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Chemical activation of tannin–furanic carbon foams

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ABSTRACT

New tannin-derived/furanic carbon foams with high surface areas were obtained by chemical activation. $ZnCl_2$ and H_3PO_4 were used as activating agents and the stability of the foams structures obtained was evaluated. In addition to conventional textural analysis, the activated foam samples were analysed by nuclear magnetic resonance (NMR) and temperature programmed desorption with mass spectrometry analysis (TPD-MS). ^{13}C NMR analysis has allowed to understand the chemical rearrangements occurring and ^{1}H NMR has allowed to study interactions of the foam with water. TPD-MS yielded information on the surface chemistry of the activated carbon. Chemical activation was found to be effective for both treatments: the surface area increasing from 36 m^2/g up to 1875 m^2/g and 1265 m^2/g for foams synthesised respectively with zinc chloride and phosphoric acid. It has been demonstrated that the final carbon foams exhibit mainly micropores. Moreover, different surface chemistry were obtained depending on the chemical treatment used. Therefore, it was shown that carbon foams with high surface areas and tailored surface chemistry can be synthesised from this biomass based precursor.

1. Introduction

During the last two decades, several synthesis processes have been developed to obtain carbon foams. The main types are xerogels (Job et al., 2004), aerogels (Biesman et al., 1998) and foams obtained by pyrolysis of polymers, pitches or coal extracts (Chen et al., 2006). The wall structure of these foams is generally vitreous carbon (reticulated vitreous carbon or RVC). Among the numerous possible precursors, tannin based rigid foams are known since a long time (Meikleham and Pizzi, 1994). Recently, several studies have contributed to improve the knowledge on this 95%-natural product (Pizzi et al., 2008; Tondi and Pizzi, 2009; Tondi et al., 2009a). RVC foams derived by natural precursor have been shown to be a viable alternative to synthetic foams for several applications in energy and environment such as filters for metallic ions adsorption (Tondi et al., 2009b) or insulating materials (Tondi et al., 2008a). Due to their excellent fire resistance properties they are also good candidates to replace phenolic and polyurethane foams in many construction and engineering applications (Tondi et al., 2009c).

Carbonisation derivatives of tannin based rigid foams have also been extensively characterised (Tondi et al., 2009a). The chemical constitution of their wall structures has been analysed by MALDI-ToF spectrometry (Tondi et al., 2008b) while the gasses emitted during the carbonisation process have been monitored by GC/MS (Tondi et al., 2008c). These foams resist well to carbonisation, mostly rearranging into structures of a more aromatic character through thermal annealing process. During carbonisation only a fraction of the oxygen atoms evolve from the material and some furanic structure even survive to the carbonisation. This induces defects in the sp^2 carbon structure and modifies the regularity of the network. Such carbon foams are typically reticulated vitreous carbons (RVC) which are not graphitised whatever the pyrolysis conditions applied. This product has very high porous volume and low surface area according with the features observed for most RVC foams. The volume is mainly constituted of large interconnected macropores. The cells connections in three-dimensional porous network formed were also analysed by microtomography (Tondi et al., in press).

High surface area is required to obtain interesting performances for several applications typical of activated carbons such as catalysis and selective adsorption. Two branches of activation can be run in order the improve surface area and volume of pores:

- Physical activation which consists in reaction with high temperature gasses such as H_2O, CO_2, and O_2.
- Chemical activation in which surface reactions of different chemicals produce micropores and small ripples increasing the active surface of carbon material (El-Hendawy, 2005; Girgis et al., 2002).
- Chemical activations is often used when high volume of micropores (i.e. pores with a size below 2 nm) and high carbon yield is required (Macia-Agullo et al., 2004). Another important

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characteristic of chemical activations is the possibility to create specific functional groups on the surface of carbon activated materials (Puziy et al., 2002a). Acids or bases properties of the surface are strongly influenced by the activation agent, and this can have great influence on performances especially when liquid–solid interactions occur (Radovic et al., 2001). The choice of the right activation system depends also by the thickness of the carbon walls. The chemical treatment must therefore be done carefully in order to preserve the morphology of the pristine material. The aims of this study were two:

- ○ Increase the surface area of tannin based RVC foams throughout chemical activation;
- ○ Characterise the chemical, textural and structural properties of the activated carbon foams.

2. Experimental

2.1. Activated carbon foam synthesis

The synthesis process of the pristine carbon foams from tannins has already been described in previous publications (Tondi et al., 2009a,b). Commercial Mimosa (Acacia mearnsii, formerly mollissima, de Wildt) bark tannin extract from Brazil, containing 84% phenolic material, was used for the preparation of the foams. Furfuryl alcohol (5.2 g), formaldehyde 37% water solution (3.7 g) and water (3.0 g) were mixed with 15 g of Mimosa tannin extract, strongly stirring the bulk. When the agglomerate was homogeneous diethylether (1.5 g) and then toluene-4-sulphonic acid 65% (6.0 g) were added and mixed during 10 s before discharging the mixture in a lined box for foaming. The resin foamed within 2 min with a temperature rise of about 40 °C to yield a black foam with a density ranging between 0.07 and 0.1 g cm^{-3}. The core of these foams has been cut with the dimensions wanted after skin removal.

Six groups constituted by four samples each of tannin based rigid foams 19 mm × 13 mm × 13 mm dimensions, have been selected considering an average density of 0.09 g cm^{-3}.

- Two groups have been carbonised without activation agents at 450 °C and 700 °C (samples C-450 and C-700, respectively);
- Two groups have been chemically activated with $ZnCl_2$ using Zn concentration of 0.24 and 1 g/g of foam (samples C-Zn-L and C-Zn-H, respectively);
- Two groups have been chemically activated with H_3PO_4 using phosphorus concentration of 0.3 and 0.9 g/g of foam (samples C-P-L and C-P-H, respectively).

The details of the synthesis of these different samples are as follows:

- *C-450 and C-700*: the carbonisation was carried out inside a fused silica sample holder, itself installed in the middle of a fused silica tube continuously flushed with a laminar flow of high-purity nitrogen. The tube was heated by an electric furnace from room temperature up to 450 °C and 700 °C for samples C-450 and C-700, respectively. Several experiments were done at different heating rates, the value which was chosen was 4 °C/min. Such a rather fast heating rate was chosen after it was observed that the quality of the samples (aspect, weight and friability) was not lower than that of material heat-treated at a few °C/min only. Once reached, the final temperature was held during 3 h, then the furnace was switched off, and the samples were allowed to cool down to room temperature under nitrogen flow.
- *C-Zn-H and C-Zn-L*: the pristine carbon foams were dept in two different solution of $ZnCl_2$. The ratios of the mass of activating agent over the mass of sample were 0.24 and 1 g/g for C-Zn-L and C-Zn-H, respectively. A vacuum of 10 mbar was applied during 30 min in order to remove the air naturally present in the foam sample. Then, the system slowly returned to ambient pressure and the system was left during 30 min to allow the solution to fill the foam cells. This process was repeated three times. Impregnated samples were then dried during 12 h at 100 °C. The carbonisation was done at 500 °C, holding this temperature during 1 h. The metal trapped into the structure was removed by washing the sample three times with a 2 M solution of HCl. The efficiency of the removal of zinc has been checked by adding $(NH_4)_2S$.
- *C-P-L and C-P-H*: for phosphoric acid activation, the procedure was the same as the one used for $ZnCl_2$ activation. The ratios of the mass of activating agent over the mass of sample were 0.3 and 0.9 g/g for samples C-P-L and C-P-H, respectively. The carbonisation was done at 450 °C and this final temperature held for 1 h have been applied. H_3PO_4 was then removed after carbonisation by four successive washing with deionized water.

2.2. Characterisations

Nitrogen adsorption–desorption isotherms at −196 °C were measured with a Micromeritics apparatus (ASAP 2020). Samples were outgassed before the experiments at 200 °C during 16 h. The specific surface area was obtained according to the BET method in the relative pressure range of 0.05–0.3. The total pore volume was determined at P/P^o of 0.95 and the volume of micropores was evaluated according to the Dubinin–Raduskevitch equation in the relative pressure range of 10^{-2}–10^{-4}. The DFT method was applied to analyse the pore size distribution (PSD) of the carbon materials, the kernel used assumed nitrogen–carbon interactions in slit pores. This kernel gives generally reliable results for conventional activated carbons (Jagiello and Thommes, 2004; Ryu et al., 1999).

The morphology of the foams was studied by scanning electron microscopy (SEM) using a Philips XL 30 scanning electron microscope (SEM) equipped with a LaB6 emission source. Solid phase nuclear magnetic resonance was done with an Avance 300 MHz Brucker NMR apparatus. The experiments were carried out with a Brucker probe of 4 mm fused zirconia rotors for ^1H and ^{13}C. The spinning rate was 12 kHz in a DBM4 probe. ^{13}C have been registered in CPMAS with contact time of 1 ms, impulsion time of 4.75 μs and recycle delays of 8 s.

In order to study the surface chemistry of the carbon materials, temperature programmed desorption with mass spectrometry analysis (TPD-MS) was done. This method allows the quantitative determination of the functional groups which are present on the surface of the carbon materials (Rietsch et al., 2009; Vix-Guterl and Ehrburger, 2003). TPD-MS experiments were done with a lab-made instrument. In this experimental set-up, around 10 mg of sample is put inside a furnace under dynamic vacuum (below 10^{-5} mbar). An outgassing at 50 °C is done to remove condensed species (mainly water), then the sample is progressively heated with heating rate of 5 °C/min up to 950 °C. The molecules which evolve from the material by desorption or by decomposition reaction are analysed by a quadrupole mass spectrometer (Figueiredo et al., 1999). These volatile products result mainly from surface groups decomposition reactions. Calibration of the experimental set-up was done for CO, CO_2, H_2O and H_2.

3. Results and discussion

The main drawback of RVC foams is their completely smooth surface at the nanometrical scale. According with this knowledge, tannin based carbon foams exhibit a high porous volume almost completely constituted of macropores (i.e. pores with a size above

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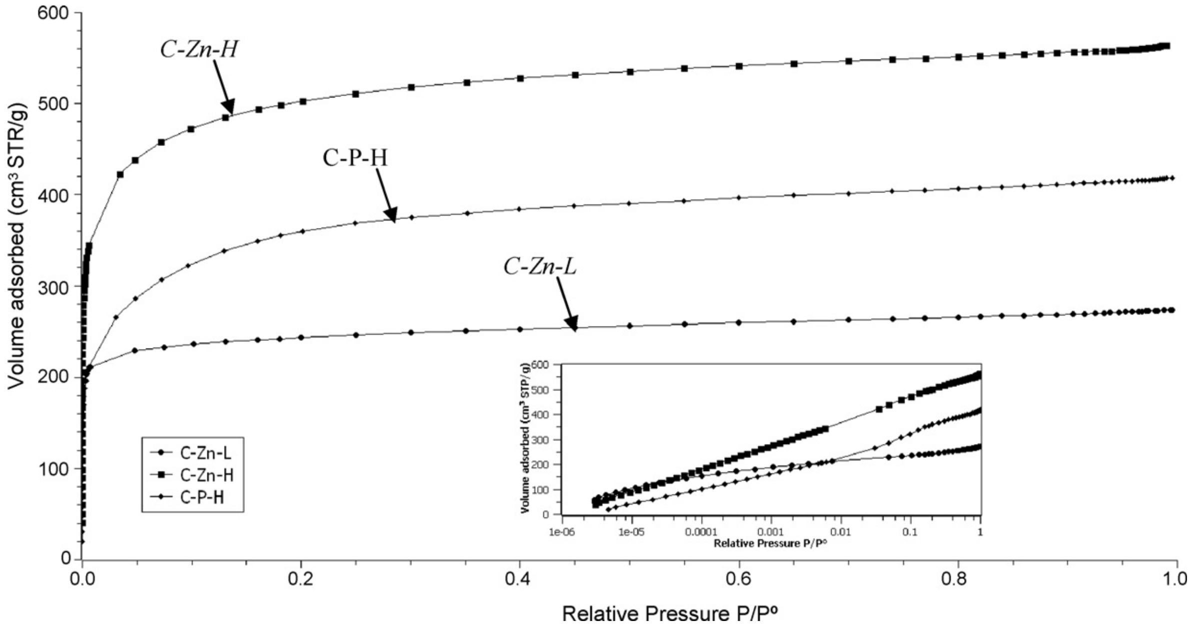

Fig. 1. Nitrogen adsorption isotherms of carbon foams at 77 K.

300 nm). The use of activating agents like $ZnCl_2$ or H_3PO_4 is useful to create a significant volume of micropores and mesopore, and therefore to increase the surface area of carbon materials (Molina-Sabio and Rodriguez-Reinoso, 2004). Nitrogen adsorption isotherms at 77 K are the most common way to analyse the porosity of materials. The main advantage of this technique is the wide pressure range (6 orders of magnitude) which allows to study the whole pore size distribution with a single measurement (Rouquerol et al., 1999). N_2 adsorption isotherms at 77 K of activated carbon foams are reported in Fig. 1 while carbonisation conditions, surface area and pores volume are reported in Table 1.

According with RVC materials, carbon foam obtained by carbonisation of the pristine foam without activating agent has a really low surface area (36 m^2/g) and it does not exhibit any porosity in the micropore or mesopore range. The activation with phosphoric acid at low activating ratio does not lead to any development of porosity (sample C-P-L). This is in agreement with the studies done on activation of other precursors: it was observed that activating ratio upper than 0.7 are necessary to achieve a significant increase of surface area and porous volumes (Girgis et al., 2002). In facts when the activating ratio increase to 0.9, the carbon foam shows a surface area of 1265 m^2/g and a porous volume of 0.65 cm^3/g. The isotherms of sample C-P-H is of type 1, showing that the pore size distribution consists mainly of micropores and small mesopores. This is confirmed by the high value of V_{DR} (0.47 cm^3/g).

The Dubinin–Radushkevich analysis gives an estimation of the total volume of micropores (V_{DR}) throughout nitrogen adsorption isotherm. This parameter is important to evaluate the performances of materials because in the most of the applications the volume of ultra-micropores can be indispensable (Gadiou et al., 2005; Frackowiak et al., 2006).

In many cases, it has been observed that phosphoric acid activation leads to carbons having a higher volume of mesopores. In this case, the low temperature applied for the carbonisation of these tannin based foams has, fortunately, prevented this effect (Puziy et al., 2002b). Details about the pore size distributions (PSD) have been achieved throughout the DFT method and they are shown in Fig. 2. It can be observed that the PSD of H_3PO_4 activated carbons exhibit a significant volume of small mesopores with a size between 2 and 4 nm. Conversely, the volume of ultra-micropores results relatively low.

It must be noticed that the hole at 1 nm in the PSD is known as an artefact of conventional DFT analysis. Some new DFT methods have been very recently presented to overcome this problem (Ravikovitch and Neimark, 2006).

In the case of $ZnCl_2$ activation, an increase of the porous volume is observed even for low values of activation ratio. It has been found that this activating agent generally leads to carbon materials with a significant microporous volume and a narrow PSD (Molina-Sabio and Rodriguez-Reinoso, 2004). The isotherm of C-Zn-L sample perfectly matches with the characteristic of a type 1 isotherm. The pore size distribution of this sample which was computed by the DFT method shows that only ultra-micropores are obtain (Fig. 2). From the PSD of this carbon foam, we can compute the volume of ultra-micropores. The value obtained is $V_{UL} = 0.27\ cm^3/g$.

When the activation ratio increases (sample C-Zn-H), the textural properties are improved in term of surface area and pore volume, but the PSD becomes wider. Nevertheless, this carbon foam is still a true microporous material with textural properties similar to microporous activated carbons (Ahmadpour and Do, 1997; Hayashia et al., 2004). The volume of ultra-micropores of the sam-

Table 1
Textural parameters of carbon foams obtained with and without activating agent.

Sample	Activation ratio	Carbonisation temperature (°C)	Weight loss (%)	S_{BET} (m^2/g)	V_P (cm^3/g)	V_{DR} (cm^3/g)
C-450	–	450	45	36	–	–
C-P-L	0.30	450	28	55	0.04	0
C-P-H	0.90	450	28	1265	0.65	0.47
C-Zn-L	0.24	500	42	945	0.42	0.37
C-Zn-H	1.00	500	56	1875	0.87	0.73

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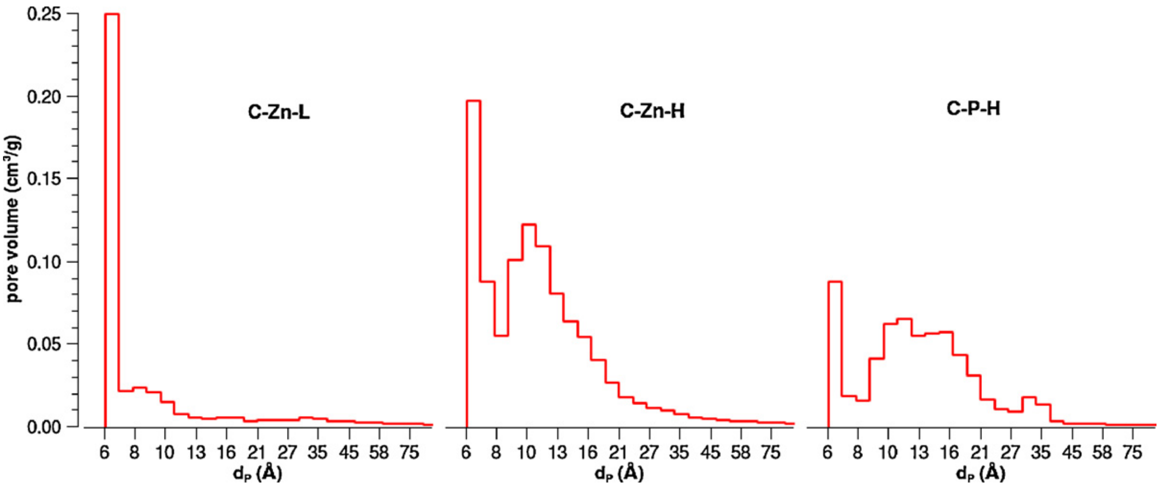

Fig. 2. Pore size distribution of activated carbon foams obtained with the DFT method.

ple C-Zn-L is V_{UL} = 0.28 cm^3/g and the increasing of pore volume is mainly related to super-micropores. Finally it is possible to deduce that Zn-activation produce a higher volume of pores and a narrower PSD, oriented in ultra-micropores in relation to H_3PO_4 activated foams.

Scanning electron microscope (SEM) images of the foam are presented in Fig. 3. As expected from the textural analysis, the sample C-450 exhibits a smooth non-porous surface. The images obtained with the activated carbon foams shows that strong modifications of the surface occur during the activation process. Ripples and dimples appear on the cell wall surfaces during $ZnCl_2$ and H_3PO_4 activation and a consequent increase of the surface area is obtained. However, the structure of the foam is preserved. The weight loss between the pristine foam and the final carbon material presented in Table 1 shows that weight loss is lower when activating agents are presents. The only exception is represented by the sample C-Zn-H which undergoes higher decomposition losing some textural properties.

Solid state NMR can be used to obtain new insights about the process which occur during the carbonisation. The ^{13}C and ^{1}H NMR analysis of the carbon foams are reported in Fig. 4. It was observed that the concentration of activation agents does not modify the signal neither in the ^{1}H NMR nor in the ^{13}C NMR spectra (data not shown). Comparing the ^{13}C NMR spectrum of C-Zn-H and C-P-H activated carbon with the non-activated one (C-450) it can be seen that carbonisation of activated foams is more effective and yields a more aromatic carbon. Alkyl groups at 15.0 and 33.9 ppm are no more present when carbon is activated and the oxo-aromatic compounds peak at 154.0 and 115 ppm disappears as well (mainly phenol groups). With this technique it is possible to have a clearer idea on what occurs during carbonisation.

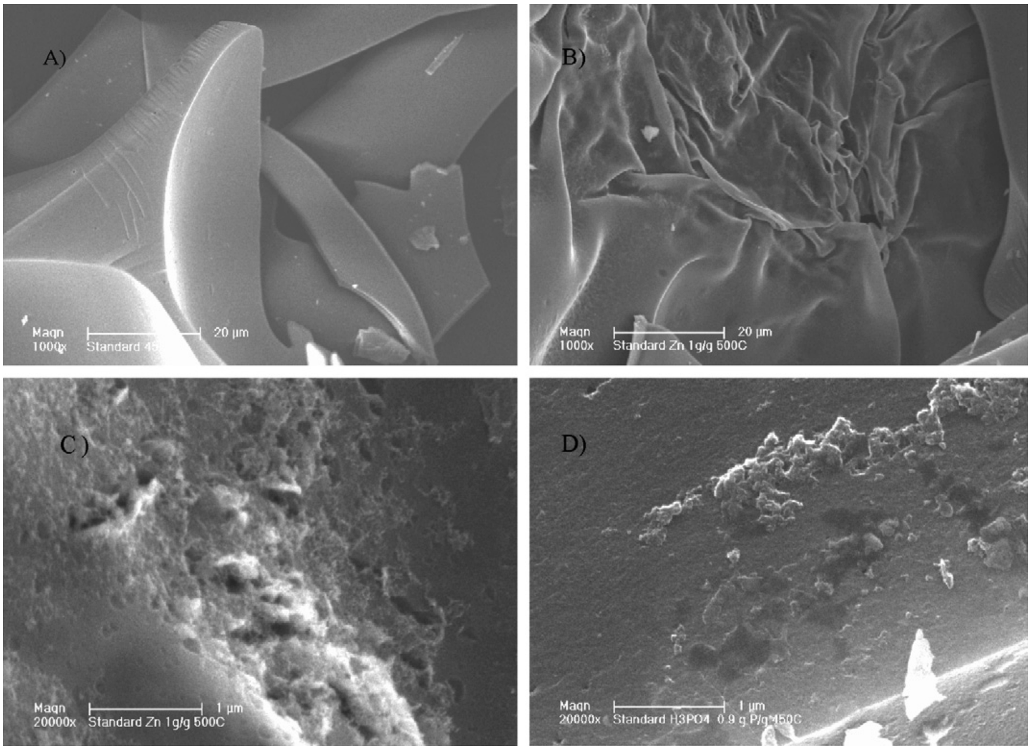

Fig. 3. MEB images of carbon foams. (a) C-450 (1000×); (b) C-Zn-H (1000×); (c) C-Zn-H (20,000×); (d) C-P-H (20,000×).

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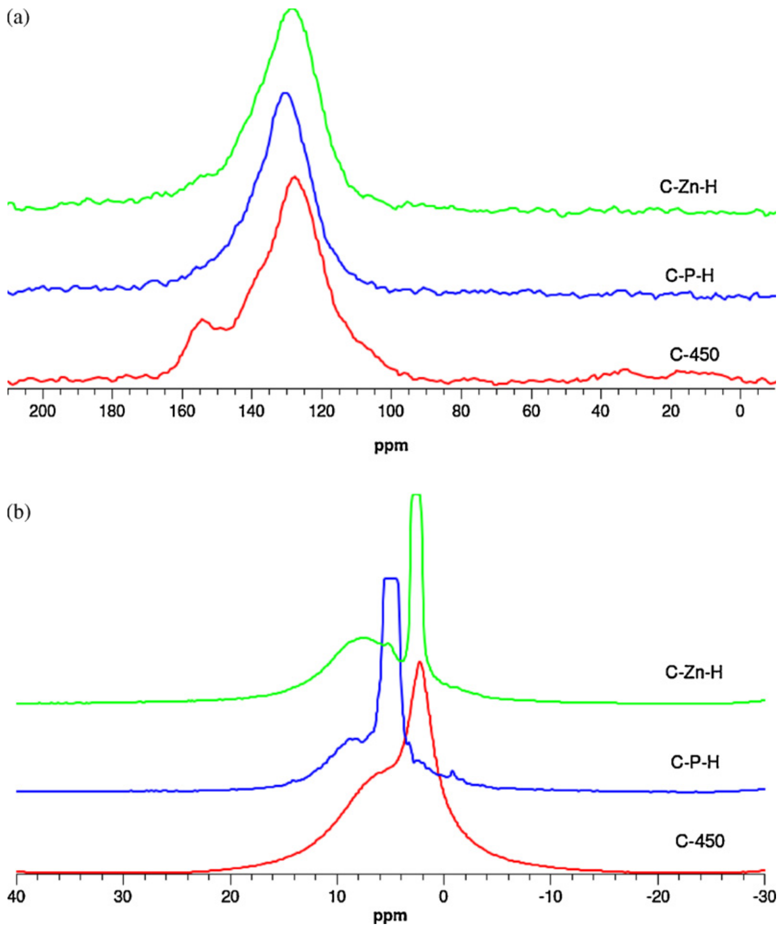

Fig. 4. NMR spectra of carbon foam synthesised with and without activating agents: (a) ^{13}C NMR; (b) ^{1}H NMR.

The ^{1}H NMR of is shown in Fig. 4b. The spectrum of Zn-activated carbons presents a broad signal of protons at 13 ppm which is attributed to strong hydrogen-bonded species (CH species are not visible in these conditions). The narrower signal at 3 ppm is attributed to bulk water. The shift from the bulk water signal, which is normally situated at 4.9–3 ppm is attributed to the paramagnetic shielding of aromatic rings. This environment seems to be unaffected by the Zn-treatment according the constant value of the water chemical shift. The decreasing of hydrophilic species after the activation causes higher water mobility and a narrower signal at 3 ppm. This means that hydrophilic centres are less present while the stronger ones are still present.

From the ^{1}H NMR spectrum of C-P-H sample is possible to see that the signal of hydrophilic species at around 8 ppm decreases strongly. The signal at 4.9 ppm is attributed to the bulk water without any paramagnetic influences from the aromatic rings. The narrow line width and the non-unshielded chemical shift of this peak reveal a proton high mobility with a poor influence of the hydrophilic species. This water clusters possibly be due to the presence of protons (H^{+}) trapped in the structure after acid activation. Indeed with bad washed samples we note a chemical shift higher than 6 ppm for acidic water medium.

Further information on the surface properties of carbon foams can be obtained from TPD-MS experiments. The TPD-MS profiles obtained for C-P-H and C-Zn-H samples are presented in Fig. 5 and it was observed that all carbon foams exhibits similar TPD-MS profiles. Two different processes are observed depending by carbonisation temperature:

- below 400 °C, the only phenomena which can occur are the desorption of molecules and the decomposition of functional surface groups;
- above 450 °C, the heating of the sample leads to pyrolysis processes, the carbon material undergoes decomposition reaction and some thermal annealing. The amount of molecules which evolve from the material during this step is generally far higher than the one detected during the low temperature surface decompositions because this process operate on the whole volume of the sample.

The four main gases analysed are H_2, H_2O, CO and CO_2. H_2 is mainly emitted during the pyrolysis process and is not indicative of the presence of surface groups. Therefore, the amounts emitted are very low until 500 °C. Above this temperature, an intense peak of hydrogen is observed around 650 °C. This peak is related to thermal decomposition of the carbon foam. CO is the other molecule, which evolves from carbon materials at relatively high temperatures. CO

Table 2
Amount of gases emitted during the temperature programmed desorption of carbon foams between 25 and 400 °C.

Sample	H_2 (mol/g)	H_2O (mol/g)	CO (mol/g)	CO_2 (mol/g)
C-450	5.1×10^{-7}	2.8×10^{-4}	1.3×10^{-4}	3.8×10^{-4}
C-P-H	1.4×10^{-5}	2.0×10^{-3}	1.3×10^{-4}	1.7×10^{-4}
C-Zn-L	5.0×10^{-6}	5.0×10^{-4}	1.4×10^{-4}	2.3×10^{-4}
C-Zn-H	1.0×10^{-4}	5.0×10^{-4}	1.6×10^{-4}	2.1×10^{-4}

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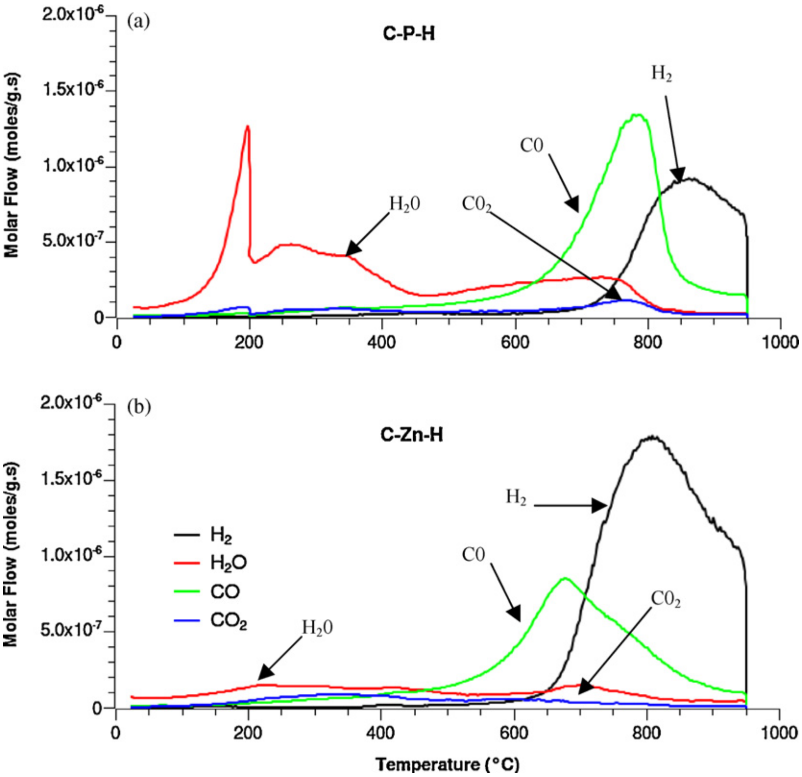

Fig. 5. TPD-MS profiles of activated carbon foams. (Bottom) with $ZnCl_2$; (top) with H_3PO_4.

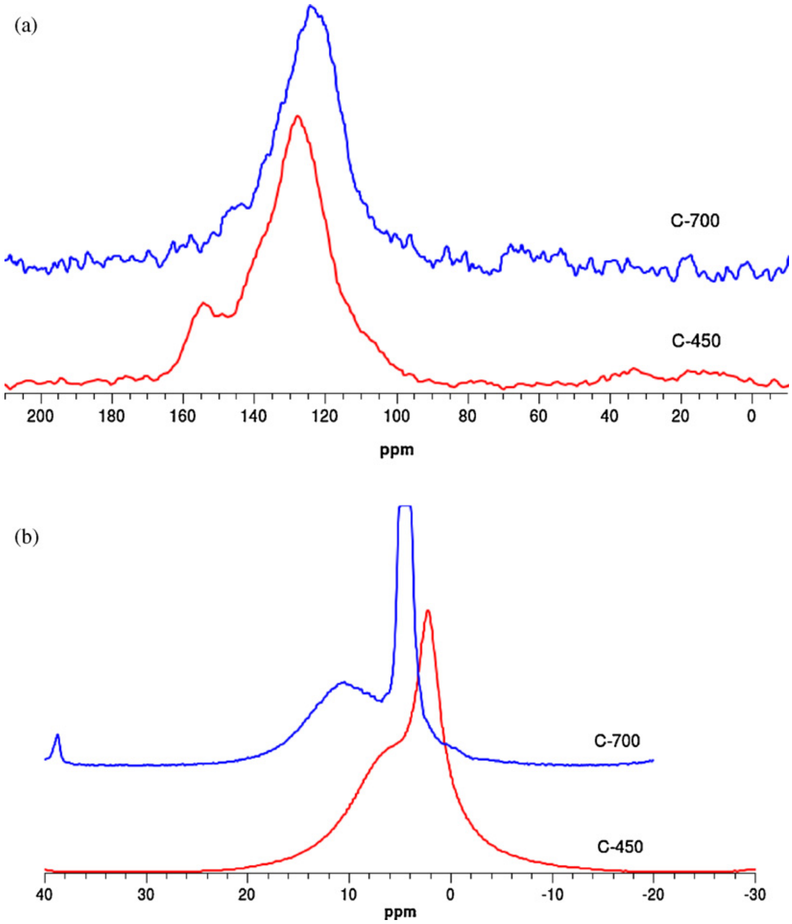

Fig. 6. NMR spectra of carbon foams obtained without any activating agent for two different carbonisation temperatures. (a) ^{13}C NMR; (b) ^{1}H NMR.

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can be emitted during the decomposition of stable surface groups like ethers, quinones, furanes or phenols, but it is also released during the pyrolysis of the carbon materials. Therefore, CO_2 and water are the main molecules released below 400 °C, the former is formed during the decomposition of carboxylic and lactone groups, the latter is generally coming from H_2O molecules strongly adsorbed on the surface by hydrogen bonds or trapped in the porosity of the material.

The TPD-MS profiles presented in Fig. 5 shows that C-P-H carbon foam has a large peak of desorption of water at 200 °C. It must be noticed that the sharp decrease at 200 °C is related to a 10 min step in the heating of the sample. This step was necessary to keep the total pressure in the experimental set-up below 5×10^{-5} mbar which is the limit pressure to achieve good measurements with our mass spectrometer. This water desorption peak is in agreement with the results of the NMR experiments presented above which showed the presence of a peak correlated with bulk water. The TPD-MS profiles are completely different for the C-Zn-H sample, the amount of water desorbed is far lower than the one measured for the foam C-P-H.

In order to obtain quantitative parameters related to the surface chemistry, the amount of gases which evolves from the carbon material between room temperature and 400 °C was integrated. The values are presented in Table 2. A general observation is that the amounts of gases released are relatively high and are indicative of a rich surface chemistry. This fact is particularly significant for the sample C-450 that exhibits low surface area (36 m^2/g). The values presented in Table 2 confirm that the amount of water trapped in the porosity of the C-P-H material is far higher than for the other carbon foams. As expected, the amount of hydrogen desorbed is very low in this temperature range for all carbon materials. Carbon dioxide is the main molecule desorbed below 450 °C. Consequently, the CO_2 desorption in this temperature range is indicative of the presence of carboxylic acid groups on the surface, but lactones and anhydrides can also be involved in the process (Marchon et al., 1988; Zielke et al., 1996).

It was observed that the use of different activating agents leads to different surface chemistries, but also to modifications in the graphitization level of the carbon foams. Further insights on this aspect have been obtained when different temperatures of carbonisation have been compared. The spectra of foams obtained by carbonisation at 450 °C and at 700 °C are shown in Fig. 6. The ^{13}C NMR spectra show that, when increasing the temperature of carbonisation, the thermal rearrangement became stronger and a higher amount of oxygen species are expelled from the structure. The ^{1}H NMR spectrum shows a great influence of paramagnetic shielding effect. The C-700 carbon foam exhibits an unshielded peak of water which shows the presence of water molecules with a high mobility. Although this ^{1}H NMR is similar to the one of the C-P-H carbon foam, the presence of bulk water could not be related to the acidity of the surface. The lower amount of hydrophilic functions and the higher amount of aromatic rings could be an explanation. This compares well with the MALDI-ToF analysis done on the carbon foams (Tondi et al., 2008b). Moreover, the study of the peaks between 0 and 40 ppm on the ^{13}C NMR allows to see that alkyl groups disappear when the carbonisation temperature increases to 700 °C. Therefore, the increase of the carbonisation temperature leads to a carbon foam with more hydrophobic surface and higher graphitization level.

4. Conclusions

In this study, we have demonstrated that chemical activation is effective to synthesise tannin based carbon foams with a high surface area. If the mass ratio of activating agent to tannin is low, the activation with $ZnCl_2$ leads to microporous carbon foams with a very narrow pore size distribution. When Zn-activation ratio increase the pore size distribution become wider and the surface area can reach 1875 m^2/g. This value compares well with microporous active carbons. H_3PO_4 has also been tested as an activation agent and a significant increase in surface area has been obtained. It was possible to obtain a surface area of 1265 m^2/g with a larger pore size distribution. It must be noticed also that in the case of phosphoric acid activation, the carbon yield is higher and the structure maintains more easily his texture.

It was confirmed that NMR can be suitable for the characterisation of such carbons materials. ^{13}C NMR allowed to evaluate the chemical composition and the aromatic character of the carbon foams, while ^{1}H NMR gave new insight on the hydrogen bonds interactions and the degree of freedom of water trapped in the porosity of the materials. It was shown that activation leads to a more aromatic structure in which the oxygens are almost completely expelled and alkyl groups are mostly rearranged to aromatic compounds. In most cases, adsorbed water interacts strongly with the surface of the carbon material. Nevertheless, for carbon foams obtained with phosphoric acid or by carbonisation at 700 °C, a high degree of freedom of water was observed. This could be related to the acidic or hydrophobic characters of the surfaces. TPD-MS analysis was used to obtain the amount of functional groups present at the surface of the foams. The surface properties of the carbon foams are different depending on the synthesis process. Anyhow a high amount of carbon dioxide is desorbed at moderate temperature (below 450 °C). This is mainly related to the presence of carboxylic groups. At higher temperature, the TPD-MS profiles of CO and H_2 confirmed that the presence of an activating agent leads to an increase of the graphitization level of the carbon foam.

Therefore, this study shows that biomass based carbon foams with interesting textural properties can be obtain by chemical activation. Further improvements will be done in order to obtain a tailored surface chemistry through specific chemical treatments. According with the information collected, these materials should be suitable for several applications such as catalyst supports or pollution scavenger.

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