysis in inert atmosphere of porous organic gels based on resorcinol – formaldehyde (RF) resins. RF formulations, prepared in water, are very expensive but are also very easy to handle, leading to nice, monolithic, big and reproducible elastic hydrogels. The latter need to be dried in a suitable way, for both removing the liquid saturating the porosity and preventing the collapse of the pores. For that purpose, convective, supercritical or freeze drying can be used, leading to xerogels, aerogels and cryogels, respectively.

Xerogels present a rather high bulk density, whereas aerogels and cryogels have a much higher porosity. Producing aerogels is a costly procedure, since drying of organic hydrogels by supercritical carbon dioxide is involved. Freeze-drying is much cheaper, and is thus a very interesting alternative drying route. Pore structures similar to those of aerogels have indeed been reported if water in the

hydrogels has been exchanged by t-butanol beforehand, a solvent having a higher vapour pressure and presenting much smaller volume changes than water when frozen. In the present work, low-cost carbon gels have been produced according to two simultaneous ways: (i) substitution of resorcinol by flavonoid tannins, and (ii) use of cheap drying modes: supercritical drying with acetone or freeze-drying. We show that, in a number of cases, carbon gels having characteristics very similar to those of their expensive RF counterparts dried in supercritical CO₂ can be obtained.

2. Materials and methods

2.1. Preparation of tannin-based gels

Information about tannins is extensively given in another paper from the present issue [1]. Briefly, tannins are commercial raw materials extracted from mimosa tree barks and widely used in leather, chemical and food industries. These are phenolic molecules able to lead to the same kind of reactions as resorcinol does. Especially, their cross-linking with formaldehyde in water produces high-quality resins, already used and commercialised for wood joining. In the present case, the formulations known for the preparation of adhesives, for which hard and highly cross-linked materials are desired, have been modified for obtaining highly porous gels. Two types of formulations have been investigated: tannin – resorcinol – formaldehyde (TRF) and tannin – formaldehyde (TF).

2.1.1. Organic tannin-based hydrogels. TRF hydrogels were prepared from a TRF resin whose composition was optimised in a former work [2], and to which formaldehyde was added. In a typical RF formulation, the stoichiometric R/F molar ratio is 0.5. In the present case, 2/3 in weight of the resorcinol was replaced by tannins. The pH of the initial TRF solution was 8.15. Small amounts of 99.8% acetic acid were added for decreasing and adjusting the pH at different values ranging from 2 to 8. Such a broad range of pH is very unusual for RF gels but, as shown below, allows obtaining rather different pore structures.

TF hydrogels were prepared by mixing tannins, first dissolved in a 20% water solution of methanol, and 37% water solution of formaldehyde, in such a way that the weight ratio T/F was 1.35. The pH of the initial TF solution was 4.3 and was increased or decreased by addition of 33% aqueous solution of NaOH or 99.8% acetic acid, respectively. Again, various solutions having a wide range of pH, ranging from 3.3 to 8.3, were obtained.

All these solutions of known pH were poured into sealed glass tubes and left for gelling and ageing in an oven at 50 and 85°C for TRF and TF formulations, respectively. Gelation of TRF solutions occurred within a few hours, whereas that of TF required several days. Because the gel point was quickly reached for TRF, its determination was easily carried out through a careful examination of the tubes. The gelation was assumed to be complete when the solution no longer flowed when tilted at an angle of 45°. A strong influence of pH was observed, see Figure 1. Because the reactions in TF solutions were much slower despite the higher temperature, gelation times of TF formulations could not be measured. Reactivity of T is lower than that of R, because electrophilic substitution is always easier with two -OH groups (case of resorcinol) than with one -OR group (case of flavonoid tannin).

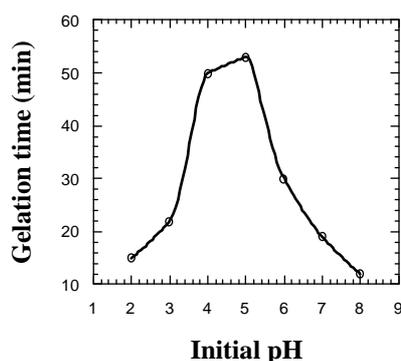


Figure 1. Gelation time of TRF solutions at 50°C as a function of pH.

2.1.2. *Tannin-based carbon gels.* After a few days of curing, during which the stiffness of the hydrogels was improved, the latter were removed from their tubes, cut into cylindrical pieces, and soaked into dry solvent. For TRF gels, the solvent was acetone, which was replaced 24 h later by t-butanol, next changed by fresh one three consecutive times every three days. Doing this, the solvent saturating the porosity was assumed to be pure t-butanol. For TF gels, the solvent was only acetone, replaced every day by fresh one, three times.

Then, exchanged TRF and TF wet gels were freeze-dried and supercritically dried, respectively. Temperature and pressure conditions used for each process are given in Figure 2. Advantages of using acetone for supercritical drying are that acetone is typically 1000 times cheaper than liquid CO₂ on one hand, and that only a few cm³ are required instead of a few hundreds of cm³ in the case of CO₂, further reducing the costs. The only drawback is the use of much higher temperature and pressure.

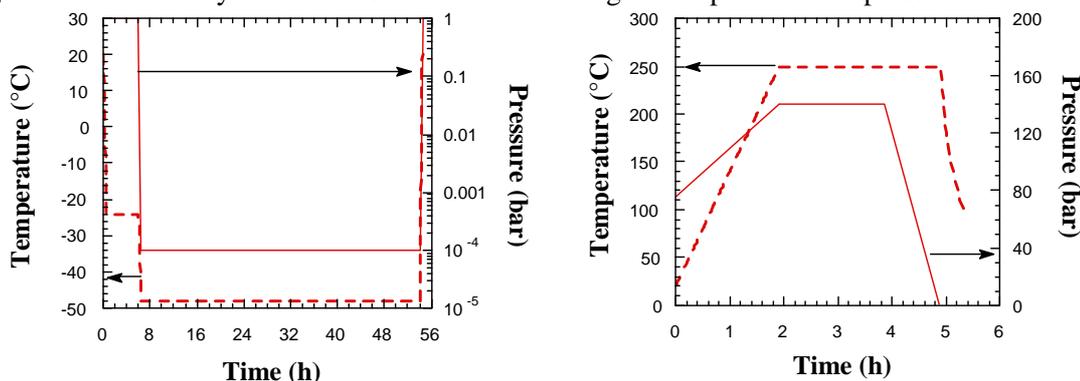


Figure 2. Temperature and pressure conditions used for: (left) freeze-drying TRF organic gels; (right) drying TF organic gels in supercritical acetone.

After drying, samples were installed inside a quartz boat placed at the center of a fused silica tube heated by a horizontal furnace and flushed with nitrogen. Heating rate and set point (maintained for 2h) were 5°C min⁻¹ and 900°C, respectively. After cooling under nitrogen flow, TRF carbon cryogels and TF carbon aerogels were recovered.

2.2. Investigation of carbon gels derived from tannins

Carbon gels were characterised in terms of total, micro (i.e. pores narrower than 2 nm) and mesoporosity, surface area and pore-size distribution. These features were obtained through the use of different techniques such as helium pycnometry and nitrogen adsorption at 77K.

2.2.1. *Pycnometry.* Helium pycnometry allowed determining the skeletal density of the carbon constituting the gels. For avoiding any bias related to possible closed porosity, the samples were finely crushed in a mortar before any measurement. Monolithic carbon gels having perfectly known dimensions and regular shapes were weighed in order to measure their apparent, or bulk, density. The total porosity was deduced from the two values of density.

2.2.2. *Adsorption.* BET surface area, micro and mesopore volumes were calculated from the nitrogen adsorption isotherms obtained at 77K according to the techniques extensively detailed elsewhere [3]. Pore-size distribution within the range of micro and mesopores was calculated by the DFT method [4].

3. Pore texture of TRF and TF carbon gels

3.1. Porosity and surface area

Whatever the tannin-based precursor, the skeletal density of the resultant carbon was always close to 2 g cm⁻³, as expected for a disordered carbon prepared at 900°C. In contrast, the bulk densities were found to range from 0.10 to 0.74 g cm⁻³, leading to total porosities within the range 56 – 95 %, see

Figure 3. The highest porosity values are typical of RF-based carbon aerogels prepared by drying of their organic precursors in supercritical CO₂, i.e., close to 95%. The same applies to the BET surface area, shown in Figure 4, whose highest values are, again, very similar to those of classical carbon aerogels, typically ranging from 500 to 700 m² g⁻¹.

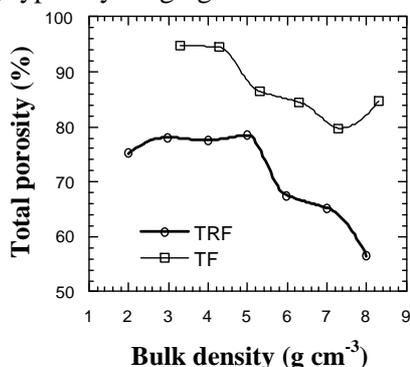


Figure 3. Total porosity of TRF carbon cryogels and TF carbon aerogels.

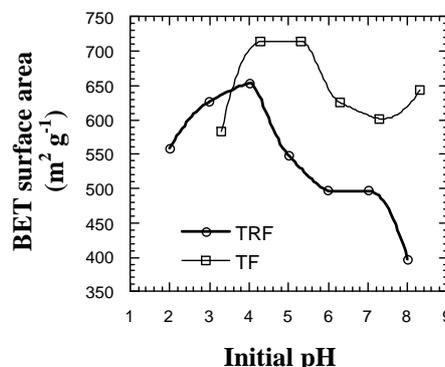


Figure 4. BET surface area of TRF carbon cryogels and TF carbon aerogels.

It is interesting to note that the maximum of both porosity and surface area clearly corresponds to the minimum of reactivity of the precursor monomers, i.e. to the pH at which the gelation time was found to be the highest: close to 5 (see again Figure 1). It can thus be assumed that fast gelation leads to strongly cross-linked polymer network and finally to dense materials. However, the strongest effect is observed at high pHs, for which gels having the lowest porosity are obtained. The higher surface area and porosity of TF gels prepared at pH 8.3 are one exception due to the NaOH used in higher amount for increasing the pH. NaOH remains in the carbon and participates to its activation.

3.2. Micro and mesoporosity

For clarity, only a few nitrogen adsorption isotherms obtained with TRF- and TF-derived carbon gels are presented in Figure 5. All are of type IV according to the IUPAC classification, and mean that the materials are essentially mesoporous. Desorption branches are parallel to, and almost merged with, adsorption curves. Such narrow hysteresis loops are H1-type, and are typical of cylindrical mesopores in which capillary condensation occurs.

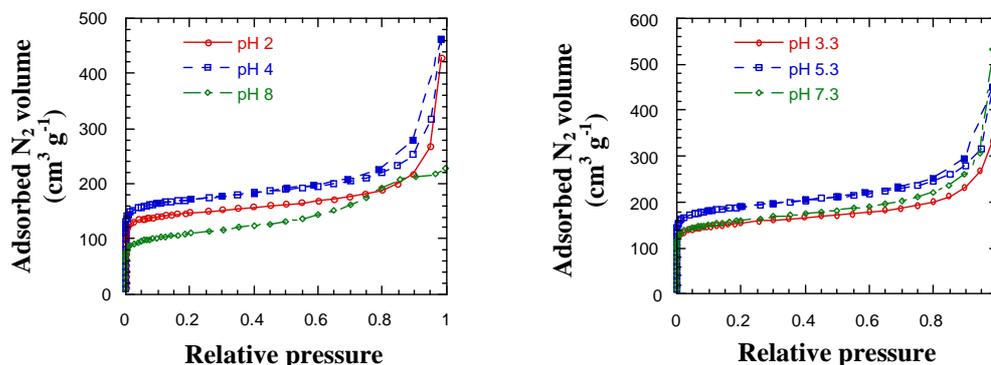


Figure 5. Nitrogen adsorption isotherms at 77K for: (left) TRF carbon cryogels; (right) TF carbon aerogels. For clarity, only one hysteresis loop is shown in each plot (at pH 4 and 5.3): adsorption (empty symbols) – desorption (full symbols).

From these curves, in addition to the BET surface areas presented above, micropore (V_{μ}) and mesopore (V_m) volumes as well as average micropore widths (L_0) could be determined. V_{μ} was derived from the Dubinin – Radushkevich method (see [3] and refs. therein), whereas V_m was assumed

to be the difference between the adsorbed volume of liquid nitrogen at a relative pressure of 0.99 minus V_{μ} . L_0 was calculated from the equation of Stoeckli et al. [5]. All these data are gathered in Table 1, as a function of the synthesis pH.

Table 1. Micropore (V_{μ}) and mesopore (V_m) volumes, and average micropore widths (L_0), of TRF carbon cryogels and TF carbon aerogels.

pH	TRF carbon cryogels			TF carbon aerogels		
	V_{μ} (cm ³ g ⁻¹)	V_m (cm ³ g ⁻¹)	L_0 (Å)	V_{μ} (cm ³ g ⁻¹)	V_m (cm ³ g ⁻¹)	L_0 (Å)
2	0.215	0.45	6.7			
3	0.243	0.23	6.6			
3.3				0.224	0.29	6.4
4	0.252	0.46	6.7			
4.3				0.276	0.36	7.2
5	0.213	0.22	6.1			
5.3				0.277	0.42	5.9
6	0.192	0.39	7.8			
6.3				0.241	0.51	6.8
7	0.19	0.40	7.5			
7.3				0.229	0.59	7.0
8	0.155	0.20	9.0			
8.3				0.246	0.89	8.9

The changes of the pore texture parameters listed in Table 1 are in agreement with the trends shown in Figures 3 and 4. For TRF carbon cryogels, pore volumes at high pH are much lower than those of materials prepared in acidic medium. At intermediate pH, a maximum is observed. The average pore width tends to increase with pH. These findings are consistent with obtaining materials of low porosity at high pH, and agree with previous studies of the effect of pH on the porosity of RF carbon xerogels carried out, however, in a much narrower range of pH [6,7].

The behavior of TF carbon gels is not exactly the same when compared to that of TRF materials. The micropore volume also goes through a maximum near pH 4 – 5, and the average micropore width also tends to increase with pH. But the mesopore volumes always and considerably increase with pH. The fraction of mesoporosity thus changes from 56 to 78% at pH 3.3 to 8.3, respectively. Such big variations of pore structures have never been observed before with RF carbon gels, whatever the way they have been prepared.

Pore-size distributions derived from Figure 5 by application of DFT are presented in Figure 6. Again, for clarity, not all synthesis pHs are shown. In the case of TRF carbon cryogels, increasing the synthesis pH has two simultaneous effects: broadening of the distribution of pore widths and shifting it towards narrower pores. These effects are modest below the pH of lower reactivity, close to 4, for which the pore texture parameters were rather similar to each other, especially the surface areas, as seen in Figure 4. But the effects of pH are strongly marked above pH 5. Thus, through the use of various synthesis pH, it is possible to tune easily and accurately the porosity. RF formulations, for which the pH cannot be changed so much, don't allow this at such extent.

In the case of TF aerogels, the pore-size distribution is neither shifted nor broadened with pH, but the relative proportions of pore families change considerably. In first approximation, two main peaks may be considered, one corresponding to micropores and centered on 0.5 nm, the other one corresponding to wide mesopores and centered on 35 nm. When the pH increases, the centers of the peaks are unchanged, but their heights increases for mesopores, and go through maximum for micropores. These features are consistent with the values of Table 1, but Figure 6 brought the additional information that these porosity changes occurred at constant pore width.

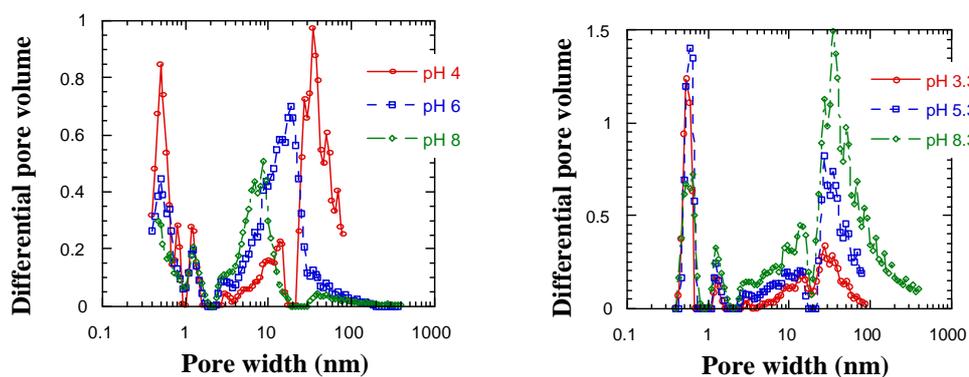


Figure 6. Micro-mesopore-size distributions derived from Figure 5 by application of DFT for: (left) TRF carbon cryogels; (right) TF carbon aerogels.

4. Conclusion

Using flavonoid tannins (T) for partial or complete substitution of resorcinol (R) allowed obtaining very different carbon gels and observing very different behaviors as well. A range of synthesis pHs much wider than that typically employed for RF gels could indeed be used, leading to the preparation of carbon gels having either pore textures close to those of classical RF aerogels, or having much lower porosity and different mesopore fractions.

If 2/3 in weight of R was replaced by T, gelation of tannin – resorcinol – formaldehyde formulations in aqueous solution was possible from pH 2 to 8. Both broadening and shifting of the pore-size distributions towards narrower pores were observed at increasingly high pH. Thus, tailoring the pore texture is easier in the case of TRF carbon gels than in the case of classical RF gels.

Complete replacement of R by T also allowed preparing new materials in a wide range of pH from 3 to 8. In this case, the pore-size distributions were not shifted with pH but the relative proportions of micro and mesopores were strongly changed instead. At constant pore diameters, mesoporosity increased considerably with pH, whereas microporosity presented a maximum near pH 5.

Tannins not only lead to carbon gels whose pore texture is more easily tailored than that of RF gels. Tannins are also non-toxic, environment-friendly, natural products which are typically thirty times cheaper than resorcinol. Combining their use with that of cheaper drying routes, such as supercritical drying in acetone and freeze-drying, low-cost carbon aerogels and cryogels, respectively, could be prepared. Such new materials are serious substitutes to expensive RF carbon aerogels for the same applications, provided that the synthesis pH was suitably chosen.

Acknowledgments

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