The formation of a hydrothermal carbon coating on graphite microfiber felts for using as structured acid catalyst

Laura Roldan1,2, Iván Santos1, Sabino Armenise1, José María Fraile2, Enrique García-Bordejé1*

1 Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, 50018 Zaragoza, Spain
2 Instituto de Síntesis Química y Catálisis Homogénea, Facultad de Ciencias, Universidad de Zaragoza - C.S.I.C., Pedro Cerbuna 12, 50009 Zaragoza, Spain

Abstract

A hydrothermal carbon layer has been coated on graphite felt using a carbohydrate solution (glucose, sucrose or starch) as precursor. The coating is uniform in thickness and coverage, and exhibits excellent adhesion to the substrate. It is highly hydrophilic, very accessible to reactants and the thickness can be tuned by the synthesis conditions. The coating was functionalized with sulfonic acid groups and its morphology and surface chemistry characterized by SEM, TPO-MS, IR-spectroscopy and XPS. The sulfonated material has been tested in the esterification of palmitic acid with methanol exhibiting significant activity and stability.

* Corresponding author: Tel.:+ 34 976733977; fax.: +34 976733318 E-mail address: jegarcia@icb.csic.es
1. Introduction

Material science devoted to valuable carbon materials has gained increasing interest because of the potential applications as catalyst support, adsorbent, electrodes or gas storage media for fuel cells or biological applications. Carbon materials have a long history as catalyst support. Carbon has been used as catalyst support for noble metals in liquid phase reactions such hydrogenations [1-3] and oxidations [4], or as electrocatalyst [5;6]. Recently, carbon materials have been also applied as metal-free catalyst for oxidative dehydrogenations of alkanes [7;8] and for different reactions catalysed by bases [9;10] or acids [11;12].

Many synthetic approaches to prepare carbon materials have been used. To name a few, carbonisation, laser ablation, chemical vapour deposition, or hydrothermal carbonisation. Each particular method allows the preparation of carbon materials with different shapes, texture, crystallinity and chemical composition. An appealing method to prepare carbon materials is hydrothermal carbonisation (HTC) [13]. This versatile method allows preparing carbon nanomaterials and composites with different morphologies. Furthermore, it is simple and sustainable because it requires a low specific energy input and uses biomass as feedstock instead of fossil fuels.

When HTC method is carried out at low temperature (<250 °C) highly hydrophilic nanocarbons, usually nanospheres, are produced with diameters ranging between hundreds of nanometers to microns. This carbon material, also denoted as hydrochar, have an external surface densely functionalised with polar functional groups such as carboxylic, hydroxyl or quinone groups [14]. These groups are located on the external surface and
hence very accessible to reactants. Moreover, these functional groups are amenable to anchorage of different active phases for catalysis or adsorption. Several approaches have been used to modulate the morphology of hydrothermal carbon or to increase its specific surface area. For instance, the use of a sacrificial hard template such as anodized alumina [15], porous silica beads [16], silica nanospheres [17;18], SBA-15 [19] or latex nanoparticles [20]. Soft templates such as anionic[21] or nonionic surfactant [22] have been also used. The approaches mentioned above usually lead to macro and mesopores. Recently, micropores have also been created by chemical activation [23;24].

Due to the small size of nanospheres, some drawbacks are encountered for application in adsorption or catalysis. For slurry operation, the separation of the carbon nanospheres can be troublesome and cost-intensive. On the other hand, if they are used in a packed bed, the high pressure drop, non-uniform flow distribution, plugging and release to the effluent preclude its practical implementation. These drawbacks would be overcome by immobilizing the hydrothermal carbon on macroscopic supports. Furthermore, supporting the catalyst on structured reactors is highly desired because it has been put forward as a key enabling factor to implement flow chemistry in organic reactions [25]. As far as we know, there is no precedent on the macroshaping of hydrothermal carbon into monolithic macroscopic structures.

Recently, sulfonated carbon materials have been used in esterification and transesterification reactions with remarkable activity [26-32]. They were prepared via incomplete carbonization of sugars (glucose), starch or cellulose. These materials are claimed to be more resistant to desulfonation than sulfonic commercial resins due to stabilizing effect exerted by the electronegative polycyclic aromatic hydrocarbons.
Furthermore, they have shown higher activity in the trans/esterification than many other solid acid catalysts used in this reaction such as silica supported Nafion, sulfonated zirconia or niobic acid. Toda and cols. [30] prepared a sulfonated carbon derived from D-glucose which showed higher activity than conventional solid acid catalyst. This catalyst did not lose activity, even for repeated reactions at temperatures between 80 and 180 °C. Goodwin and cols. [26] prepared a sulfonated carbon that was tested in esterification (acetic acid and caprilic acid) and transesterification (triacetine, tricapriline and soy oil). It exhibited a catalytic activity during 1-hour cycle comparable to H$_2$SO$_4$ and superior than the catalytic activity using Nafion SAC-13. As far as we know, there is only one publication employing sulfonated carbon microspheres prepared via hydrothermal carbonization as acid catalyst [33]. The target reaction was the esterification of oleic acid with ethanol. This catalyst exhibited slightly larger turnover frequencies than H$_2$SO$_4$ and p-toluene sulfonic acid and much larger than Amberlyst-15.

Herein, the coating of a hydrothermal carbon (HC) layer on a macrostructured support such as carbon felt (CF) using one-pot synthesis method is described. Several synthesis conditions have been employed such as pretreatment or not with nitric acid, different carbohydrate precursor (glucose, sucrose and starch) and different concentrations. The morphology and surface chemistry of the hydrothermal carbon coated carbon felt has been characterised by SEM, IR, XPS and TPO-MS. The adhesion strength of the coating layer has been assessed by ultrasonic tests. Finally, the coated felt has been functionalised with sulfonic acid groups and tested in esterification of palmitic acid.
2. Experimental

Graphite felt was purchased from Carbon Lorraine. It consists of an entangled network of carbon microfilaments of a few centimetres length and around ten micrometres of diameter. A 1 cm diameter circular piece was cut from 5 mm-thick graphite felt sheet. The piece of felt was washed with acetone. In some preparations, it was also treated with nitric acid (65%) at 80 ºC during 16 hours and washed with distilled water until neutrality. For the hydrothermal carbon synthesis, a solution of the carbohydrate (glucose, sucrose or starch) was prepared at different concentrations in 25 ml distilled water. The solution was poured into the autoclave vessel. Subsequently, the piece of felt was immersed into the carbohydrate solution. The HNO₃-treated felt kept immersed without forcing it. However, the as-received felt floated on the solution and it was necessary to force the felt inside the solution by fixing its borders to the autoclave wall.

The autoclave vessel was closed and the hydrothermal synthesis was carried out under autogenous pressure at 195 ºC for 18 h. After cooling down the autoclave, the felt was introduced in ethanol and sonicated for 15 min (frequency 40 KHz) to remove loosely adhere hydrothermal carbon. After drying, the ultrasonic treatment was repeated again. Finally, the sulfonated materials was washed thoroughly with distilled water and subsequently with ethanol and dried in an oven at 105 ºC. The carbon felt coated with a hydrothermal carbon layer was denoted as HC-CF.

The sulfonation of the hydrothermally treated felt was carried out with concentrated (>96%) sulfuric acid (1 g felt/20 mL H₂SO₄) at 150ºC under argon atmosphere for 16 h.
The resulting graphite felt was then washed thoroughly with hot distilled water and dried overnight at 105°C. The sample of HC-CF after sulfonation was denoted as HO_3S-HC-CF.

Esterification reaction of palmitic acid with methanol was carried out in a round flask under reflux using 7.5 mmol of palmitic acid (1.92 g), 75.0 mmol of methanol (3.04 ml), 210 mg of graphite felt and 2.1 mmol of 1-methylnaphthalene (0.30 g) as internal standard. Small aliquots were withdrawn at different reaction times and analyzed by means of a gas chromatograph (HP-5890-II).

SEM analysis was carried out with a microscope SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and with an analyzer EDX Röntec XFlash of Si(Li). The images were obtained both from the secondary and backscattered signal.

Temperature-programmed oxidation experiments (TPO) were performed in a SETARAM Setsys Evolution. About 10 mg of sample was heated at 10 °C/min rate until 700 °C under air while monitoring the weight. In parallel, TPO-MS experiments were carried out in the same conditions in a quartz reactor and the gases were analysed using a quadrupole mass spectrometer (Balzers) connected in line with the reactor.

For infrared analysis, monolith samples were first ground in an agate mortar to produce fine powder that was mixed with pure KBr (Merck for spectroscopy) by a weight ratio of 1:100. About 250 mg of the mixture was used to prepare each pellet by compressing at 10 tonnes cm^{-2} for 10 min using a hydraulic press. Infrared spectra were recorded with a Vertex 70 Bruker spectrometer over the wavenumber range of 4000-400 cm^{-1} with 30 scans being taken at 2 cm^{-1} spectral resolution. The spectrum of a pure KBr pellet was used as background.
XPS spectra were recorded with an ESCAPlus Omnicrom system equipped with a Al Kα radiation source to excite the sample. Calibration of the instrument was done with Ag 3d5/2 line at 368.27eV. All measurements were performed under UHV, better than $10^{-10}$ Torr. Internal referencing of spectrometer energies was made using the dominating C 1s peak of the support at 284.6 eV and Al 2p, at 74.3eV. The program used to do curve fitting of the spectra was XPS Peak4.1 and XPS Graph routines after baseline Shirley method.

3. Results and discussion

When hydrothermal synthesis from a glucose solution is carried out in absence of graphite felt, carbon nanospheres of diameters ranging between 500 and 1000 nm are produced (figure 1a) in agreement with other works [13]. When hydrothermal synthesis is carried out after introducing a piece of graphite felt (figure 1b) in the carbohydrate solution, the carbon felt becomes coated by a uniform layer of hydrothermal carbon with some carbon nanospheres attached to it (figures 2-4). The variation of synthesis parameters, i.e. carbohydrate type and concentration and pre and post treatments, led to different morphologies and loadings of hydrothermal carbon coating, which is explained in detail below.
Figure 1. SEM images of different materials used and synthesised in this work: (a) hydrothermal carbon nanospheres synthesised in the absence of graphite felt (HC); (b) as-received graphite felt (CF).

Figure 2. SEM images of carbon felt after hydrothermal carbon synthesis from three different concentrations of glucose solution: (a, b) 0.3 M glucose solution; (c, d) 0.5 M glucose solution; (e, f) 1M glucose solution.
3.1. Effect of the carbohydrate concentration

Figure 2 shows SEM images prepared from glucose parent solutions of three different concentrations (0.3, 0.5 and 1 M). It is apparent that the amount of produced carbon nanospheres and layer thickness increase as the carbohydrate concentration increases. From some SEM images in which the coating is abruptly interrupted, it is possible to measure the hydrothermal carbon layer thickness, which is ~ 200 nm and ca. 4000 nm for hydrothermal carbon coating derived from the 0.3 M (figure 2b) and 1 M glucose solutions (figure 2f), respectively. Thus, a large range of thicknesses can be prepared depending on the concentration of carbohydrate solution. Nevertheless, for the thinnest coatings, SEM observations cannot unambiguously prove that the coverage is complete.
3.2. Effect of the pre-treatment with nitric acid and post-treatment in ultrasound

Figure 3 shows samples after synthesis of hydrothermal carbon using the same 0.5 M glucose solution but two different carbon felts, namely as-received carbon felt (figure 3a, b) and carbon felt pre-treated with 65% HNO₃ at 80º C during 16 h (figure 3c, d). Comparison of the two figures shows that HNO₃-treated carbon felt yielded higher amount of hydrothermal carbon spheres than as-received carbon felt. Agglomerates of nanospheres even clog the macropores between the felt microfibers for HNO₃-treated carbon felt (figure 3c and d). Hydrothermal carbon loading determined by thermogravimetric analysis was 16 wt% and 26 wt% for the as-received and HNO₃-treated hydrothermal carbon, respectively. The higher amount of hydrothermal carbon on the HNO₃-treated carbon felt can be explained because graphite felt becomes more hydrophilic after HNO₃ treatment. Therefore, it is more easily wetted by aqueous carbohydrate solution, which can access readily to the whole porosity of carbon felt.

Some produced carbon nanospheres are weakly attached to the carbon felt surface or just entrapped within the macropores of the felt. In order to remove the hydrothermal carbon that is not well attached, ultrasound treatment was carried out previously to further
characterisation. The hydrothermal carbon content determined by thermogravimetric analysis was 16.1 wt% and 7.3 wt% before and after ultrasound treatment, respectively. Figure 3(e) and (f) shows SEM images of the hydrothermal carbon coated carbon felt after ultrasound treatment. Most nanospheres were removed and only the hydrothermal carbon coating layer remains after ultrasound treatment. Ultrasound treatment is very aggressive and commonly employed to check coating adhesion [34-36]. After this treatment, only the well-attached coating remains with some semi-spheres embedded within the coating (figure 3f). Therefore, the adhesion of the remaining hydrochar layer to the graphite felt is excellent, which underscores the mechanical resistance of coating for a real catalytic application under flow conditions.

![SEM images of hydrothermal carbon coated carbon felt prepared using 0.3 M solutions of two different carbohydrates: (a) sucrose or (b) starch](image)

3.3. Influence of the carbohydrate precursor type

Hitherto, the shown results correspond only to hydrothermal carbon prepared using glucose as precursor. Besides glucose, other carbohydrate types have been tested such as sucrose
and starch (figure 4). The morphology of coating surface varies depending on the precursor. The surface of sucrose-derived carbon is rough, with no embedded nanospheres but sharp elongated features (figure 4a). In contrast, the surface of starch-derived carbon is smoother and with rounded features (figure 4b), resembling the morphology of samples prepared using glucose (figure 3f).

The loading of hydrothermal carbon on graphite felt can be accurately quantified by gasification under air atmosphere in temperature programmed thermogravimetric analysis as explained in next section. For the same carbohydrate molar concentration, the hydrothermal carbon loading follows this increasing order, glucose < starch < sucrose (figure S1 supplementary information).

3.4. Characterisation of HTC coating by TPO-MS and proposed formation mechanism

Figure 5 shows TPO gravimetric experiments for pure graphite felt, for felt coated with hydrothermal carbon derived from glucose, starch and sucrose, respectively. All samples were previously treated by ultrasound to remove looser nanospheres. Graphite felt does not lose weight until temperatures above 930 K. On the other hand, hydrothermal carbon coating is less stable to oxidation. It starts to be burnt out already at 500 K and it is completely burn-out at 850 K. Therefore, the weight loss until 850 K gives an accurate measure of the hydrothermal carbon loading.
Figure 5. Normalized weight loss in temperature programmed oxidation experiments under air atmosphere for original carbon felt (CF) and carbon felt coated with hydrothermal carbon (HC-CF) prepared from 0.3 M solutions of the three different types of saccharides (glucose, starch and sucrose). Inset shows the derivative of weight loss.

Before hydrothermal synthesis the graphite felt is superhydrophobic and it floats on water surface. After hydrothermal carbon synthesis, the felt remains immersed within water indicating the functionalisation of the carbon coating (figure S2, supplementary information). Some preliminary information about surface chemistry can be obtained using temperature programmed oxidation coupled to mass spectrometry (TPO-MS). The derivative of weight loss (inset in figure 5) shows two different burn-out rates, which take place at similar temperatures for all the samples irrespective of the synthesis conditions (saccharide type and concentration). The slower burn out is centred at \textit{ca.} 585 K and the faster one occurs at \textit{ca.} 750 K. These two rates seem to indicate a heterogeneous functionalisation along the coating thickness. This is confirmed by the analysis of MS
signal (figure S3 supplementary information). The slower rate is mainly associated with the formation of \( H_2O \) (trace d in figure S3) by reaction of \( O_2 \) gas with hydrogen on the highly functionalised external surface. In the period of faster burning-out at \( ca. \ 750 \) K the formation of \( CO_2 \) prevails, which is produced by reaction of \( O_2 \) gas with the less functionalised inner part in contact with the felt surface. Thus, the innermost part of hydrochar layer is hydrophobic, which creates a good anchorage with the graphite surface while the external surface of the layer, which is in contact with the aqueous solution, is hydrophilic. This agrees with the structure reported for carbon nanospheres, which have a hydrophobic core and a hydrophilic surface [14;34]. Elsewhere, it was confirmed that the hydrocarbon produced by condensation of saccharide has a composition based on furan groups [37].

Based on SEM observations and TPO-MS, we propose the mechanism depicted in figure 6 for the synthesis of HT-carbon coating on graphite felt. Hydrothermal carbon nanospheres are generated both in the carbohydrate solution and on graphite microfiber surface. As hydrothermal process proceeds further, HT-carbon that is not in contact with aqueous carbohydrate solution becomes enriched in carbon by dehydration as in the mechanism reported for HT-carbon nanospheres [14;38]. When the carbon felt surface is densely covered by nanospheres, they coalesce to form a HT-carbon layer. This layer has increasing carbon content, \( i.e. \) decreasing functionalisation, towards the direction of the graphite microfiber. This hydrofobicity gradient enhances the interaction of HT-carbon and graphite felt surface leading to a good anchorage. As synthesis time increases, coalescence of new spheres with the HT-carbon layer contributes to its thickening. This mechanism explains
the observations of increasing HTC layer thickness as time and carbohydrate concentration rises.

Figure 6. Scheme proposed for the synthesis of HTC coating on graphite felt. The darkest contrast of HTC indicates higher carbon content.

3.5. Surface chemistry characterisation by spectroscopic techniques
Figure 7. Infrared spectra of original carbon felt (CF), carbon felt coated with hydrothermal carbon (HC-CF) and after subsequent sulfonation (HO$_3$S-HC-CF).

The surface chemistry of the original carbon felt (CF), the carbon felt composite coated with hydrothermal carbon (HC-CF) and after subsequent sulfonation (HO$_3$S-HC-CF) was characterised exhaustively by IR and XPS spectroscopy. Figure 7 shows the characterisation by IR. The original graphite felt is almost featureless indicating the absence of functionalisation. After hydrothermal synthesis many bands emerge which indicate a high degree of functionalisation in agreement with the increased hydrophilicity. The bands are similar for all the used saccharides types and for all the tested synthesis conditions. Among the most prominent bands, that at 1710 cm$^{-1}$ can be attributed to C=O (carbonyl, quinone, ester, or carboxyl) whereas the bands at 1620, 1505 and 1428 cm$^{-1}$ are attributed to skeletal C=C vibrations, and the bands at approximately 2900 and 3000–3700 cm$^{-1}$ correspond to stretching vibrations of aliphatic C–H (methyl and methylene groups) and O–H (hydroxyl or carboxyl), respectively [39-42]. In HO$_3$S-HC-CF sample, the –SO$_2$OH groups could be identified with the intense band at 1221 cm$^{-1}$, representing the O=S=O asymmetric and symmetric stretching modes [27;43]. In the low frequency range, the band at 590 cm$^{-1}$ is assigned to C–S stretching mode, suggesting the existence of covalent sulfonic acid groups [27]. It is evident that the H$_2$SO$_4$ treatment at high temperature enables the intensive covalent sulfonation of hydrothermal carbon.
Figure 8. X-ray photoelectron spectra of C1s (a) and O1s (b) peaks for graphite felt (CF), graphite felt coated with glucose (0.5 M)-derived hydrothermal carbon (HC-CF) and this latter after sulfonation (HO₃S-HC-CF). (c) S2p peak of HO₃S-HC-CF and sulfonated carbon felt (HO₃S-CF).

Additionally, X-ray photoelectron spectroscopy (XPS) was used to characterise the surface functionalities. The detailed XPS C1s and O1s spectra are shown in figure 8. The relative abundance of each peak after fitting of C1s and O1s region are displayed in tables S1 and S2 (supplementary information). The C1s core-level spectrum of the carbon felt (CF) exhibits a dominant peak at 284.6 eV due to carbon atoms of the graphene sheets (C=C, C-H, C-C). However, the spectrum is remarkably different after coating with hydrothermal carbon (HC-CF) and after subsequent sulfonation (HO₃S-HC-CF). In these later samples,
the peak-fitting allowed the identification of three additional signals at 285.7, 287.2, and 289.0 eV. They are attributed, respectively, to carbon coordinated to a single oxygen in hydroxyl groups or ethers (C-O-R), to carbonyl or quinone groups (>C=O), and carbon having a total of three bonds to oxygen in carboxylic groups (COOH/R) [44-46]. C-S bonds cannot be distinguished from C-C bonds because of the similarity in electronegativity between sulfur and carbon [47]. Comparing the intensity of the C1s peaks before and after sulfonation (table S1), the decrease of the peak at 285.7 eV and the increase of peak at 287 eV could be attributed to the strong oxidising ability of H2SO4 treatment which generates more carbonyl and carboxylate groups from hydroxyl groups.

The O/C ratio determined by XPS is 0.03, 0.17 and 0.22 for CF, HC-CF and HO3S-HC-CF, respectively. Therefore, the functionalisation increases progressively in each preparation step. For curve fitting of the O1s peak, the functional groups shown in figure 9 were considered, namely, C=O groups at 531.1 eV, carbonyl oxygen atoms in esters, amides, anhydrides and oxygen atoms in hydroxyls or ethers at 532.2 eV, the ether oxygen atoms in esters and anhydrides at 533.3 eV, and the oxygen atoms in carboxyl groups at 534.2 eV [40;42]. Additionally, the band at 535.5 eV is associated to chemisorbed water [42]. This later band was especially characteristic of the highly hydrophilic sulfonated samples.

The bands in the sulfur 2p region were also analysed. No sulfur band was observed for CF and HC-CF as expected. Figure 9 shows the S 2p bands of sulfonated as-received carbon felt (HO3S-CF) and HO3S-HC-CF. The peak at 169 eV is assigned to a higher oxidation state (+6) of sulfur in SO3H groups, while the peak at 163.5 eV is not present, which is assigned in the literature to reduced forms of sulfur [39;48]. This shows that all the sulfur fixed in the hydrothermal carbon coating is associated to sulfonic groups. The S/C ratio
determined by XPS was 0.34 wt% and 1.44 wt% for HO$_3$S-CF and HO$_3$S-HC-CF, respectively. Therefore, the original carbon felt is more difficult to functionalise than the hydrothermal carbon coated one.

3.6. Sulfonation and testing in esterification reaction

Previously to testing in esterification reaction, the carbon samples were sulfonated to create the catalytic acid sites. The HT carbon coating was not removed after sulfonation when glucose and starch were used as precursors. However, sulfonation of the sucrose-derived composite led to the complete removal of carbon coating. Therefore, using these sulfonation conditions, a suitable acid catalyst can be prepared from glucose or starch precursors but not from sucrose precursor. SEM image of glucose-derived HT carbon (figure 9a) after sulfonation shows that the morphology of the coating and the spheres deposited on it are apparently unaltered by sulfonation process. In order to explain the different chemical reactivity upon sulfonation and the different morphology of HT carbon coating for the several carbohydrate precursors, it is necessary to look into the mechanism of HT carbon formation. It is reported that the mechanism is a complex cascade of coexisting reaction paths of furfural polymerization and aldol condensation reactions involving both furan motifs and decomposition products, such as levulinic acid [37]. Depending on carbohydrates type, different types and proportions of furans (hydroxyfurfural, furfural) and decomposition products are produced. These different monomers will have various emulsification behaviours and connecting functions. Therefore, the polymerization process will differ from one carbohydrate to another. In
reference [38], it is shown that hydrothermal carbon spheres prepared from glucose and starch are smaller and more cross-linked than those prepared from sucrose. The lower degree of cross-linking of carbon moieties for sucrose-derived coating could account for its removal upon sulfonation.

Figure 9. SEM images of HT carbon coating (a) after sulfonation and (b) after esterification reaction of sample prepared from 0.5 M glucose. Image (a) shows clearly that the HT coating has uniform thickness of about 350 nm.

As a proof of concept, the catalytic activity of HO$_3$S-HC-CF prepared using 0.5 M glucose solution was tested in the esterification reaction of palmitic acid with methanol. The HO$_3$S-HC-CF catalyst led to 87% yield after 26 h (Figure 10). The hydrothermal carbon loading on the felt was very similar before and after reaction (TPO, S4 supplementary information). The loading is only slightly smaller after reaction due to the removal of some species desorbing at the highest temperatures in TPO. The coating morphology after reaction (figure 9b) is also comparable to that before reaction, corroborating the stability of the
hydrothermal carbon coating. Therefore, the HO$_3$S-HC-CF composite was not damaged even though it underwent intensive stirring during reaction. The direct sulfonation of the graphite felt without hydrothermal carbon (HO$_3$S-CF) gave no activity in the acid catalysed reaction. Although the lower functionalisation of this support, \textit{i.e.} 0.33 wt\% sulfur determined by XPS, may account for a lower activity, the total lack of activity might be related to the different nature of the acidic sites, aryl-SO$_3$H in the case of felt and alkyl-SO$_3$H in HC\cite{37}, and the corresponding lower pK$_a$ of the aromatic sulfonic groups.

A catalyst consisting of sulfonated hydrothermal carbon nanospheres (HO$_3$S-HC) was also prepared at the same synthesis conditions as HO$_3$S-HC-CF, \textit{i.e} from 0.5 M glucose solution, but without introducing the carbon felt in the synthesis autoclave. The sulfur content determined by XPS was 1.50 wt\% and 1.44 wt\% for HO$_3$S-HC and HO$_3$S-HC-CF, respectively. Therefore, the density of sulfonic acid groups in both samples is similar. The determination of sulphur content in HO$_3$S-HC-CF sample by elemental analysis was not possible due to difficulty of sample grinding for analysis that entailed irreproducible measures. HO$_3$S-HC sample could be grinded and a sulphur content of 1.7 wt\% was determined by elemental analysis, which is very coincident with that determined by XPS. Therefore, sulphur contents determined by XPS is adopted as an approximation of sulfonic acid groups density for comparison between samples. In the catalytic tests, the amount of HO$_3$S-HC catalyst was set equivalent to the amount of hydrothermal carbon coating on HO$_3$S-HC-CF. The conversion to palmitate using HO$_3$S-HC was slightly smaller than that of HO$_3$S-HC-CF. The initial reaction rate was 38 and 81 mmol g$^{-1}$h$^{-1}$ for HO$_3$S-HC and HO$_3$S-HC-CF, respectively. Thus, catalytic sites in the sulfonated hydrothermal carbon
coating the felt are more efficiently used than the sulfonated carbon nanospheres. The preparation and catalytic tests were repeated twice, exhibiting similar performance.

HO$_3$S-HC-CF catalyst was used as macroscopic square pieces of the felts (~0.5 cm side) in contrast to the nanospheres (500 nm average size). The macrostructure of the felt has the advantage of being easier to handle and separate from reaction medium than carbon nanospheres. In addition, the higher ester yield using the HO$_3$S-HC-CF catalyst demonstrates that the liquid diffuses easily within the macropores of the felt. Work is underway studying the stability and reuse of the catalyst.

![Figure 10](image.png)

**Figure 10.** Esterification of palmitic acid with methanol catalyzed by sulfonated catalyst.

Reaction conditions: 7.5 mmol palmitic acid; 75 mmol methanol; 0.210 g catalyst; under reflux. HO$_3$S-HC-CF and HO$_3$S-HC were prepared from 0.5 M glucose precursor.
For continuous operation, the macroporous structure of the felt will enable that the liquid reactant can flow through the monolithic felt with low pressure drop. Monolithic pieces of graphite felt can be readily implemented inside microreactor plates [49], thus paving the way for its use in flow chemistry. The carbon felt scaffolding imparts to the composite physical reinforcement, versatility to mould in different macroscopic shapes and additional heat and electric conductive pathways while the hydrothermal carbon layer provides surface to anchor functionalities as demonstrated for sulfonic groups, showing high performance in esterification reactions. The high thermal conductivity inherited from the graphitic framework guarantees isothermal operation and rapid heating/cooling down in chemical reactions performed at moderate or high temperatures. In addition, the high electrical conductivity of the graphitic felt broadens the potential application field of hydrothermal carbon for electrochemical devices.

4. Conclusions

The nanocoating of hydrothermal carbon layer on graphite microfibers felts is reported for the first time. This macroporous structure is rarely achieved by standard chemistry and processing of hydrothermal carbon. The method described here is one-pot, energy efficient and uses biomass as feedstock. The coating is mechanically stable and uniform in thickness and coverage. Furthermore, the thickness can be tailored depending on the synthesis conditions down to a thickness of a few hundreds of nanometers. The sulfonation of the hydrothermal carbon coated felt gave rise to an active and stable catalyst in esterification reaction.
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