Research article

Sulfonated porous carbon catalysts for biodiesel production: Clear effect of the carbon particle size on the catalyst synthesis and properties

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ABSTRACT

Sulfonated porous carbons (PCs-SO₃H) are prepared by the sol-gel reaction of resorcinol and formaldehyde. The porosity is maintained during drying using a cationic polyelectrolyte as pore stabilizer. It was found that varying the Resorcinol/Na₂CO₃ molar rate, different resins are produced which, after pyrolysis, give carbonaceous materials with different textural properties. It seems that a Resorcinol/Na₂CO₃ molar ratio of 200:1 was the optimal condition to produce a well-developed porous structure. Both resins and carbon materials are sulfonated by treatment with sulphuric acid. The relation between the carbon particles size, the sulfonation efficiency and its performance as a catalyst is studied. The higher amount of sulfonic groups, and thermal stability, as well as better catalytic performance, was obtained when smaller porous carbon particles were chosen by sieving. PCs-SO₃H exhibited high efficiency for the esterification reaction and high performance for biodiesel production. The catalysts can be recycled several times with a minimal loss of activity. Thermal analysis evidenced stability up to ca. 200 °C, allowing the use of this catalyst at high temperature. The simple synthesis and low cost of the PCs-SO₃Hs make them promising catalysts for the synthesis of biodiesel.

1. Introduction

Fuels derived from natural fats (e.g. vegetable oils) have become attractive owing to the fact that they are made of renewable resources [1]. However, the cost efficiency of its production is still a challenge. Therefore, the design of new and eco-friendly techniques needs to be investigated to make this process more competitive in the actual market. Enzymatic, heterogeneous or homogeneous catalysis are the actual technologies for biodiesel production [2–4]. Different lipases systems have been used in enzymatic catalysis for this purpose with high yields [5–7]. Despite the high production levels, enzymes constitute a major drawback for commercialization due to their high cost and low recyclability. In this sense, homogeneous catalyst (NaOH or KOH) can reduce substantially the production costs [8–10]. The reaction can be performed at low temperature and ambient pressure with high conversion rates, avoiding undesirable intermediate steps. Leung et al. demonstrate those homogeneous alkaline catalysts have as major drawbacks that they are highly hygroscopic and they adsorb water during its storage, diminishing the catalytic performance [11,12]. Furthermore, the alkaline catalyst produces soap in contact with water and free fatty acids,

making the separation of biodiesel (esters) and glycerol a very difficult task. Alternatively, heterogeneous acid catalysts have been proposed as a proper alternative for biodiesel production. In this sense, the catalysis carry out using homogeneous acids compounds (e.g. H₂SO₄) is effective but it is hard to eliminate the acid from the reaction product. In that context, the heterogeneous catalysts are advantageous because they can be easily separated from the reaction product by filtration. However, a proper quantity of the active sites and accessibility to these sites is a stepping stone towards an optimum performance of the catalyst [13, 14]. Several researchers have been studied different materials that can be used as acidic heterogeneous catalysts [2]. For example Twaiq et al. demonstrate that the zeolites are effective as catalysts in the palm oil cracking process [15]. Palm oil conversion of 80–100 wt.% and yield of gasoline fraction of 38–47 wt.% were obtained from the composite catalysts. Wenlei Xie et al., synthesized several heterogeneous acid catalysts based on SnO₂/SiO, WO₃/SnO and WO₃ supported on AlPO₄. In all the cases the catalysts were effective to transesterificate soybean oil giving fatty acids ethyl esters with an oil conversion between 70% to 82% [16–18]. Other materials which present capability for biodiesel catalyst are sulfated zirconium, Amberlite resins [19], and Nafion [20]. Common problems associated with solid acid catalysts are the low concentration of active sites, the hydrophilic nature of the catalyst surface, and the leaching of the active groups. The high cost of several catalysts production is also an obstacle to be produced in large-scale. In order to avoid the problems mentioned, has been reported various types of heterogeneous

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acid catalysts from sulfonated carbon [21,22]. In this type of catalysts, higher catalytic activity due to the presence of mesopores interconnected with micropores was observed. Lee demonstrates the ability of the carbonaceous materials to catalyze biodiesel reaction [23]. However, no detailed studies of the influence of the pore sizes, and the catalyst size have been made so far. Our group have previously synthesized porous carbons [24–28]; by pyrolysis of synthetic resins. The resins were made by sol-gel polycondensation of resorcinol and formaldehyde in the presence of a pore stabilizer, like a cationic polyelectrolyte (polydiallyl, dimethylammonium chloride) (PD). It has been demonstrated that the pore stabilizer allows maintaining the porosity during drying of the wet resin [29] avoiding complex drying method such as the use of supercritical fluids [30]. The use of PD as pore stabilizing agent makes the synthesis process cheaper and more environmentally friendly. Take into account the importance of the porosity and the porous size distribution; we study for the first time the influence of the Resorcinol/Na_2CO_3 ratio during the resin synthesis.

Finally, these types of porous carbons were sulfonated by reaction with concentrated sulfuric acid, in order to use it as an acid heterogeneous catalyst for biodiesel production. This work describes an in-depth study of the influence of the carbon size not only during biodiesel synthesis but also during sulfonation. To fulfill this aim, a previous sieving step was performed in order to study the influence of the particle size in the efficiency of the sulfonation procedure and then, its catalytic behavior. Based on the results it is demonstrated that the size of the catalyst particles is a very important parameter to take into account not only at the moment of produce biodiesel but also when this material is sulfonated. Moreover to test the efficiency of the produced catalyst, all the samples were used for two important reactions in biofuels production, i) the esterification of acetic and oleic acid with ethanol and ii) the transesterification of commercial sunflower oil with ethanol.

In summary, the novelty of this work are; 1) the influence of the molar ratio between resorcinol and sodium carbonate on the porosity of the catalyst is investigated; 2) it has been demonstrated that the sulfonation procedure is more effective if the carbon size is controlled; 3) not only the esterification reaction but also de transesterification reaction (biodiesel production) is performed more efficiently by

controlling the catalyst size; 4) The sulfonic group are strongly attached to the carbon being stable upon heating to 200 °C; 5) the sulfonation of small porous carbon microparticles seems a suitable method to produce cheap and environmentally friendly heterogeneous acid catalysts combining a high surface area and an excellent catalytic performance (Scheme 1), thus making this material a promising candidate for industrial scale production.

Moreover, it is demonstrated that the catalyst can be employed several cycles remaining its catalyst activity.

2. Experimental

2.1. Materials

Resorcinol (Fluka), Formaldehyde (Cicarelli), sodium carbonate (Cicarelli), and polydiallyl, dimethylammonium chloride (BDH) were employed to synthesize porous resins. For sulfonation procedure concentrated H_2SO_4 (Cicarelli, 98%) was used. In order to obtain the catalyst acid groups quantity $NaHCO_3$ (Sigma-Aldrich), Na_2CO_3 (Sigma-Aldrich), NaOH (Sigma-Aldrich, 99.998%), Na_2SO_4 (Sigma-Aldrich) and HCl (Sigma–Aldrich, 99.999%), were employed. All the chemicals were analytical quality reagents.

The esterification reactions were carried out using acetic (Fluka, analytical quality) or oleic (Riedel-de Haën, analytical quality) acid and bioethanol (98%, provided by BIO4 Bioetanol Río Cuarto S.A., Río Cuarto, Argentina). KOH (Sigma-Aldrich, analytical quality) was used to obtain the acetic acid conversion. The transesterification was performed using commercial sunflower oil (Natura). The chromatogram of the commercial oil (Natura) gave the following composition: Linoleic acid: 74%, Oleic acid: 14%, Palmitic acid: 8%, Stearic acid: 4%. For comparison with the carbon based catalysts prepared in this work, commercial solid acid catalysts were also tested: Nafion® 117 and Amberlite®-IR 120. Nafion® 117 (Dupont) is a fluorinated aliphatic polymer bearing sulfonic groups ($—CF_2CF_2SO_3H$). The material used in this work is in the form of cylindrical and spherical pellets, lengthwise striations. The mean size of the pellets is below 200 μm. A number of sulfonic groups is 1.10 ± 0.07 meq/g. Amberlite®-IR 120 is a cation exchange resin
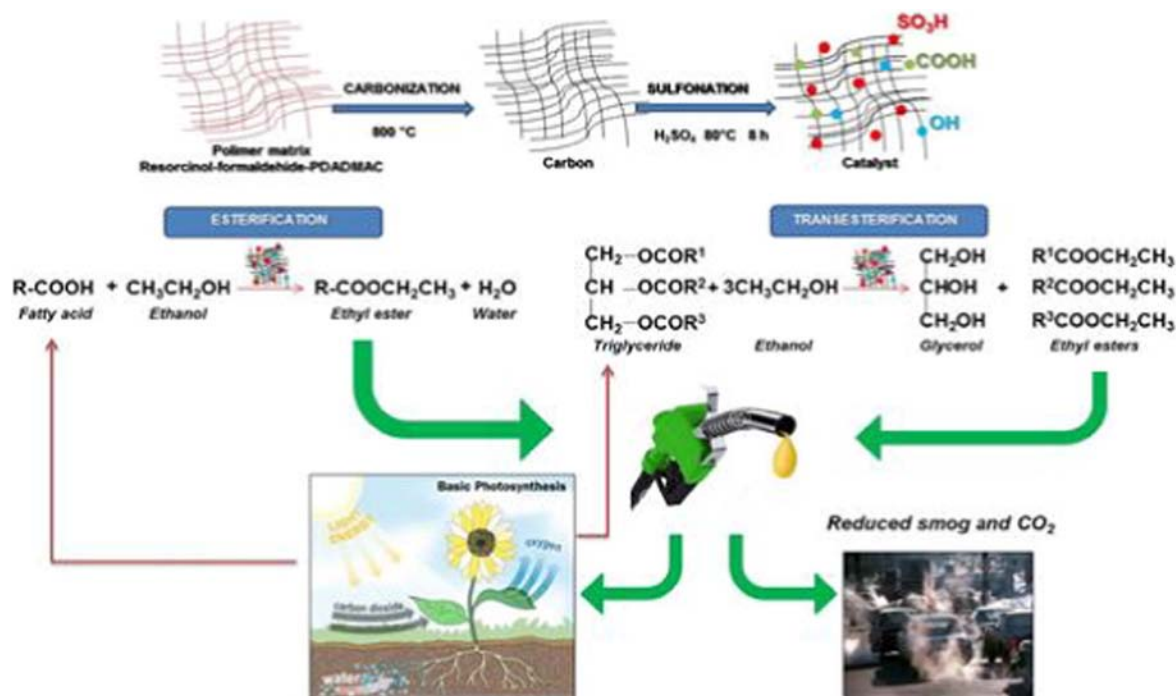
Scheme 1. Biodiesel production cycle from renewable bio-oils via catalytic transesterification and esterification using heterogeneous acid catalyst based on porous carbon obtained from the sol-gel polycondensation of resorcinol and formaldehyde in the presence of a PD.

based on polystyrene crosslinked with divinylbenzene (8%) and sulfonated. The moisture content is of 53–58%. The particle size is between 0.62 and 0.83 mm. The acid group content is 1.8 meq/mL (wet).

2.2. Synthesis of sulfonated porous carbon catalysts

Monolithic porous carbons were synthesized by polycondensation of resorcinol (R) with formaldehyde (F) in the presence of PD as pore stabilizer and sodium carbonate (C) as a basic catalyst [31,32]. The molar ratio of resorcinol to formaldehyde (37 wt.% in an aqueous solution) (R/F) and the ratio of resorcinol to water (R/W) were fixed at 0.5 g/mL. Furthermore, the PD/R ratio was kept constant at 7. In order to study the influence of the molar ratio Resorcinol/Na$_2$CO$_3$ (R/C) on the porous structure of the synthesized carbons, this ratio was varied from 100 to 500.

All components were mixed and stirred for 10 min. Then the samples were polymerized by heating at 70 °C, in a closed system, for 24 h. to obtain a porous organic gel. The organic gel was dried at 70 °C in air for 6 h. Finally, porous carbons (PCs) were obtained by pyrolysis of the dried monolithic gels at 800 °C for 1 h under an argon atmosphere with a heating rate of 40 °C/h. The samples obtained were denoted as PCx, where x represents the molar ratio R/C (100, 200, 300, 400, and 500).

Before the sulfonation process, synthesized carbons were sieved in order to isolate particle size between 0.149 and 0.210 nm. A series of PCx without sieving was also sulfonated for the sake of comparison. The sulfonation process was carried out as follow: 0.2 g of carbon was added to a concentrated H$_2$SO$_4$ solution (10 mL). The solution was heated for 8 h at a constant temperature (80 °C) under reflux and then cooled to room temperature. Finally, the samples were washed with distilled water and centrifuged in order to isolate the black precipitate from the reaction mixture. [33,34]. The sulfonated carbons were dried at 100 °C for 12 h. The catalysts obtained by this way were labeled PCxS-SO$_3$H.

2.3. Characterization techniques

The textural properties of the synthesized carbons and catalysts were evaluated by nitrogen adsorption measurements at −196 °C using N$_2$Gsorb-G (Gas to Materials Technologies) equipment. The samples were previously degassed for 8 h at 100 °C. Apparent surface area (S$_{BET}$) was calculated by application of the B.E.T. equation to the nitrogen adsorption data [35]. The Dubinin–Radushkevich equation was used to calculate the micropore volume (V$_0$) and volume of narrow micropores (V$_n$) from the nitrogen (−196 °C) and carbon dioxide (0 °C) adsorption data, respectively [36]. The values of V$_0$ corresponds to the total micropore volume, whereas V$_n$ provides the volume of micropores below 0.7–0.8 nm [37]. The mesopore volume (V$_{meso}$) was deduced from the N$_2$ adsorption isotherm, by subtracting the value V$_0$ (N$_2$) from the total amount adsorbed at P/P$_0$ = 0.98 [38]. Mesopore size distribution was estimated by application of the Barrett–Joyner–Halenda (BJH) method to the desorption branch of the nitrogen isotherm.

2.4. Determination of acid groups by titration

The content of acids groups on the catalyst surface was determinate by titration using the technique published by Tamborini et al. [39]. 0.5 g of the catalyst was added to (a) 17.00 mL of NaHCO$_3$ 0.05 M (b) 17.00 mL of Na$_2$CO$_3$ 0.05 M solution (c) 17.00 mL of NaOH 0.05 M solution and (d) 20.00 mL of Na$_2$SO$_4$ (0.1 M). The samples were agitated for 24 h and then filtered to remove the catalyst. After that, 5.00 mL aliquots of the solutions a–c were extracted. The aliquot of the solution (a) was acidified with 10.00 mL of 0.05 M HCl. The aliquot of the reaction (b) was acidified with 15.00 mL of 0.05 M HCl and, the aliquot of the (c) was acidified with 10.00 mL of 0.05 M HCl. After that, the samples were placed in a sealed tube equipped with a needle; nitrogen

was bubbled through the samples for 2 h, and the samples were heated at 80 °C for 30 min, in order to eliminate the dissolved gases. The acid group content (carboxylic, phenols, lactones groups) was determined by back potentiometric titration using a NaOH (0.05 M) solution. The sulfonic group content was determined by a direct titration of (d) with a NaOH (0.05 M) solution, using a pH-meter (Adwa AD 110). The standardization of NaOH solution was carried out using potassium phthalate monoacid (FtHK) as primary standard and phenolphthalein as indicator. The average of three measurements was used to make the calculations.

The amount of the acidic groups on carbon was determined using the Eq. (1) when back-titration was employed.

$$n_{csf} = \frac{n_{HCl}}{n_B} \cdot [B] \cdot V_B - ([HCl] \cdot V_{HCl} - [NaOH] \cdot V_{NaOH}) \cdot \frac{V_B}{V_a} \tag{1}$$

where, n$_{csf}$ denotes the moles of carbon surface functionalities that reacted with the base, while [B] and V$_B$ are the concentration and volume of the base mixed with the carbon, respectively. V$_a$ is the volume of the aliquot taken from the V$_B$, and [HCl] and V$_{HCl}$ are the concentration and volume of the acid added to the aliquot taken from the original sample, respectively.

The content of sulfonic group was determined using a direct titration with the Eq. (2).

$$n_{csf}^t = V_{NaOH} \cdot [NaOH] \tag{2}$$

The NaOH reacts with all acid groups, (carboxylic acids, lactones, phenols and sulfonic groups), therefore, the value of n$_{csf}^t$ includes all of these groups. The n$_{csf}'$ obtained from the titration with Na$_2$CO$_3$ gives the quantity of carboxyl, lactonic and sulfonic groups. The difference between n$_{csf}^t$ and n$_{csf}'$ denotes the phenol moles quantity. Similarly, since NaHCO$_3$ reacts with carboxylic and sulfonic groups (n$_{csf}''$), the difference between n$_{csf}'$ and n$_{csf}''$ corresponds to the lactonic moles. The Na$_2$SO$_4$ reacts only with the sulfonic group (n$_{csf}^s$); the difference between the n$_{csf}''$ and the n$_{csf}^s$ refers to the carboxylic acid moles.

X-ray photoelectron spectroscopy (XPS) analysis of PC200S-SO$_3$H was used to determine the surface species bonded to the catalyst and was performed with the Thermo-Scientific K-Alpha instrument equipped with a hemispherical electron analyzer using a Mg Kα (1253.6 eV) 300 W X-ray source. Carbon, oxygen and sulfur content were analyzed in an elemental analyzer (EA1112 Thermofinnigan FLASH). All the determinations were done in triplicate.

2.5. Catalytic experiments

2.5.1. Esterification of acetic and oleic acid with ethanol

The catalytic activity of sulfonated carbon towards the esterification of acetic or oleic acid with bioethanol was measured following the procedure used by Marchetti et al. [40,41].

In a typical run, 0.1 mol of organic (acetic or oleic) acid per 1 mol of ethanol and 0.2 g of catalyst were mixed for 10 h at 75 °C under constant stirring and reflux [42]. The reaction products were evaluated every 1 h. Aliquots of 5 mL of the reaction mixture were extracted at different times, and they were washed with distilled water to stop the reaction. The acetic acid (AcH) conversion was determined from a direct titration with a solution of KOH (0.1 M), using a pH electrode to determining the equivalent point. In the reaction with oleic acid (OlH), the excess of ethanol was removed from the oil phase and finally to achieve a better separation the mixture was centrifuged for 20 min. The oil phase obtained was dissolved in ethanol and sulfuric ether for titration analysis, which was conducted from a direct titration with a solution of KOH (0.1 M), using a pH electrode to determine the equivalent point. The conversion value is calculated from Eq. (3). The catalytic activity was expressed as

conversion of free fatty acids (FFA) (%).

$$X(\%) = \frac{molFFA_{initial} - molFFA_{end}}{molFFA_{initial}} \cdot 100 \qquad (3)$$

Esterification was carried out with commercial solids: Nafion® 117 and Amberlite-IR 120 catalyst for comparison.

2.5.2. Transesterification of commercial sunflower oil with ethanol

Transesterification reaction was performed in a 250 mL refluxing equipment heating with a glycerin bath at 75 °C under magnetic stirring. The amount of regional commercial sunflower oil used was 10 g; a molar ratio of ethanol to oil (20:1) was added. The raw biodiesel yield was calculated by weighing raw biodiesel (BD) and the initial oil mass using the Eq. (4). In order to obtain raw biodiesel, the reaction mixture was transferred to a decantation ampule of 50 mL. When the mixture reached the room temperature (18–20 °C) the three phases present in the mixture were separated. The bottom semisolid phase corresponds mainly to glycerol and solid catalyst, the upper phase contained the bioethanol and the other phase consisted of biodiesel (FAEE phase). The FAEE phase was washed with warm water three times and, then water to provide a purified FAEE, finally, the FAEE was distilled. The procedure depicted ensure the elimination of unreacted bioethanol, but this layer content also unreacted free fatty acids, mono-, di- and triglycerides and even unsaponifiable compounds coming from the raw material.

$$\% \text{ FAEE yield} = \frac{\text{weight of biodiesel}}{\text{weight initial oil}} \times 100 \qquad (4)$$

The percentage of ethyl ethers (f) was determined by gas chromatography using dodecane as an internal standard. Monitoring of the reaction was performed using the same technique. In both cases, a Hewlett Packard 5890 series II coupled to a mass detector 5972 series of the same brand was used. A column HP-1 MS 30 m long, 0.25 mm internal diameter and a film thickness of 1 μm was used. The oven temperature was programmed as follows: initial temperature: 60 °C, final temperature: 260 °C, a heating rate of 4 °C/min. Helium carrier gas was used at a rate of 0.8 mL/min, at constant volume. The injector temperature was 200 °C and the injection volume was 1 μL. The column head pressure was 5 psi. The fatty acid ethyl ester standards were employed in order to obtain the residence time of each ethyl ester. The % of biodiesel was calculated using Eq. (5).

$$\% \text{ of Biodiesel} = \% \text{ FAEE yield} \times f \qquad (5)$$

2.5.3. Catalysts reusability

In order to study the stability of sulfonic acid groups and the possibility to reuse the catalyst, PCxS-SO$_3$H was recovered by filtration after the first 10 h of reaction. Then, the catalyst was washed with water, ethanol, and hexane and finally dried. After that, the PCxS-SO$_3$H was incorporated into the fresh reaction mixture. Before each cycle, the content of sulfonic groups is re-evaluated by titration.

2.5.4. Thermal stability

The thermal stability of the original and reused PCxS-SO$_3$H was studied by thermogravimetric analysis (TGA) under flowing N$_2$. A Mettler Toledo model TGA/SDTA851e/SF/1100 instrument was used. The heating rate was 10 °C/min and the temperature range of 25 to 1000 °C.

3. Results and discussion

3.1. Textural characteristics of porous carbon and sulfonated catalysts

In Fig. 1a are shown the N$_2$ adsorption isotherms (at 77 K) for a porous carbon (PC200) and its sieved microparticles (PC200S). The isotherms PC200 and PC200S are identical, suggesting that sieving of the material does not produce a variation in the micro and mesoporosity. Fig. 1b shows PC100S and PC100S-SO$_3$H isotherms and pore size distribution. All isotherms are type IV, characteristic of samples combining a micro and mesoporous structure. The presence of mesoporosity is clearly confirmed by the presence of a characteristic Type H1 hysteresis loop due to the metastable fluid state of nitrogen during adsorption. As it is possible to observe the variation in the ratio R/C produces changes in the porosity of the PC. It was demonstrated that the porosity of the material plays an important role to anchor the sulfonic groups and that the carbons that present a high S$_{BET}$ volume with connected meso and micropores facilitate the incorporation of such groups [39]. PC200 presents the largest porosity values. Therefore, this seems to be the optimal resorcinol/catalyst ratio in order to reach a highly developed porous structure (S$_{BET}$ ca. 695 m^2/g).

In Fig. 1b, it can be seen that the sulfonation process decreases the nitrogen adsorption capacity of the carbon. It is likely that the process of sulfonation produces corrosion of the micropore walls and some of the collapse decreasing the porosity. The effect is more remarkable in the case of the PC200S-SO$_3$H sample, implying that the sulfonation process is affecting not only the microporosity but also the mesoporosity of this carbon. A closer look at the pore size distribution (inset of Fig. 1b) suggests that the sulfonation mainly affects the largest pores since the peak at ca. 20 nm of the original sample disappears after the functionalization treatment. Textural parameters of PCs and sulfonated PCxS are listed in Table 1.
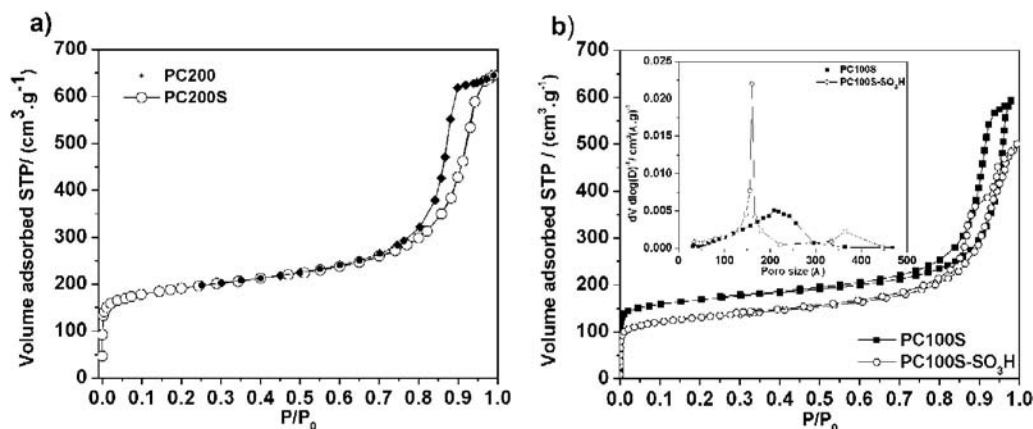

Fig. 1. a) Nitrogen adsorption-desorption isotherms a 77 K to PC200 and PC200S. b) Nitrogen adsorption-desorption isotherms a 77 K and BJH pore size distribution (inset) of PC100S and PC100S-SO$_3$H.

Table 1
Textural properties of PCs and PCxS-SO₃H.

Samples	S_{BET}[a] (m²/g)	V_0[b] (cm³/g)	V_{meso} (cm³/g)	V_t[c] (cm³/g)	D_p[d] (nm)
PC100S	630	0.25	0.67	0.92	21
PC100S-SO₃H	470	0.19	0.58	0.77	16
PC200S	695	0.33	0.67	1.00	18
PC200S-SO₃H	140	0.00	0.34	0.34	17
PC300S	630	0.27	0.44	0.71	4
PC300S-SO₃H	405	0.19	0.55	0.74	3
PC400S	360	0.14	0.56	0.70	20
PC400S-SO₃H	275	0.11	0.14	0.25	4
PC500S	395	0.16	0.60	0.76	15
PC500S-SO₃H	255	0.11	0.19	0.30	9

[a] Determined from BET theory.
[b] Determined from Dubinin-Radushkevich.
[c] Volume adsorbed at p/p₀ of 0.98.
[d] Determined from the BJH desorption method.

3.2. Contents of acidic groups of porous materials

Table 2 shows the content of acidic groups in the synthesized porous materials. The sulfonated samples previously sieved were included for the sake of comparison. The results in Table 2 show that applying a sieving step prior to the sulfonation process causes a drastic effect on the amount of surface functional groups incorporated at the carbon. While the content of sulfonic groups increases, both the phenolic groups, and carboxylic groups diminishes. Apparently, the reduction of the particle size enhances the contact between the carbon surface and H_2SO_4 raising the effectiveness of the sulfonation process. As it can be seen the catalyst with the highest sulfonic content is PC200S-SO₃H and PC300S-SO₃H.

Fig. 2 shows the XPS spectra for the PC200S-SO₃H catalyst. Three signals can be clearly observed at 168 eV, 284 eV and 530 eV corresponding to S 2p, C1 s, and O 1 s, respectively. The deconvolution of the C1 s, Fig. 2b, gives four bands at a binding energy of 290.4 eV, 288.4 eV, 286.1 eV, and 284.3 eV, corresponding to the C-S, C=O, C-O, and C-C, respectively. These results confirm the presence of the sulfonic, carboxylic and phenolic groups. In the case of the S 2p signal two bands are observed at a binding energy of 168.6 eV and 169.9 eV, corresponding to the C—SO₃H and C—S bonds, respectively; these signals confirming the successful functionalization of the carbon surface with sulfonic groups (Fig. 2c). Table 3 shows the elemental analysis of PC200S-SO₃H catalyst.

All these results verify the presence of sulfonic, carboxylic, lactonic and phenolic groups at the surface of the carbons. However, since XPS

Table 2
Content of acidic groups in the synthesized porous materials. The sulfonated samples previously sieving were included for the sake of comparison.

Without sieving				
Catalyst	Phenols (mmol/g)	Lactones (mmol/g)	Carboxylic acid (mmol/g)	Sulfonic acid (mmol/g)	Total (mmol/g)
PC100-SO₃H	0.46	–	0.40	0.70	1.56
PC200-SO₃H	0.48	–	0.26	0.78	1.12
PC300-SO₃H	–	–	0.61	0.98	1.59
PC400-SO₃H	–	–	0.47	1.00	1.47
PC500-SO₃H	–	–	0.89	0.76	1.65

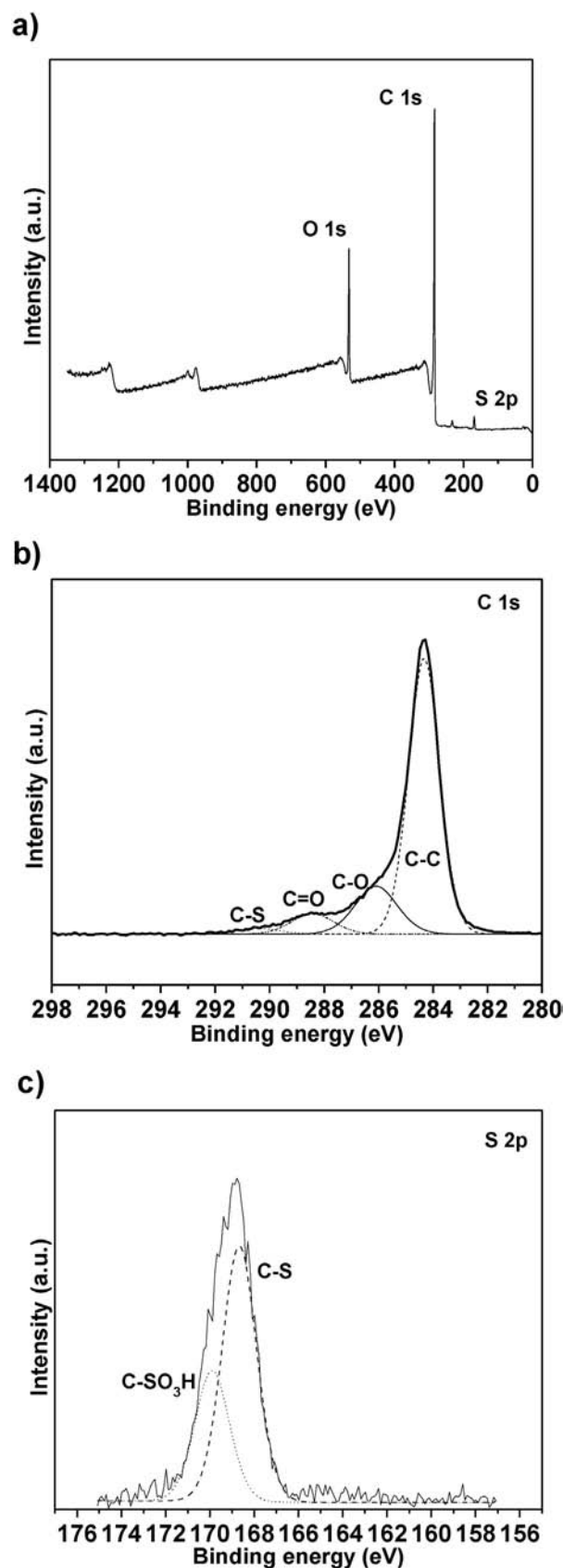| With sieving before the sulfonation reaction				
Catalyst	Phenolic (mmol/g)	Lactonic (mmol/g)	Carboxylic acid (mmol/g)	Sulfonic acid (mmol/g)	Total (mmol/g)
PC100S-SO₃H	0.31	–	0.33	0.98	1.62
PC200S-SO₃H	0.29	–	0.23	1.06	1.58
PC300S-SO₃H	–	–	0.51	1.10	1.61
PC400S-SO₃H	–	–	0.40	0.52	0.92
PC500S-SO₃H	–	–	0.74	0.43	1.17

Fig. 2. a) XPS survey scan, b) high-resolution C1 s XPS spectrum and c) high-resolution S 2p XPS spectra of the PC200S-SO₃H catalyst.

Table 3
Elemental analysis by XPS of PC200S-SO$_3$H catalyst.

Element	Position (eV)	Area (%)	Atomic (%)
O 1s	530	49,536.50	14.65
C 1s	284	105,139.31	81.60
S 2p^3	168	4412.55	3.76

is a surface technique, it is not useful to quantitatively determinate the total content of these groups inside the catalyst.

3.3. Catalytic activity evaluation

The catalytic performance of the PCxS-SO$_3$H catalyst for the acetic and oleic acid esterification with ethanol was evaluated at 75 °C for 10 h. Fig. 3a and b show the evolution of acetic acid conversion versus reaction time for the different PCx-SO$_3$H catalysts (heterogeneous particle size distribution, Fig. 3a and for PCxS-SO$_3$H catalysts (particle size in the range of 0.210 to 0.40 mm, Fig. 3b. Esterification was also carried out with commercial catalysts: Nafion® 117 and Amberlite-IR 120.

Comparing the results of Fig. 3a and b, a drastic increase in the acetic acid conversion at smaller times can be clearly appreciated by both series of catalysts comparing the sieved sample with the non-sieved one. For instance, the PC200-SO$_3$H catalyst, at 1 h of reaction the conversion value is ca. 10%, while for the same catalyst sieved the conversion reaches 50%. A similar behavior is obtained for all of the samples synthesized. The same results can be observed in Fig. 3 c. As it can be seen in all the cases the sieving carbons present the double initial velocity compared with the non-sieved catalyst. Moreover, all the measurements with sieved catalyst reach the maximum value of conversion (90%) at 3 h, in contrast to non-sieved materials which do not reach this value even after 10 h of reaction. Therefore, when the carbons are sieved before the sulfonation process, 2 h of reaction are more than enough to achieve the maximum conversion (more than 80% for most of the samples and 60% for PC500S-SO$_3$H). From the point of view of the industrial application, these results are very promising in order to reduce the time to obtain the final product and increase the yield of the process if a preliminary sieving step is applied to the carbon. Apparently, the diffusion of the reactants into the solid sieve catalysts is highly favored when the catalyst particle size is diminished. Furthermore, among all the samples evaluated, PC200S-SO$_3$H seems to be the best material, this catalyst reaches more than 90% acetic acid conversion in the esterification reaction in 4 h. The commercial catalysts Nafion 117, Amberlite-IR 120 cannot reach a plateau in conversion at the time reaction studied, the conversion values being lower compared to the all sulfonated porous carbon catalyst. Table 4 shows the percentage of conversion of acetic acid obtained using the PCxS-SO$_3$H catalysts and its textural properties.

The results in Table 4, show that the catalysts which achieve higher acid acetic conversion are those which present higher content of sulfonic groups, more mesopore volume and greater pore size (PC100S-SO$_3$H, PC200S-SO$_3$H and PC300S-SO$_3$H). These results indicate that mesopores facilitate the reactants diffusion, increasing the contact of them with internal and external sulfonic groups. PC300S-SO$_3$H has a peak pore size of 3 nm, however, it is clearly observed that present a size pore distribution more developed than the other catalysts indicating that present pores with different diameters ranging from 10 to 60 nm (Fig. 1b). This fact explains its high content of sulfonic groups and good catalytic efficiency. The catalyst PC200S-SO$_3$H has the highest catalytic efficiency due to its high content of sulfonic groups and textural properties. Based on the excellent results shown by PC200S-SO$_3$H, its catalytic behavior was also evaluated in the oleic acid esterification with ethanol. The Fig. 4 shows the oleic acid conversion using PC200-SO$_3$H, PC200S-SO$_3$H, Nafion 117 and Amberlite-IR 120 as a catalyst during 10 h of reaction. As it can be seen, the catalytic behavior of the sulfonated material is enhanced when the particle size is minimized. The value of oleic acid
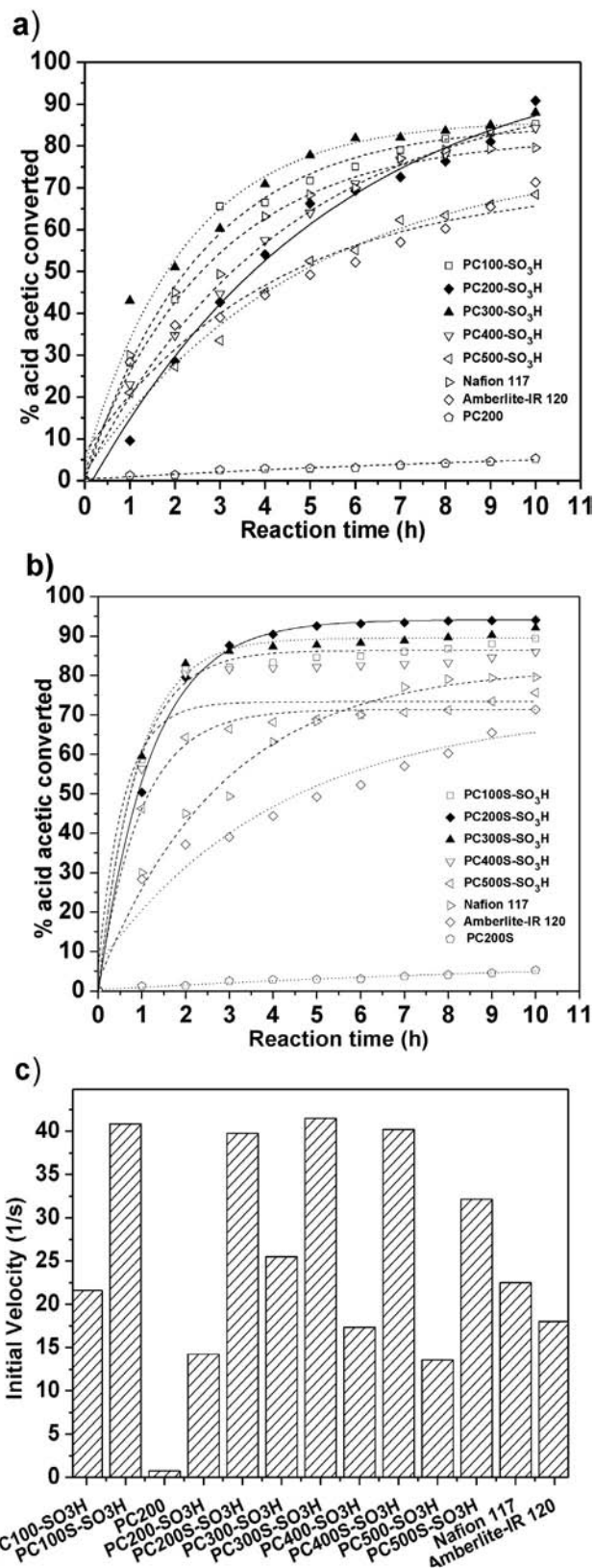

Fig. 3. Esterification of acetic acid with ethanol (molar ratio 1:10), 75 °C using 0.2 g of catalysts a) PCx-SO$_3$H and b) PCxS-SO$_3$H. c) Initial esterification velocity of the sieved and non-sieved catalyst. Nafion 117 and Amberlite-IR 120 catalysts were included.

conversion for PC200-SO$_3$H non-sieved achieves 25%, in contrast, the same catalyst sieved reach a 50% of oleic acid conversion in the first hour of reaction. The maximum conversion achieved by PC200S-SO$_3$H

Table 4
Catalytic and textural properties of PCxS-SO₃H.

Catalyst	D_p^a (nm)	V_{meso}^b (cm³/g)	Sulfonic acid[c] (mmol/g)	% acid acetic conversion[c] (10 h)
PC100S-SO₃H	16	0.58	0.98	89.2
PC200S-SO₃H	17	0.34	1.06	94.0
PC300S-SO₃H	3	0.55	1.10	92.0
PC400S-SO₃H	4	0.14	0.52	86.0
PC500S-SO₃H	9	0.19	0.43	75.6

[a] Determined from the BJH desorption method.
[b] Determined by $(V_t - V_0)$.
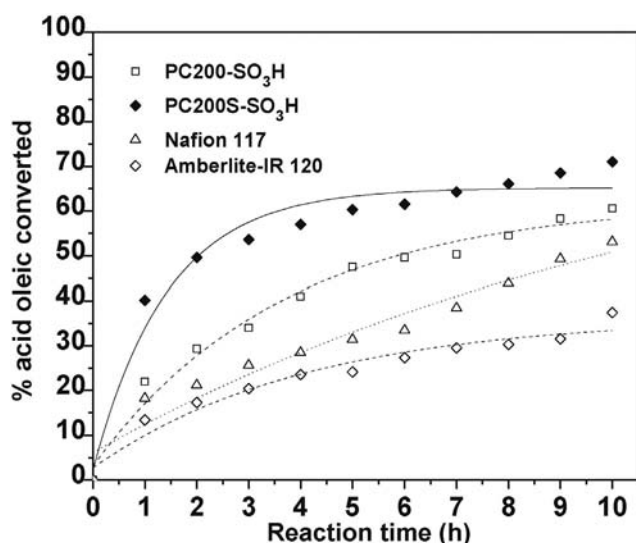[c] Determined by potentiometric titration.

Fig. 4. Esterification of oleic acid with ethanol at 75 °C (molar ratio 1:10) using 0.2 g of the corresponding catalysts: PC200-SO₃H and PC200S-SO₃H compared with the Nafion 117 and Amberlite-IR 120 catalysts.

after 10 h of reaction is 70%, this value is higher than the value of 60% achieved by the non-sieved carbon. These results are detailed in Table 5.

PC200S-SO₃H was employed to produce biodiesel (fatty acid ethyl esters) from sunflower commercial oil. While it is common to produce biodiesel using ethanol, bioethanol is used instead to assure that the biodiesel contains 100% renewable carbon [43–45]. Moreover, both vegetable oil and bioethanol are obtained from local industrial sources,
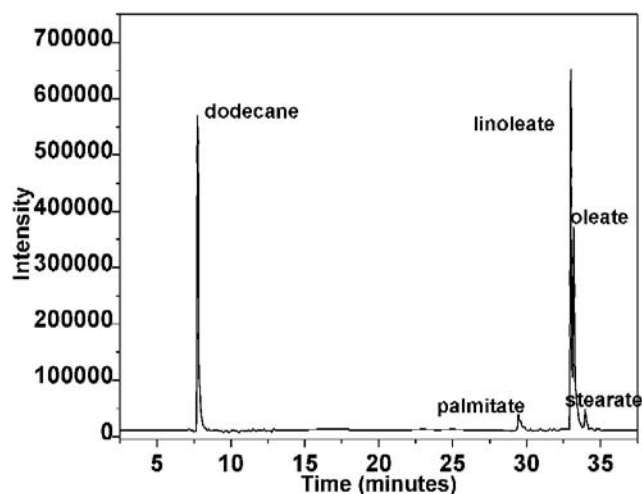

Fig. 5. Ethyl esters generated in the transesterification reaction of sunflower oil with ethanol; 10 wt.% to the PC200S-SO₃H catalyst, 90 °C and 10 h.

reducing significantly the transportation and making the biodiesel a true biofuel.

The amount of the mixture of ethyl esters obtained was to 7 g. The main components of the mixture of ethyl esters were identified by gas chromatography using the internal standard method (Fig. 5).

In Table 5, the % FAEE yield obtained from Eq. (4) and the conversion of ethyl esters for the transesterification reaction of sunflower oil-ethanol (1:20) at 90 °C for 10 h is shown, using a weight of 10% to PC200-SO₃H in relation with the weight to sunflower oil. If the conversion values are divided by the amount of sulfonic groups in the materials, the Turnover Number (TON) is obtained. The TON values at 2 h of reaction are shown in Table 5. As it can be seen in Table 5 the sieving improves the TON value for all the catalysts tested. In summary, PC200S-SO₃H is suitable as a catalyst for the synthesis of biodiesel (transesterification of sunflower oil with ethanol), in that sense, % FAEE yields as high as 70%. The percentage of conversion of vegetable oil to ethyl esters (f) is 90% after 10 h of reaction time. This result is very promising for the biodiesel process since the use of this catalyst not only increase the conversion but also decrease the time to reach it. Both situations improve the yield and the production of the process, generating at the same time a more rentable process. Moreover, the biodiesel only has to be washed with water to remove impurities (glycerol, free acid) without neutralization steps. One of the biggest advantages of
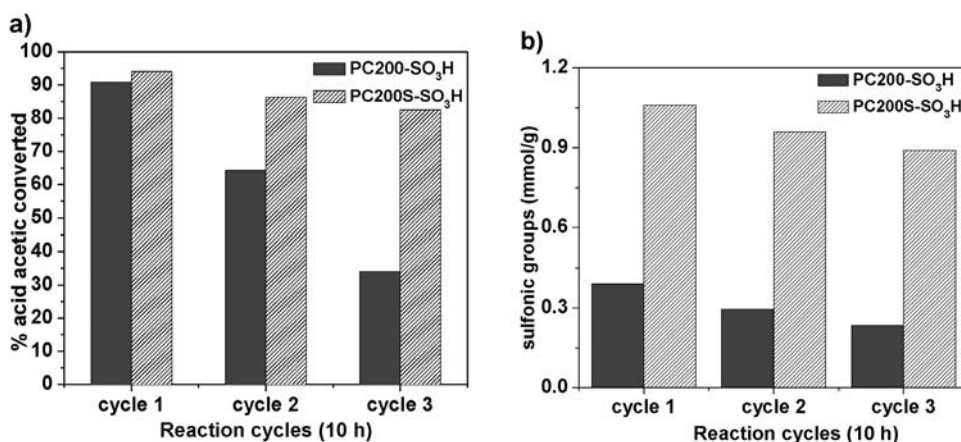
Table 5
Catalytic properties.

	Esterification		Transesterification			
	% acid acetic conversion[a] (10 h)	% acid oleic conversion[a] (10 h)	TON[b] (2 h)	% yield FAEE[c]	f = % ethyl ethers (10 h)[d]	% of biodiesel[e]
PC100-SO₃H	85.3	–	3.08	–	–	–
PC200-SO₃H	90.8	60.6	1.82	–	–	–
PC300-SO₃H	88.0	–	2.60	–	–	–
PC400-SO₃H	84.3	–	2.17	–	–	–
PC500-SO₃H	68.4	–	1.80	–	–	–
PC100S-SO₃H	89.2	–	4.17	–	–	–
PC200S-SO₃H	94.0	71.0	3.75	70 ± 0.5	90	63
PC300S-SO₃H	92.0	–	3.77	–	–	–
PC400S-SO₃H	86.0	–	7.73	–	–	–
PC500S-SO₃H	75.6	–	7.47	–	–	–
Nafion 117	79.5	53.1	2.71	0	0	0
Amberlite-IR 120	71.3	37.4	0.81	0	0	0

[a] Determined by potentiometric titration.
[b] mmol acid acetic converted/mmol sulfonic group.
[c] Calculated using Eq. (4).
[d] Analysed by gas chromatography (sunflower oil, 10 h, 10% catalyst, molar ratio 1:20, 90 °C).
[e] Calculated using Eq. (5).

Fig. 6. a) Acetic acid conversion and b) sulfonic groups content for PC200-SO₃H and PC200S-SO₃H catalysts versus the number of reaction cycles (after 10 h of esterification reaction).

a solid catalyst is the possibility to reuse the catalyst. However, since aromatic sulfonation is a reversible reaction, the sulfonic group could be lost during the reaction (leaching).

To check the reusability of the catalyst, the materials (PC200-SO₃H and PC200S-SO₃H) were used during three reaction cycles. The evolution of the acetic acid conversion and content of sulfonic groups with the number of cycles is depicted in Fig. 6a and b.

Along three reaction cycles, 0.17 mmol/g of sulfonic groups is lost (16% of the initial concentration) for the sample PC200S-SO₃H. However, for the sample PC200-SO₃H in the second cycle, the sulfonic group losses is 0.095 mmol/g (c.a. 25% respect to the initial amount of sulfonic groups), and in the third cycle 0.156 mmol/g is lost, that represents c.a. 40%. The loss of the active sites is reflected in the percentage of acid acetic conversion. While the catalytic behavior decreases slightly for the sieved catalyst in the second and third cycle, 8%, and 12% respectively, the sample non-sieved shows a more accused loss of activity 29% and 62% in the same cycles. These results again the importance of the carbon particle size. It has been clearly demonstrated that the smaller particles not only shows enhanced diffusion of the reactants into the sample but also improves the sulfonation process making the sulfonic groups more stable. Both processes are crucial to getting high conversion rate (more than 80%).

One way to accelerate the kinetic of the reaction is to increase temperature. However, when a heterogeneous catalyst is used, the stability of the active groups is the main limitation. Thermogravimetric measurements of thermal stability (Fig. 7) of PC200S-SO₃H were performed. The material show weight loss profiles which can be divided into two zones:
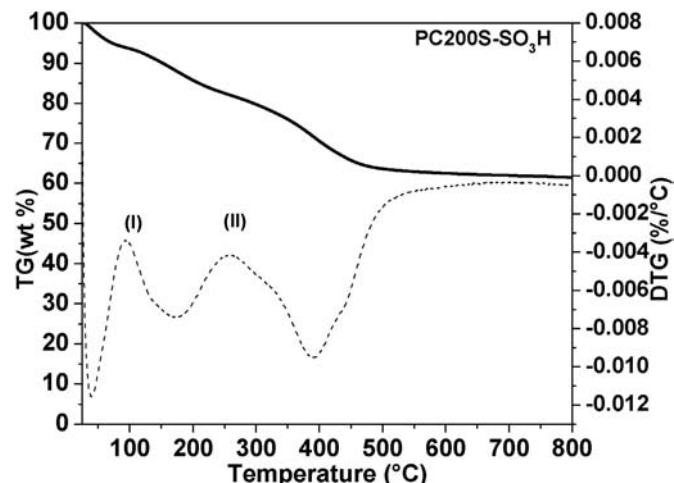

Fig. 7. TG weight loss curves and d(M)/dT for PC200S-SO₃H (0.210 to 0.149 mm).

(I) from room temperature to 150 °C attributed to water desorption and (II) between 200 and 400 °C attributed to thermal decomposition of sulfonic groups attached to the catalyst surface [46,46–48], this result demonstrate that it is possible to reach temperatures up to 200 °C without loss of sulfonic groups. Therefore, the sulfonated porous carbon catalyst could be used at higher temperatures.

4. Conclusions

A novel kind of catalysts are synthesized and tested for the acetic and oleic acid esterification reaction with ethanol, along with the transesterification reaction of triglycerides (sunflower oil) with ethanol. The catalysts are synthesized by sulfonation of porous carbons which are themselves produced by carbonization of porous resins made of a resorcinol/formaldehyde cross-linked matrix. The porous carbons act as a solid support where acid (sulfonic) groups are attached. The resins synthesis is carried out using a cationic polyelectrolyte (poly(diallyl, dimethylammonium chloride)) as pore stabilizer. The use of this additive allows drying the sample in dry air, an inexpensive and simple way, which does not require costly and complex solvent exchange and supercritical or vacuum drying. The use of the porosity stabilizer avoids the pore collapse and maintains the porosity of the catalyst during air drying making possible to produce the catalyst in an economical way. Changing the resorcinol/catalyst (R/C) ratio allows controlling the textural properties of the carbons. In this way, it is possible to select the optimal synthesis condition in order to obtain the best porosity and pore size distribution of the carbon to be employed as catalyst's support. Additionally, the particle size is controlled by milling and sieving the resulting powder. The process does not produce any changes in the textural properties of the catalyst. However, the material has an increased sulfonation degree and also shows higher initial velocities, esterification and transesterification catalytic efficiencies, and improved turnover numbers (TON). Additionally, the use of sieved particles enhances the final conversion of reactant and diminishes the time to reach the maximum conversion. Moreover, the reusability of the catalysts is clearly improved since both a number of sulfonic groups and catalytic efficiencies are maintained during several cycles. Studies of the catalyst's thermal stability demonstrate that it is possible to reach temperatures up to 200 °C without loss or decomposition of the sulfonic groups.

The facile synthesis, the high separation efficiency, and the low synthesis cost, make the sulfonated porous carbons, described here, promising materials for the industrial catalysis of biodiesel synthesis.

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