Bimodal activated carbons derived from resorcinol-formaldehyde cryogels

Andrzej Szczurek1, Gisele Amaral-Labat1, Vanessa Fierro1, Antonio Pizzi2 and Alain Celzard1,3

1 Institut Jean Lamour—UMR CNRS 7198, CNRS—Nancy-Université—UPV-Metz, Département Chimie et Physique des Solides et des Surfaces. ENSTIB, 27 rue Philippe Séguin, BP 1041, 88051 Épinal cedex 9, France
2 ENSTIB-LERMAB, Nancy-Université, 27 rue Philippe Séguin, BP1041, 88051 Epinal cedex 9, France
3 Member of the Institut Universitaire de France
E-mail: Alain.Celzard@enstib.uhp-nancy.fr

Received 24 February 2011
Accepted for publication 22 March 2011
Published 3 May 2011
Online at stacks.iop.org/STAM/12/035001

Abstract
Resorcinol-formaldehyde cryogels prepared at different dilution ratios have been activated with phosphoric acid at 450 °C and compared with their carbonaceous counterparts obtained by pyrolysis at 900 °C. Whereas the latter were, as expected, highly mesoporous carbons, the former cryogels had very different pore textures. Highly diluted cryogels allowed preparation of microporous materials with high surface areas, but activation of initially dense cryogels led to almost non-porous carbons, with much lower surface areas than those obtained by pyrolysis. The optimal acid concentration for activation, corresponding to stoichiometry between molecules of acid and hydroxyl groups, was 2 M l⁻¹, and the acid–cryogel contact time also had an optimal value. Such optimization allowed us to achieve surface areas and micropore volumes among the highest ever obtained by activation with H₃PO₄, close to 2200 m² g⁻¹ and 0.7 cm³ g⁻¹, respectively. Activation of diluted cryogels with a lower acid concentration of 1.2 M l⁻¹ led to authentic bimodal activated carbons, having a surface area as high as 1780 m² g⁻¹ and 0.6 cm³ g⁻¹ of microporous volume easily accessible through a widely developed macroporosity.

Key words: carbon cryogels, activated carbons, bimodal porosity, resorcinol

1. Introduction
Gelation of diluted polymers in a solvent leads to highly porous materials where pore volumes are saturated by the liquid in which the polymers have been prepared. Such solids are called hydrogels or alcogels, whether the solvent is water or alcohol, respectively. The solid phase is highly dispersed, so that if the solvent can be removed from the wet gel without pore collapse, extremely lightweight dry gels can be obtained. Zero shrinkage is almost impossible in practice, and the capillary forces exerted on the thin solid parts usually reduce the pore volume. The way the gels are dried thus has a major effect on the bulk density, and hence, on the porosity, of the resultant dried gels [1, 2]. Three main drying methods have been suggested: subcritical, supercritical and freeze-drying, leading to xerogels, aerogels and cryogels, respectively. From these materials, carbonaceous counterparts may be obtained by controlled pyrolysis, and carbon xero-, aero- and cryogels are thus obtained. Their structure is similar to that of their precursors, but the porosity is narrower due to the shrinkage induced by the pyrolysis.

Carbon aerogels and cryogels, when suitably prepared, have the highest pore volumes, whereas capillary forces unavoidably decrease the pore volumes of xerogels. Carbon aerogels are rather expensive because their preparation often involves supercritical CO₂. However, much cheaper supercritical solvents have been suggested and were shown to be interesting alternatives (see [3] and references therein). Carbon cryogels are even cheaper, but their synthesis requires longer periods, typically at least 5 days. It involves
several cycles of solvent exchange, followed by deep freezing and sublimation of the ice in vacuum [4]. Such process produces only a very low pore collapse, and bulk densities as low as those of typical aerogels can be obtained. However, the pore structure is generally coarser for cryogels [4]. Freeze-dried hydrogels, in which water ice crystals act as templates, can have very wide pores, sometimes called ‘megalopores’, leading to microhoneycomb structures [2, 5]. For some applications requiring highly available pores, a coarse structure may be of interest in which narrower pores can be developed. This situation is that of adsorbents used under dynamical conditions, porous electrodes for supercapacitors and catalyst supports [6, 7].

For the last two cases, in addition to the desired high diffusion rates of molecules flowing through the pores, high purity of the carbon is required. Inorganic impurities may indeed alter the catalytic behaviour, for example, by poisoning noble metals, and also considerably decrease the shelf life of supercapacitors working in organic electrolyte at high potential (see [8] and references therein). The production of pure carbons requires pure organic precursors; therefore, biosourced raw materials generally have to be avoided except if scrupulously washed with various solvents and/or acids. Synthetic polymers with a high carbon yield are thus preferred, particularly phenolic resins. Resorcinol and phenol are valuable precursors of carbonaceous solids. Phenol is less reactive than resorcinol but is cheaper [9–11]. Resorcinol, although expensive, presents several advantages for the preparation of gels. It is very easy to handle, is water-soluble, and gives rise to nice, monolithic, big and reproducible elastic hydrogels. For these reasons, it is the most studied carbon gel precursor. Many reports are available for comparing past results with new gels and gel-derived materials.

In the present work, carbon cryogels prepared from resorcinol–formaldehyde (RF) resin have been either pyrolysed or activated with phosphoric acid. The former process led to carbon cryogels, whereas the latter produced activated carbon cryogels. Phosphoric acid was chosen because it is easy to handle and allows preparation of activated carbons at moderate temperature, in inert or self-generated atmosphere, and even in air (see [12, 13] and references therein). The aim of this work was to study how activated carbons can be obtained from RF cryogels prepared at different dilutions. This has not been attempted before, and the previous works refer to the chemical activation of either RF aerogels with phosphoric acid [14] or of RF xerogels with KOH [15]. Different results are reported here, and for some of the produced activated carbons, comparison with pyrolysed RF gels is meaningful.

2. Materials and methods

2.1. Synthesis of carbonaceous materials derived from resorcinol–formaldehyde cryogels

2.1.1 Preparation of carbon cryogels. RF hydrogels were prepared by polycondensation reaction of resorcinol with formaldehyde in an aqueous solution, basing on the method described elsewhere [16]. In the present case, resorcinol (R) was diluted in distilled water (W) at four different R/W mass ratios: 0.05, 0.1, 0.2 and 0.5, yielding the samples labelled as RF0.05, RF0.1, RF0.2 and RF0.5, respectively. These solutions were then mixed with a 37% aqueous solution of formaldehyde (F), in such a way that the ideal stoichiometry was reached, corresponding to an R/F molar ratio of 0.5. Potassium carbonate (K), frequently but improperly called ‘catalyst’, was added in such a way that the R/K molar ratio was 100. Resorcinol (98%), formaldehyde (37%, stabilised by 10.6% methanol) and potassium carbonate (97%) were supplied by Dyno Kjem Norge (Norway), VWR (France) and Prolabo (France), respectively. All the reactants were mixed to obtain a homogeneous solution that was poured into tubes of 1 cm inner diameter, which were sealed afterwards. Gelation and aging of RF hydrogels were carried out as follows. The tubes were first kept for 48 h at room temperature, then baked in an oven at 50 °C for 24 h and next at 85 °C for 48 h. Orange-red transparent hydrogels were recovered.

The hydrogels were removed from the tubes and cut into cylindrical pieces with a typical thickness of 1 cm. The samples were soaked in dry acetone for 24 h and then in pure tert-butanol, which was refreshed every day. After three days, the exchange of water and all types of liquid by-products of RF polycondensation initially contained in the pores of the hydrogels was assumed to be complete [17]. The samples were frozen at −25 °C for 24 h and placed in a freeze-dryer (Christ Alpha 1-2Dplus) for 48 h. During the freeze-drying process, the working pressure and temperature varied from 0.064 to 0.12 mbar and from −48 to −41 °C, respectively. Once dried, RF cryogels had different colours, depending on the R/F molar ratio of the initial solution: from orange for sample RF0.05 to dark red for RF0.5.

Organic RF cryogels were carbonized in a horizontal tubular furnace. The samples were placed in quartz boats and transferred to a fused silica tube continuously flushed with high-purity nitrogen at a flow rate of 50 ml min⁻¹. The tube was heated in a furnace at 5 °C min⁻¹ up to 900 °C, and the final temperature was held for 2 h. Next, the furnace was allowed to cool to room temperature under nitrogen flow. The resultant samples were named CRFx, where C means carbon and x is the R/W weight ratio varying from 0.05 to 0.5.

2.1.2 Chemical activation of organic cryogels. Monolithic organic cryogels were chemically activated with aqueous solutions of orthophosphoric acid. Chemical activation, as well as drying after impregnation and washing after heat treatment, partially destroyed the initial monolithic shape. Different concentrations of phosphoric acid, between 0.25 and 4 M1⁻¹, were used. Each organic cryogel was immersed in a beaker containing such amount of diluted acid solution that the sample/acid ratio was 20 mg m⁻¹. The beaker was next put in a vacuum vessel for 2 h, allowing deep impregnation of the sample to occur; however, bubbles coming out of the porous cryogels disappeared much earlier. Samples were subsequently taken from the acid, installed in glass beakers and dried in an oven heated at 103 °C for periods ranging from...
0.5 to 12 h. As demonstrated below, drying has a considerable impact on the pore texture of the resultant activated carbons. Dried samples were pyrolysed under the same conditions as used for CRFx materials, except that the final temperature was fixed at 450 °C.

After pyrolysis, the samples were thoroughly washed with distilled water in a Soxhlet extractor for 4 days. Finally, they were dried in an oven heated at 103 °C for 24 h. Activated cryogels were termed ARFx-c-t, where x has the same meaning as before, c is the acid concentration (M−1) and t is the drying time (h) before the pyrolysis.

2.2. Characterization methods

2.2.1 Scanning electron microscopy (SEM). Samples of carbon aerogels were observed using an FEI Quanta 600 FEG scanning electron microscope. Only secondary electrons were used for observing the topographic contrast.

2.2.2 Adsorption studies. Nitrogen adsorption isotherms were obtained at −196 °C using a Micromeritics ASAP 2020 automatic adsorption apparatus. The samples were outgassed for 48 h in vacuum at 250 °C prior to any adsorption experiment. Surface areas, \( S_{BET} \), were determined by the Brunauer–Emmett–Teller (BET) calculation method [18] applied to the adsorption branch of the isotherms. The micropore volume, \( V_{DR} \), was determined according to the Dubinin–Radushkevich (DR) method (see [19] and references therein), with correlation coefficients equal to or higher than 0.999. The total pore volume measurable by adsorption, \( V_{0.99} \), was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure \( P/P_0 = 0.99 \) [20]. The mesopore volume, \( V_{meso} \), was assumed to be the difference \( V_{0.99} - V_{DR} \). Finally, the pore size distributions (PSD) were calculated by application of the density functional theory (DFT) model [21] supplied by Micromeritics software, considering slit-shaped pores.

2.2.3 Pycnometry. The bulk density, \( \rho_b \), defined as the mass of material divided by the total volume it occupies, was calculated from the weights of cylindrical or parallelepipedal samples of accurately known dimensions. The skeletal density, \( \rho_s \), defined as the density of the solid from which the considered material is made, was measured by helium pycnometry (Accupyc II 1340, Micromeritics). For avoiding errors related to closed porosity, the samples were finely crushed in an agate mortar. After drying overnight at 120 °C in vacuum, they were introduced to a calibrated volume (1 cm³) flushed ten times with high-purity helium. From bulk and skeletal densities, the porosity, \( \Phi \) was calculated as \( \Phi = 1 - \rho_b/\rho_s \). The specific pore volume \( V_p \) (cm³ g⁻¹), i.e. the total pore volume per unit mass of material, was calculated as \( V_p = 1/\rho_b - 1/\rho_s \). The macropore volume, \( V_{macro} \) (cm³ g⁻¹), was thus assumed to be \( V_p - V_{0.99} \).

---

Figure 1. Bulk density and BET surface area of CRF carbon cryogels.

2.2.4 Porosimetry. Meso and macropore size distributions were determined by mercury porosimetry (AutoPore IV 9500, Micrometrics). The experiments were performed at low pressure (0.001–0.24 MPa) and at high pressure (0.24–414 MPa). This method was used to obtain information on pores larger than 3.6 nm. No compression of the materials was observed at any mercury pressure, and thus, the Washburn equation was applied as \( D = -4\gamma \cos \theta/P \), where \( D \) (nm) is the pore diameter, and \( P \) (MPa), \( \gamma \) (485 mJ m⁻²) and \( \theta \) (140°) are the isostatic pressure, surface tension and contact angle of mercury, respectively.

3. Results and discussion

3.1. Pore structure of CRF carbon cryogels

Helium pycnometry revealed no significant difference between carbon cryogels. An average skeletal density of \( 1.99 \pm 0.04 \) g cm⁻³ was obtained, independent of the original R/W ratio. In contrast, bulk densities changed by one order of magnitude from 0.17 to 1.14 g cm⁻³, as shown in figure 1. The trend is remarkably linear. The corresponding porosities thus ranged from 42.7 to 91.5%. Such a trend was expected since a lower R/W ratio corresponds to a higher dilution of the resin before gelation, and hence, to a more porous material after curing, drying and pyrolysis. Likewise, BET surface areas derived from nitrogen adsorption experiments were found to increase with the porosity of the cryogels (see figure 1). Sample CRF0.05 had a surface area close to 780 m² g⁻¹, other samples having values of 670–715 m² g⁻¹. Such values are comparable and sometimes higher than those reported for other carbon cryogels based on resorcinol-formaldehyde [4, 16, 17].

Figure 2(a) shows N₂ adsorption-desorption isotherms at 77 K. All of them exhibit a sharp increase in the volume adsorbed at \( P/P_0 < 0.05 \), indicating the presence of narrow micropores. A narrow knee corresponding to adsorption into micropores was followed by the gradual filling of wider micropores and mesopores at higher \( P/P_0 \). The isotherms had approximately the same slope up to \( P/P_0 = 0.4 \), where the hysteresis cycles emerged. The main differences observed concerned the total N₂ adsorbed volume and the relative
pressure at which this maximum occurred. Thus, materials prepared from gels at intermediate R/F ratios, CRF0.1 and CRF0.2, adsorbed similar N$_2$ volumes of about 850 cm$^3$ g$^{-1}$, CRF0.05 and CRF 0.5 adsorbed about 600 and 400 cm$^3$ g$^{-1}$, respectively. For CRF0.5, the maximum N$_2$ volume was reached at $P/P_0 = 0.8$ indicating that the PSD shifted towards lower mesopore diameters compared with those of CRF0.05, CRF0.1 and CRF 0.2.

Figure 2(b) shows the PSD calculated using the DFT model from the N$_2$ adsorption data. The results are in good agreement with the trends anticipated above. The micropore size distribution was very similar for all the materials. Concerning mesopores, the broadest PSD was observed for CRF0.1, and no mesopores wider than 10 nm were found for CRF0.5.

Figure 3 shows macro, meso and micropore volumes of CRF carbon cryogels. The highest micropore volume was obtained with the most porous material, i.e. having the lowest R/W mass ratio. $V_{DR}$ indeed continuously decreased when the R/W ratio increased. The corresponding curve is thus similar to that of $S_{BET}$, since micropores essentially contributed to the latter. Consistently, lower micropore volumes corresponded to higher mesopore volumes, on average. This trend was not fully obeyed, since the lowest dilution (R/W = 0.5) led to the lowest total porosity. In other words, the mesopore volume could not constantly increase with the R/W ratio, and a maximum was logically observed at R/W = 0.2, in agreement with figure 2(b). It is interesting to note from figure 3 that carbon cryogels are highly macroporous with a significant amount of micro and mesoporosity at high dilution (R/W = 0.05–0.1); they are meso and microporous at medium dilution (R/W = 0.2) and are truly microporous at low dilution (R/W = 0.5). It can be expected from these results that impregnation of RF gels, and hence, efficiency of activation by phosphoric acid will be the highest for materials prepared at low R/W ratios, whereas poorly porous materials like those having R/W = 0.5 will be of no interest.

Figure 4(a) shows raw data on mercury intrusion into carbon cryogels prepared at different dilution ratios. Two noticeable features are present. The first one is the marked decrease in the intruded volume when the R/W ratio increased, in agreement with the above calculations of total porosity. Thus, the curves for CRF0.5 were so close to the $x$-axis that an inset was added to figure 4(a) to magnify them. The second characteristic is that intrusion occurred at increasingly high pressures when the R/W ratio increased, suggesting that the pores tend to become narrower when the porosity decreases.

PSDs calculated from figure 4(a) are presented in figure 4(b). However, differences with PSDs obtained by direct application of Washburn’s equation are negligible and only concern the widest pores, not visible on the plots. Again, an inset has been added to figure 4(b) to better present the results for the CRF0.5 sample. The peak diameters are significantly shifted towards narrower pores when the R/W ratio increases, as expected from the intrusion curves. Their values are listed in table 1. In the case of CRF0.5, part of the porosity is out of the range that can be measured by
Figure 4. Mercury porosimetry results: (a) raw intrusion (open symbols)-desorption (solid symbols) curves, and (b) corresponding pore size distributions. For clarity, the data of CRF0.5 are presented in the insets.

Table 1. Comparison of the peaks of pore-size distributions derived from mercury porosimetry and nitrogen adsorption within the range of pore widths 3–50 nm.

| Carbon cryogel sample | Peak pore width (nm) determined by |
|----------------------|-----------------------------------|
|                      | Hg porosimetry       | N$_2$ adsorption |
| CRF0.05             | 7 and 13              | 7 and 13         |
| CRF0.1              | 26                    | 9 and 27         |
| CRF0.2              | 15                    | 19               |
| CRF0.5              | 4                     | 7                |

mercury porosimetry, i.e. it is narrower than 3.6 nm (see inset of figure 4(b)).

It is interesting to compare the mesopore size distributions obtained by the techniques so different as nitrogen adsorption and mercury porosimetry, both based on models having their own limitations. Despite expected differences, which can be explained not only by the methods but also by their associated models (thus pores are neither ideal cylinders nor ideal slits, and their geometry may depend on their size), the agreement between figures 2(b) and 4(b) within the width range of 3–50 nm is rather satisfactory, as shown in table 1.

3.2. Pore structure of ARF activated carbon cryogel

Microscopy could not show any clear difference between carbon cryogels obtained by pyrolysis and activated cryogels on one hand, nor between samples activated with different concentrations of phosphoric acid on the other hand. This finding suggests that the initial structure of the RF cryogel precursor was always retained, hence, the interest on chemical activation. Consequently, only SEM images of ARF0.05 material prepared from 1 M H$_3$PO$_4$ and dried for 1 h, are presented in figure 5. A coarse pore structure, typical of cryogels, is clearly seen at low magnification. Despite the care with which water was exchanged with tert-butanol, and despite the small changes in volume occurring upon freezing ($-3.4 \times 10^{-4}$ g cm$^{-3}$ [4], against $-7.5 \times 10^{-2}$ g cm$^{-3}$ for water), organic ice crystals probably induced internal stresses and cracks, leading to the somewhat ‘exfoliated’ structure.

Images taken at the highest magnification reveal the typical granular structure known for carbon aerogels, xerogels or cryogels based on resorcinol–formaldehyde or on other resins [1, 22–26]. Connected nodules are seen, whose diameter was independent of the R/W ratio, as reported previously [24, 27]. In the present case, the nodules have diameters of 40–60 nm, typical of what is usually observed for carbon aerogels derived from RF resins and having the same composition [3]. The use of potassium carbonate as ‘catalyst’, instead of conventional sodium carbonate or
sodium hydroxide, had no visible effect on the average size of the nodules. Obviously, no effect of the activation process, i.e. creation of micro and mesopores, could be seen at the magnification available to SEM. The pictures shown in figure 5 are thus completely similar to those of the carbon cryogel counterparts. They demonstrate that the structure is open, allowing the deep penetration of orthophosphoric acid, and hence, the effective activation of the inner parts of the monoliths.

More than 35 activated carbons have been obtained from the combination of the different types of experimental parameters described in section 2. It is thus not possible to present all the results in detail. However, systematic trends have been observed, which can be described through the use of a few examples only. For instance, nitrogen adsorption-desorption isotherms of activated cryogels are given in figure 6 for a few materials that have been prepared and characterized in the present work, namely, for those impregnated with acid at a concentration lower or equal to 1 M. Figure 6(a) shows the effect of the concentration of H₃PO₄ on RF0.05 impregnated and dried for 1 h, figure 6(b) presents the effect of the initial R/W mass ratio for samples submitted to 1 M H₃PO₄ for 1 h, and figure 6(c) illustrates the effect of the drying time for RF0.1 activated with 1 M H₃PO₄. Comparing figure 6 with figure 2(a) reveals obvious differences between ARF and CRF series related to, as detailed below, the increase or decrease in microporosity, depending on the material, and to a systematic and significant loss of mesoporosity after activation.

Figure 6(a) shows that the adsorbed volume strongly increased with the acid concentration, but the shape of the isotherm was fully maintained within the series, suggesting that the micropore size distribution was barely affected. In contrast, the width of the hysteresis loop decreased, corresponding to lower mesopore volumes. Such a trend is unmistakable and was observed systematically, with only one exception: RF0.05 activated with 1 M H₃PO₄ and dried for 12 h had a lower surface area than the material treated with acid at a concentration of 0.75 M under otherwise the same conditions. In this unique case, it can be assumed that the long contact time promoted the attack of the resin by the acid, destroying part of its porous structure. Increasing the initial
Figure 7. Pore size distribution deduced from figure 6 by application of the DFT method: (a) ARF0.05-c-1 series, (b) ARF-x-1-1 series and (c) ARF0.1-1-t series.

R/W mass ratio led to less porous materials, as expected and as shown in figure 6(b): both micropore and mesopore volumes decreased. Finally, increasing the drying time after impregnation with the acid decreased slightly the micropore volume, whereas the mesopore volume remained roughly constant, as suggested by the data shown in figure 6(c).

The PSDs deduced from figures 6(a)–(c) by application of the DFT method are shown in figures 7(a)–(c), respectively. All the aforementioned trends are clearly observed: an increase in the micropore volume and decrease in the mesopore volume with increasing acid concentrations up to 1 M l⁻¹; a decrease in both the micropore and mesopore (however, to a lesser extent) volumes with the R/W ratio, and a slight decrease in the mesopore volume and almost no effect on the mesopore volume with drying time. Figure 7 shows the additional information that such changes occurred at rather a constant pore size, given that the distributions always peak at the same pore width values. However, the micropore size distribution tends to be distorted when the acid concentration increases, with a higher contribution of wider micropores. In other words, the average micropore width slightly increased with the acid concentration. Comparison with figure 2(b) straightforwardly shows that activation with phosphoric acid and simple pyrolysis led to comparable PSDs, but their peak intensities are very different. Activated cryogels are essentially microporous, whereas pyrolysed cryogels are essentially mesoporous. Only the positions of the peaks are more or less the same, because of the same precursor.

The bulk density of activated cryogels, as well as their average skeletal density measured by helium pycnometry, 1.90 ± 0.5 g cm⁻³, was used for calculating the macro-porosity. Macro, meso and micropore volumes of materials activated with acid concentrations lower or equal to 1 M l⁻¹ are presented in figure 8. A very few data of VDR are lacking because they were too low for accurate measurements—the corresponding BET surface areas were much lower than 100 m² g⁻¹. The mesopore volumes were always lower than 0.20 g cm⁻³ and, in most cases, lower than 0.15 g cm⁻³. The micropore volumes were always higher, except for those corresponding to the low-porosity materials within the ARF0.2-1-t series, with a maximum close to 0.6 g cm⁻³. The considerable decrease in all the categories of pore volumes
Figure 8. Macro, meso and micropore volumes of ARF activated cryogels as a function of the H$_3$PO$_4$ concentration and drying time.

The precursor organic cryogels had initial R/W mass ratios of (a) 0.05, (b) 0.1 and (c) 0.2.

is clearly seen for higher R/W ratios. Finding such a low porosity at R/W = 0.2 fully justifies that no activation of the RF0.5 series was carried out.

Figure 8 clearly shows the multimodal character of the porosity, whose major part is macroporosity. A very efficient transport towards narrower pores is thus expected for such structure. From this point of view, the sample ARF0.05-1-1 is a good compromise between the high availability of narrow pores and the high micropore volume. For this material, the fractions of macro, meso and micropores are 79, 2 and 19%, respectively, so ARF0.05-1-1 can be considered as a bimodal porous activated carbon. Such characteristics are fully comparable to those of activated foams, whose microporosity is only superficial but is fully accessible through a connected network of cells [28]. In the present case, the macroporosity is typically ten times narrower, but is sufficiently broad to enable the diffusion of molecules towards the micropores, thus improving the adsorption kinetics.

Figure 9 shows the BET surface areas in the form of 3D graphs, so that the effects of both the acid concentration and the initial R/W mass ratio are simultaneously taken into account. Each of the graphs of figure 9 corresponds to a certain acid-cryogel contact time. The changes in $S_{\text{BET}}$ are similar to those of the micropore volume, namely, $S_{\text{BET}}$ increases with the acid concentration (except for ACR0.05-1-12) and decreases with the increase of both the R/W mass ratio and drying time. The strongest effect is that of the concentration, followed by the R/W ratio, and finally, by the drying time. The most microporous sample is thus the one having the lowest initial R/W ratio, impregnated with 1 M H$_3$PO$_4$ and dried for 1 h before the heat treatment. Such a material has a BET surface area of 1440 m$^2$ g$^{-1}$. Low concentrations of acid led to small surface areas, even smaller than those of the pyrolysed carbon cryogels. The latter had values ranging from 680 to 780 m$^2$ g$^{-1}$, which were never exceeded by activated cryogels prepared from 0.25 M H$_3$PO$_4$. Almost non-porous materials were produced at a high initial R/W mass ratio. This is the reason why, given the negligible porosity of the ARF0.2 series, no activation of RF0.5 has been carried out. When R/W was raised from 0.05 to 0.2, increasingly high acid concentrations were required for obtaining surface areas higher than those of their CRF counterparts. Thus, the surface areas of the ARF0.2 series were all markedly lower than those of the CRF0.2 series, regardless of the experimental conditions: concentration or drying time.

3.3. Search for an optimal concentration of phosphoric acid

Additional experiments were carried out to check whether the surface area and related micropore volume could go through
Figure 9. BET surface area of ARF activated cryogels having different initial R/W mass ratios and heat treated with phosphoric acid at different concentrations, using a drying time of (a) 1 h, (b) 2 h and (c) 12 h.

a maximum value in the most interesting cryogels, i.e. those prepared with the R/W mass ratio of 0.05. For that purpose, other concentrations of acid, 1.2, 1.5, 2, 3 and 4 M l\(^{-1}\), were tested at 1 h drying time, whereas 0.5 h impregnation time was tested with 1 M l\(^{-1}\) acid. The corresponding results are given in table 2, with other previous data added for comparison.

From table 2, the increase in both the BET surface area and micropore volume is clearly shown when the acid concentration was increased from 0.25 to 2 M l\(^{-1}\), and a decrease is observed at higher concentrations. At 1.2 M l\(^{-1}\), the surface area is already quite high, 1780 m\(^2\) g\(^{-1}\), and the corresponding isotherm (not shown) is typical of an ideal microporous material. Given its still high macropore volume, close to 5 cm\(^3\) g\(^{-1}\), ARF0.05-1.2-1 may be considered as an authentic bimodal activated carbon with high adsorption and diffusion kinetics. If the micropore fraction is defined, just like in many other works dealing with activated carbons, as the \(V_{DR}/V_{0.99}\) ratio, then such a micropore fraction reaches 94%. Materials ARF0.05-1.5-1 and ARF0.05-2-1 have even higher macro and micropore volumes and should perform even better. Thus, at 2 M l\(^{-1}\), the BET surface area reaches a maximum of as high as 2195 m\(^2\) g\(^{-1}\). However, a significant amount of mesopores has been created; hence, such materials are no longer bimodal but rather show three different types of porosity.

It is interesting to plot several quantities taken from table 2, illustrating the effect of acid concentration on the pore texture. Figure 10(a) shows that the BET surface area and macropore volume simultaneously increase with the acid concentration until the optimum of 2 M l\(^{-1}\) is reached. This finding is extremely interesting because it shows that diffusion throughout the pore network can be significantly improved without the loss of microporosity. Such macropore volumes are even higher than those already high volumes reported for bimodal activated carbons derived from rigid foams [28]. Figure 10(b) shows that, as expected, the BET surface area strongly correlates with the micropore volume. Finally, it can be seen from Figure 10(c) that the volume of mesopores, in
Table 2. Effect of acid concentration and drying time on the pore texture parameters of ARF activated cryogels prepared with a mass ratio R/W = 0.05.

| Synthesis parameters | Pore texture parameters |
|----------------------|-------------------------|
| R/W ratio | Concentration (M) | Time (h) | Sample name | \( S_{BET} \) (m\(^2\) g\(^{-1}\)) | \( V_{macro} \) (cm\(^3\) g\(^{-1}\)) | \( V_{meso} \) (cm\(^3\) g\(^{-1}\)) | \( V_{micro} \) (cm\(^3\) g\(^{-1}\)) |
| 0.05 | 0.25 | 1 | ARF0.05-0.25-1 | 575 | 3.82 | 0.20 | 0.22 |
| 0.05 | 0.5 | 1 | ARF0.05-0.5-1 | 890 | 2.02 | 0.14 | 0.35 |
| 0.05 | 0.75 | 1 | ARF0.05-0.75-1 | 945 | 2.74 | 0.07 | 0.37 |
| 0.05 | 1 | 1 | ARF0.05-1-1 | 1440 | 2.41 | 0.07 | 0.57 |
| 0.05 | 1.2 | 1 | ARF0.05-1.2-1 | 1780 | 4.98 | 0.04 | 0.60 |
| 0.05 | 1.5 | 1 | ARF0.05-1.5-1 | 1905 | 8.47 | 0.32 | 0.63 |
| 0.05 | 2 | 1 | ARF0.05-2-1 | 2195 | 8.54 | 0.50 | 0.69 |
| 0.05 | 3 | 1 | ARF0.05-3-1 | 1960 | 11.64 | 0.63 | 0.61 |
| 0.05 | 4 | 1 | ARF0.05-4-1 | 1870 | 6.55 | 0.66 | 0.60 |
| 0.05 | 1 | 0.5 | ARF0.05-1-0.5 | 1200 | 3.94 | 0.06 | 0.47 |
| 0.05 | 1 | 2 | ARF0.05-1-2 | 1300 | 1.75 | 0.09 | 0.50 |
| 0.05 | 1 | 12 | ARF0.05-1-12 | 665 | 3.14 | 0.08 | 0.25 |

Figure 10. Pore texture parameters of ARF activated cryogels having an initial R/W mass ratio of 0.05, impregnated with phosphoric acid at different conditions, and dried for 1 h before the heat treatment.

contrast with micropores, first decreases and then increases with the acid concentration. The micropore fraction is the highest at a concentration of 1.2 M 1.1.

The existence of an optimum acid concentration has been reported in several past works. If H\(_3\)PO\(_4\) reacts with hydroxyl groups, then about 27% of the weight of the RF gel should react at stoichiometry. This assumption, based on the molecular model of Lin and Ritter [29], takes all the OH groups into account, i.e. those of the resorcinol rings and those of the methylol groups. If only aromatic OH groups are considered, then the weight fraction, \( f \), of the cryogel, which should react at stoichiometry, is 24%. Given that
For the most favourable drying time, 1 h, the optimum mass fraction $P_{RF}$, is
\[
\frac{P}{RF} = \frac{M_{H_3PO_4}}{M_{OH}} \times f \times 0.85^{1.5}
\]
(1)

where $M$ denotes molecular weights (98 and 17 g mol$^{-1}$ for $H_3PO_4$ and $OH$, respectively). When $f$ is 27 or 24%, the optimum mass fraction $P_{RF}$ is 1.83 or 1.63, respectively. These values, particularly the last one, can be compared with those reported for lignin: 1.4 [12, 13]; rice straw: 1 [30]; rubber wood sawdust: 1.06 [31]; xylan: 1; cellulose and kraft lignin: 1.5 [32]; peanuts: 1 [33]; almond shell: 1–1.17 [34]; date pits: 1.2–1.44 [35]; and coconut shell: 1.7 [36]. The optimum observed in the present work was obtained for a concentration of 2 M$^{-1}$. Assuming the complete reaction of a volume of acid solution saturating the whole pore volume, such concentration corresponds to a mass of 9.2 g of 2 M $H_3PO_4$ per gram of RF gel. This calculation was based on an RF0.05 gel having a specific pore volume of $8.4 \text{cm}^3\text{g}^{-1}$ and a skeletal density of $1.5 \text{g cm}^{-3}$, using a density of $1.1 \text{g cm}^{-3}$ for 2 M $H_3PO_4$ [37]. Given that 2 M corresponds to 18 wt% orthophosphoric acid, the reaction should be complete for a mass fraction of 85% $H_3PO_4$ to RF cryogel of 9.2/(0.85/0.18) = 1.95, in good agreement with the result from equation (1) using $f = 27\%$.

Table 2 also clearly shows the existence of an optimal impregnation time, 1 h, at a constant acid concentration. It may be assumed that short drying times are insufficient for an effective reaction of phosphoric acid with a porous solid, whereas long ones induce the digestion of the solid by acid, leading to the partial collapse of the porosity [13].

4. Conclusions

Activation of mesoporous resorcinol–formaldehyde cryogels with orthophosphoric acid produced mainly microporous materials having either lower or higher porosities than their carbonized counterparts, depending on the experimental conditions. Activation was ineffective when diluted solutions of acid were used, whereas enhancement of surface area was observed at higher concentrations. However, in the case of the initially most porous material, an optimum concentration was evidenced, attributed to a detrimental effect of an excess of acid. In most cases, much lower mesopore volumes than those of the pyrolysed cryogels were obtained. The general trends observed in this work can be summarized as follows. After pyrolysis only, the resultant CRF carbon cryogels had the following properties:

1. Surface areas were larger than 650 m$^2\text{g}^{-1}$.
2. Mesopores were easily accessible through a large amount of macropores, provided the initial R/W mass ratio of the RF precursors was lower than 0.5.

After impregnation by phosphoric acid at concentrations lower than 1.2 M$^{-1}$ and subsequent heat treatment, the activated cryogels had the following properties:

3. Increasingly high acid concentrations strongly increased the surface area and significantly decreased the mesopore volume.
4. Higher initial R/W mass ratios led to much lower surface areas and slightly decreased the mesopore volumes.
5. Higher solid-acid contact times slightly decreased the surface area and did not affect the mesopore volume.
6. A drying time of 1 h after impregnation of the RF cryogels with acid was found to be optimal for obtaining the highest surface areas after heat treatment.
7. Initial R/W mass ratio of 0.05, acid concentration of 1.2 M$^{-1}$ and drying time of 1 h led to authentic bimodal activated carbons with a surface area as high as 1780 m$^2\text{g}^{-1}$.

After impregnation by phosphoric acid at concentrations higher than 1.2 M$^{-1}$, the followings were obtained.

8. Activated carbons having exceptionally high surface area and micropore volume, 2195 m$^2\text{g}^{-1}$ and 0.69 cm$^3\text{g}^{-1}$, respectively, were obtained at an optimum acid concentration of 2 M$^{-1}$.
9. For the most favourable drying time, 1 h, the optimum acid concentration corresponded to the stoichiometry between acid molecules and hydroxyl groups of the gel.

Acknowledgments

The authors gratefully acknowledge the financial support of the CPER 2007-2013 ‘Structuration du Pôle de Compétitivité Fibres Grand’Est’ (Competitiveness Fibre Cluster), through local (Conseil Général des Vosges), regional (Région Lorraine), national (DRRT and FNADT) and European (FEDER) funds.

References

[1] Czakkel O, Marthi K, Geissler E and Laszlo K 2005 Micropor. Mesopor. Mater. 86 124
[2] Job N, Théry A, Pirard R, Marien J, Kocon L, Rouzaud J N, Beguin F and Pirard J P 2005 Carbon 43 2481
[3] Szczurek A, Amaral-Labat G, Fierro V, Pizzi A, Masson E and Celzard A 2010 Mater. Chem. Phys. submitted
[4] Tamon H, Ishizaka H, Yamamoto T and Suzuki T 1999 Carbon 37 2049
[5] Nishihara H, Mukai S R and Tamon H 2004 Carbon 42 885
[6] Hu X and Do D D 1993 Chem. Eng. Sci. 48 1317
[7] Scholl S, Kajszka H and Mersmann A 1993 Gas Sep. Purif. 7 207
[8] Azais P, Duclaux L, Florian P, Massiot D, Lillo-Rodenas M A, Linares-Solano A, Peres J P, Jehoulet C and Béguin F 2007 J. Power Sources 171 1046
[9] Pekala R W, Alvisco C T, Lu X, Gross J and Fricke F 1995 J. Non-Cryst. Solids 188 34
[10] Wu D, Fu R, Sun Z and Yu Z 2005 J. Non-Cryst. Solids 351 915
[11] Mukai S R, Tamitsuji C, Nishihara H and Tamon H 2005 Carbon 43 2628
[12] Fierro V, Torré-Fernández V, Montané D and Celzard A 2005 Thermochim. Acta 433 153
[13] Fierro V, Torné-Fernández V, Montané D and Celzard A 2006 Micropor. Mesopor. Mater. 92 243
[14] Conceição F L, Carrott P J M and Ribeiro Carrott M M L 2009 Carbon 47 1867
[15] Zubizarreta L, Arenillas A, Pirard J P, Pis J P and Job N 2008 Micropor. Mesopor. Mater. 115 480
[16] Babic B, Kaladerovic B, Vraca L and Krstajic N 2004 Carbon 42 2617
[17] Tamon H, Ishizaka H, Yamamoto T and Suzuki T 2000 Carbon 38 1099
[18] Brunauer S, Emmett P H and Teller E 1938 J. Am. Chem. Soc. 60 309
[19] Dubinin M M 1989 Carbon 27 457
[20] Gregg S J and Sing K S W 1982 Adsorption, Surface Area and Porosity 2nd edn (New York: Academic Press)
[21] Tarazona P 1995 Surf. Sci. 331–333 989
[22] Szczurek A, Jurewicz K, Amaral-Labat G, Fierro V, Pizzi A and Celzard A 2010 Carbon 48 3874
[23] Li J, Wang X, Huang Q, Gamboa S and Sebastian P J 2006 J. Power Sources 158 784
[24] Petricevic R, Reichenauer G, Bock V, Emmerling A and Fricke J 1998 J. Non-Cryst. Solids 225 41
[25] Horikawa T, Hayashi J and Muroyama K 2004 Carbon 42 1625
[26] Albert D F, Andrews G R, Mendenhall R S and Bruno J W 2001 J. Non-Cryst. Solids 296 1
[27] Bock V, Emmerling A and Fricke J 1998 J. Non-Cryst. Solids 225 60
[28] Zhao W, Fierro V, Pizzi A and Celzard A 2010 J. Mater. Sci. 45 5778
[29] Lin C and Ritter J A 1997 Carbon 35 1271
[30] Fierro V, Muñiz G, Basta A H, El-Saied H and Celzard A 2010 J. Hazard. Mater. 181 27
[31] Srinivasakannan C and Abu Bakar M Z 2004 Biomass Bioenergy 27 89
[32] Guo Y and Rockstraw D A 2006 Carbon 44 1464
[33] Girgis B S, Yunis S S and Soliman A M 2002 Mater. Lett. 57 164
[34] Izquierdo M T, Martínez de Yuso A, Rubio B and Pino M R 2011 Biomass Bioenergy 35 1235
[35] Girgis B S and El-Hendawy A N A 2002 Micropor. Mesopor. Mater. 52 105
[36] Gratuito M K B, Panyathanmaporn T, Chumnaklang R A, Sirinuntawittaya N and Dutta A 2008 Biores. Technol. 99 4887
[37] Weast R C 1981 Handbook of Chemistry and Physics 62nd edn (Boca Roton, FL: CRC Press)