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## ORIGINAL ARTICLE

# Application of sulfonated nanoporous carbons as acid catalysts for Fischer esterification reactions

L.H. Tamborini<sup>a</sup>, M.P. Militello<sup>a</sup>, J. Balach<sup>b</sup>, J.M. Moyano<sup>a</sup>, C.A. Barbero<sup>a,\*</sup>,  
D.F. Acevedo<sup>a,c,\*</sup>

<sup>a</sup> *Departamento de Química, Facultad de Ciencias Exactas, Físicoquímicas y Naturales, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina*

<sup>b</sup> *Leibniz Institute for Solid State and Materials Research (IFW) Dresden, Institute for Complex Materials, Helmholtzstraße 20, D-01069 Dresden, Germany*

<sup>c</sup> *Departamento de Tecnología Química, Facultad de Ingeniería, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina*

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## KEYWORDS

Sulfonated porous carbon;  
Sulfonation;  
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**Abstract** Heterogeneous acid catalysts were prepared by sulfonation of nanoporous carbons (NPCs). The NPCs were produced by pyrolysis of resorcinol–formaldehyde nanoporous resins (NPRs). The NPRs were synthesized as wet gels by condensation of resorcinol and formaldehyde in a sol–gel polycondensation using  $\text{Na}_2\text{CO}_3$  as catalyst. A cationic polyelectrolyte (poly(diallyl dimethyl ammonium chloride)) was used as pore stabilizer, allowing to dry the gels in air without any special procedures. Five NPRs with different properties were synthesized by varying the monomer to catalyst ratio (Resorcinol/ $\text{Na}_2\text{CO}_3$ , R/C). The morphological and textural characterizations of the NPCs were performed by scanning electron microscopy and nitrogen adsorption–desorption isotherms. The results indicate that using a molar ratio of R/C = 200, a nanoporous carbon NPC with large surface area ( $695 \text{ m}^2/\text{g}$ ) is obtained. This NPC was sulfonated by reaction with three different sulfonating agents: (i) concentrated sulfuric acid; (ii) fuming sulfuric acid and (iii) chlorosulfonic acid in order to obtain a novel Fischer esterification catalyst. The amount of acid groups attached to the NPC surface was determined by titration using a modified Boehm method. The catalytic activity, for Fischer esterification reaction of different sulfonated NPCs, was compared with sulfonated NPRs, sulfonated commercial porous carbons and polymeric acid catalyst (cationic ion exchange resins, sulfonated fluoropolymers). The modification of NPCs with concentrated sulfuric

\* Corresponding authors at: Departamento de Tecnología Química, Facultad de Ingeniería, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina (D.F. Acevedo).

E-mail addresses: [cbarbero@exa.unrc.edu.ar](mailto:cbarbero@exa.unrc.edu.ar) (C.A. Barbero), [dacevedo@ing.unrc.edu.ar](mailto:dacevedo@ing.unrc.edu.ar) (D.F. Acevedo).

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acid seems to render the materials with more catalytic activity. The best sulfonated material NPC (PC200-H<sub>2</sub>SO<sub>4</sub>) shows a high catalytic activity for the esterification of acetic acid (90.8%) and oleic acid (60.6%) with ethanol. The conversion and conversion rate values are better than commercial acid catalysts. The results suggest that sulfonated NPC catalysts are promising materials for the synthesis of biodiesel and related reactions.

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## 1. Introduction

The depletion of world oil reserves and the increasing concerns about maintaining better environmental conditions, generate a high demand for alternative fuel sources. Biodiesel has been recently regarded as the best candidate to replace diesel fuel. It is a clean, renewable fuel, which can be used on any diesel engine without the need for modification (Vasudevan and Briggs, 2008).

Chemically, the biodiesel is a mixture of alkyl esters of long chain fatty acids and is typically made from biological, non-toxic triglycerides, such as vegetable oils (Abreu et al., 2004), animal fats (Liu et al., 2004), or even used cooking oil (Issariyakul et al., 2008). The current biodiesel production technology involves the trans-esterification of triglycerides with methanol or ethanol using basic or acid catalyst (Ma and Hanna, 1999). Two types of catalysts can be used: homogeneous or heterogeneous type. The use of NaOH or KOH as homogeneous catalysts reduces the production costs (Shimada et al., 2002), because the reaction can be performed at low temperature and ambient pressure, with high conversion rates and without intermediate steps. However, homogeneous alkaline catalysts are highly hygroscopic and absorb water from the air during storage affecting its performance (Leung and Guo, 2006). Furthermore, basic catalysts in contact with water or free acids lead to the formation of soap. That saponification reaction decreases the yield of biodiesel and makes the separation of the esters and glycerol difficult. The most frequently used homogeneous acid catalyst is H<sub>2</sub>SO<sub>4</sub>. This catalyst causes equipment corrosion, resulting in higher production costs and decreasing the catalytic activity. This homogeneous acid catalyst is also soluble in the reaction mixture which makes difficult to completely wash it out from the biodiesel. Heterogeneous catalysts are solid and can be easily separated from the product by filtration, eliminating the necessity to wash out the catalyst (Reinoso et al., 2012). However, the active sites are less accessible for the reactants decreasing its activity (Van Gerpen, 2005). Several acidic heterogeneous catalysts (Sani et al., 2014; Wilson and Lee, 2015) have been studied such as zeolites (Twaiq et al., 2004), MCM-41 (Twaiq et al., 2003), sulfated zirconium, Amberlyst-15 (Klepáčová et al., 2006), Nafion (López et al., 2007) and mesoporous silica (SBA-15) (Zuo et al., 2013). Sulfonic acid SBA-15 catalysts are particularly attractive materials with activities comparable to Nafion and Amberlyst resins in palmitic acid esterification. It has been reported that sulfonic acid-functionalized silicas possess small pore sizes (6 nm) and long, isolated parallel channels, that produce slow in-pore diffusion and catalytic turnover in esterification (Lee et al., 2014). Using other approach poragen agents were used to produce SBA-15. The synthesis produces ordered mesoporous silicas with diameters spanning 5–30 nm (Woodford

et al., 2012). These silicas were functionalized and they were effective in both palmitic acid esterification and transesterification. However the ordered structures of SBA-15 are known to hamper rapid molecular exchange with the bulk reaction media (Lee et al., 2014). As the last paragraph describes, several methods have been used to improve the SBA-15 materials to be used as catalyst. Nevertheless, the extremely strict synthetic procedure to obtain the SBA-catalyst makes impossible its production in a large scale, in comparison with the carbon catalyst proposed in this manuscript. Solid acid catalysts present common problems: low concentration of active sites and microporosity, the hydrophilic nature of the catalyst surface, and leaching of active groups. The high cost of production is also an obstacle to commercialize many existing acid heterogeneous catalysts. Recently, it has been reported the synthesis of new acidic heterogeneous catalysts by sulfonation of porous carbons, either sulfonated ordered mesoporous carbons (Liu et al., 2008; Wang et al., 2007) or sulfonated carbons derived from the incomplete pyrolysis of sugars (Mo et al., 2008). The transesterification and esterification using mesoporous order carbons as catalyst produce acceptable yield; however, the several steps to generate the catalyst are the main deficiency. Porous carbons obtained from biomass pyrolysis have already been used as catalyst for biodiesel production; nevertheless, in this kind of materials it is very difficult to obtain a reproducibility in the morphology (size pore, connectivity) of the catalyst (Aldana-Pérez et al., 2012). The sulfonated carbon catalysts showed better activity than many other solid acid catalysts used for this purpose, including silica on Nafion, sulfated zirconium and Niobic acid. In this work taking into account our experience in the synthesis of porous carbons from polymeric resins (Balach et al., 2013, 2012; Bruno et al., 2010, 2009) it demonstrates a simple synthetic path to produce catalysts with reproducible morphology (size pore, connectivity) and inexpensive, condition that are necessary for producing this material in an industrial scale.

Our approach to obtain the carbon employs nanoporous gels obtained by sol-gel polycondensation of resorcinol (R) and formaldehyde (F) in the presence of a basic catalyst (e.g. sodium carbonate) using poly(diallyl dimethyl ammonium chloride) (PD) as a pore stabilizing agent (Bruno et al., 2010) and conventional drying. This procedure presents advantages over, other complex drying methods supercritical fluids (aerogels) (Job et al., 2005), low surface tension solvents (ambigels) or the sublimation of a solid solvent (cryogels) (Tamon et al., 2000). All these processes require complex procedures for drying and solvent exchange, making the obtained material expensive and difficult to produce at industrial scale (Al-Muhtaseb and Ritter, 2003). In this work, we used the relative amount of catalyst (sodium carbonate) to control the pore structure. After drying, the nanoporous resins (NPRs) were pyrolyzed

to obtain nanoporous carbons (NPCs). In order to generate active sites to catalyze the esterification reaction, the NPC with the larger surface area was sulfonated by three different approaches. Besides, a new method to quantify the sulfonic groups attached to the catalysts is demonstrated. The method is based on the titration of Boehm (Goertzen et al., 2010; Kim et al., 2012; Oickle et al., 2010), which was modified to take into account the acidity of sulfonic groups. Finally, the catalytic activity of sulfonated NPCs was studied by the measurement of the Fischer esterification of acetic acid and oleic acid with ethanol. The method described in this work allows preparing heterogeneous acid catalysts with high surface areas and good catalytic activity. The simplicity of the synthetic procedures is promising for the fabrication of low cost catalysts for biodiesel production.

## 2. Experimental

### 2.1. Synthesis of NPCs

Monolithic porous carbons were synthesized by polycondensation of resorcinol (R) (Fluka) with formaldehyde (F) (Cicarelli) in the presence of a cationic polyelectrolyte (PD) (BDH) as a pore stabilizer and sodium carbonate (C) (Cicarelli) as basic catalyst of the reaction. 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 (Pekala et al., 1998, 1992) and the PD/R = 7 ratio was kept constant. In order to study the influence of the conditions for sol-gel polycondensation on the porous structures of the carbon samples, the molar ratio of R/C was varied in the range of 100–500. 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 porous organic gels. The organic gels were dried at 70 °C in air for 6 h. The resins generated using different R/C ratios were denoted PR $x$ , where  $x$  represents the molar ratio of R/C. Finally, porous carbons (NPCs) 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 obtained samples were denoted as PC $x$ , where  $x$  represents the molar ratio of R/C (100, 200, 300, 400, and 500).

### 2.2. Catalysts preparation

Sulfonic acid groups were bound to the carbon PC $x$  using three methods. In the first method, 0.2 g of carbon was added to 10 mL of concentrated H<sub>2</sub>SO<sub>4</sub>. The same procedure was used to sulfonate the PR200 and the product is namely PR200-H<sub>2</sub>SO<sub>4</sub>. In the second method 0.2 g of carbon was added to 10 mL of fuming H<sub>2</sub>SO<sub>4</sub> (Aldana-Pérez et al., 2012; Takagaki et al., 2006; Toda et al., 2005). The suspensions of the first and second method were heated for 8 h at constant temperature ( $T = 80$  °C) under reflux and then they were cooled to room temperature. In a subsequent step, the samples were washed with distilled water until sulfate ions were no longer detected in the wash water with the barium chloride test and centrifuged in order to isolate the black precipitate from the reaction mix. Then, the sulfonated carbon materials were dried at 70 °C for 12 h. The obtained catalysts in this manner were named as PC $x$ -H<sub>2</sub>SO<sub>4</sub> and PC $x$ -H<sub>2</sub>SO<sub>4</sub>-fuming,

respectively. In the third method, 0.2 g of carbon was added to a mixture of HClSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> with a molar ratio of 2:10. The solution was heated for 8 h at 80 °C under reflux and constant stirring. Then the catalyst was allowed to cool at room temperature. After that, it was washed with distilled water and the sulfonated carbon powder was dried at 70 °C for 12 h. The obtained catalysts were named PC $x$ -HClSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. For comparison, a commercial porous carbon (Vulcan XC-72R) was sulfonated using the first procedure. The Vulcan XC-72R has a BET surface area of 222 m<sup>2</sup>/g, a micropore volume to 0.031 cm<sup>3</sup>/g and a pore size of 11.8 nm. The obtained material was named Vulcan-H<sub>2</sub>SO<sub>4</sub> (Holade et al., 2014).

### 2.3. Measurement of textural properties

Nitrogen adsorption-desorption experiments were performed with a Micrometrics ASAP 2020 at liquid nitrogen temperature, and data analysis was performed with the Micrometrics software. The samples were degassed at 180 °C for 20 h before measurements. BET surface area was calculated using the Brunauer-Emmett-Teller theory. Micropore volume ( $V_0$ ) was deduced from Dubinin-Radushkevich. The mesopore volume ( $V_{\text{meso}}$ ) was deduced from the N<sub>2</sub> adsorption isotherm, by subtracting the value  $V_0$  (N<sub>2</sub>) from the total ( $V_t$ ) amount adsorbed at  $P/P_0 = 0.984$ . Mesoporous size distribution was estimated by Barrett-Joyner-Halenda (BJH) method to the desorption branch of the isotherms.

#### 2.3.1. Scanning electron microscopy (SEM)/EDX

A Carl Zeiss EVO MA10 scanning electron microscope with an integrated EDX system was used to examine the surface morphology and characterization of the PC $x$ -H<sub>2</sub>SO<sub>4</sub> catalysts. All observations and analyses were made using software (INCA) that collects for a certain time the photons emitted by the sample, classifying them according to their energy.

#### 2.3.2. Determination of the different acid groups on the carbon surface

The content of acids groups on the surface of the catalyst was determined by titration using the technique described by Boehm. A known mass of catalyst (0.5 g) was added to 17.00 mL of each one of four bases (0.05 M): solution (a) NaHCO<sub>3</sub> (Sigma-Aldrich), solution (b) Na<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich), solution (c) NaOH (Sigma-Aldrich, 99.998 %) and solution (d) 0.5 g of catalyst with 20 mL of Na<sub>2</sub>SO<sub>4</sub> (0.1 M). The samples were agitated for 24 h, and then filtered to remove the catalyst. After that, 5.00 mL aliquots of each of the solutions a–c were extracted. The aliquot of the reaction base NaHCO<sub>3</sub> (solution a) was acidified by addition of 10.00 mL of 0.05 M HCl (Sigma-Aldrich, 99.999%). The aliquot of the reaction base Na<sub>2</sub>CO<sub>3</sub> (solution b) was acidified by the addition of 15.00 mL of 0.05 M HCl and, the aliquot of the reaction base NaOH (solution c) was acidified by the addition of 10.00 mL of 0.05 M HCl (Sigma-Aldrich, 99.999%). After that, the samples were placed in a sealed tube equipped with a needle; nitrogen was bubbled through the samples for 2 h while 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 from a direct titration from solution 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 reactions of the acid groups are shown in Scheme 1.

The equations used to determine the quantity of surface groups depend on the titration method: back-titration or direct titration. For a back-titration, the amount of the acidic groups on carbon was determined by Eq. (1) as follows:

$$n_{\text{csf}} = \frac{n_{\text{HCl}}}{n_{\text{B}}} \cdot [\text{B}] \cdot V_{\text{B}} - ([\text{HCl}] \cdot V_{\text{HCl}} - [\text{NaOH}] \cdot V_{\text{NaOH}}) \cdot \frac{V_{\text{B}}}{V_{\text{a}}} \quad (1)$$

where  $n_{\text{csf}}$  denotes the moles of carbon surface functionalities that reacted with the base, while  $[\text{B}]$  and  $V_{\text{B}}$  are the concentration and volume of the base mixed with the carbon, respectively.  $V_{\text{a}}$  is the volume of the aliquot taken from the  $V_{\text{B}}$ , and  $[\text{HCl}]$  and  $V_{\text{HCl}}$  are the concentration and volume of the acid added to the aliquot taken from the original sample, respectively.

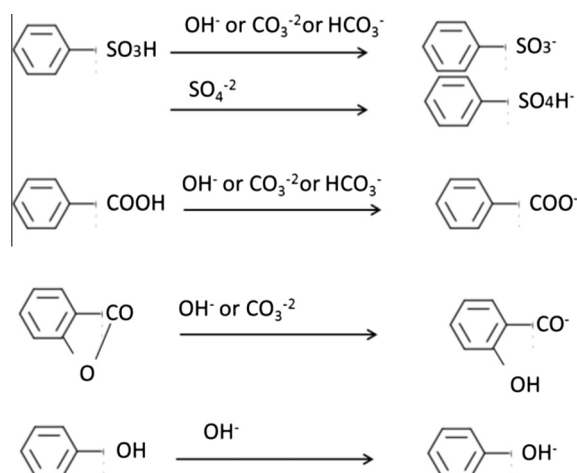
The content of sulfonic group was determined using a direct titration with the following Eq. (2):

$$n_{\text{csf}}^{\text{t}} = V_{\text{NaOH}} \cdot [\text{NaOH}] \quad (2)$$

The NaOH reacts with all surface groups, (carboxylic acids, lactones, phenols and sulfonic groups), and will therefore have an  $n_{\text{csf}}^{\text{t}}$  that includes all of these groups. The  $n_{\text{csf}}^{\text{t}}$  obtained from the titration with  $\text{Na}_2\text{CO}_3$  gives the carboxyl, lactonic and sulfonic groups. The difference between  $n_{\text{csf}}^{\text{t}}$  and  $n_{\text{csf}}^{\text{r}}$  denotes the number of moles of phenols on the surface. Similarly, since  $\text{NaHCO}_3$  reacts with carboxylic and sulfonic groups ( $n_{\text{csf}}^{\text{r}}$ ), the difference between  $n_{\text{csf}}^{\text{t}}$  and  $n_{\text{csf}}^{\text{r}}$  corresponds to the number of moles of lactonic groups. The  $\text{Na}_2\text{SO}_4$  reacts only with the sulfonic group ( $n_{\text{csf}}^{\text{s}}$ ); the difference between the  $n_{\text{csf}}^{\text{r}}$  and the  $n_{\text{csf}}^{\text{s}}$  refers to the number of moles of carboxylic acid groups.

### 2.3.3. Measurement of catalytic activity

The catalytic activity of the catalysts was evaluated on esterification reactions of acetic and oleic acid with ethanol. 0.1 mol of acetic acid (HAc) per 1 mol of ethanol with 0.2 g of catalyst was employed in order to carry out the esterification



**Scheme 1** Reaction of the acid groups in the Boehm method.

reaction. The reaction was performed for 10 h at 75 °C under constant stirring and reflux. The reaction mix was sampled every 1 h. Aliquots of 5 mL of the reaction mix were extracted at different times, and they were washed with distilled water to stop the reaction. The percent conversion of acetic acid was determined by direct titration with a solution of KOH (0.1 M), using a pH electrode to determine the equivalence point. The conversion value was calculated from Eq. (3), in order to determine the conversion vs. time profile. Esterification was also carried out with commercial solids: Nafion® 117, Amberlite IR-120 and sulfonated Vulcan® carbon as catalyst for comparison. The esterification of oleic acid (HOI) with ethanol was carried out using the same molar ratio and the same conditions as in the HAc reaction. The reaction mix was sampled every 1 h. Aliquots of 5 mL of the reaction mix were extracted, and they were washed with distilled water to stop the reaction in order to determine the conversion of the reaction vs. time. The excess of ethanol was removed from the oil phase by centrifugation for 20 min. The obtained oil phase was dissolved in ethanol and sulfuric ether for titration analysis, which was conducted by direct titration with a solution of KOH (0.1 M), using a pH electrode to determine the equivalence point. The conversion value was calculated from Eq. (4). The catalytic activity was expressed as conversion of oleic and acetic acid ( $X\%$ ):

$$X(\%) = \frac{\text{molHAc}_{\text{initial}} - \text{molHAc}_{\text{end}}}{\text{molHAc}_{\text{initial}}} \cdot 100 \quad (3)$$

$$X(\%) = \frac{\text{molHOI}_{\text{initial}} - \text{molHOI}_{\text{end}}}{\text{molHOI}_{\text{initial}}} \cdot 100 \quad (4)$$

## 3. Results and discussion

### 3.1. Synthesis of NPCs

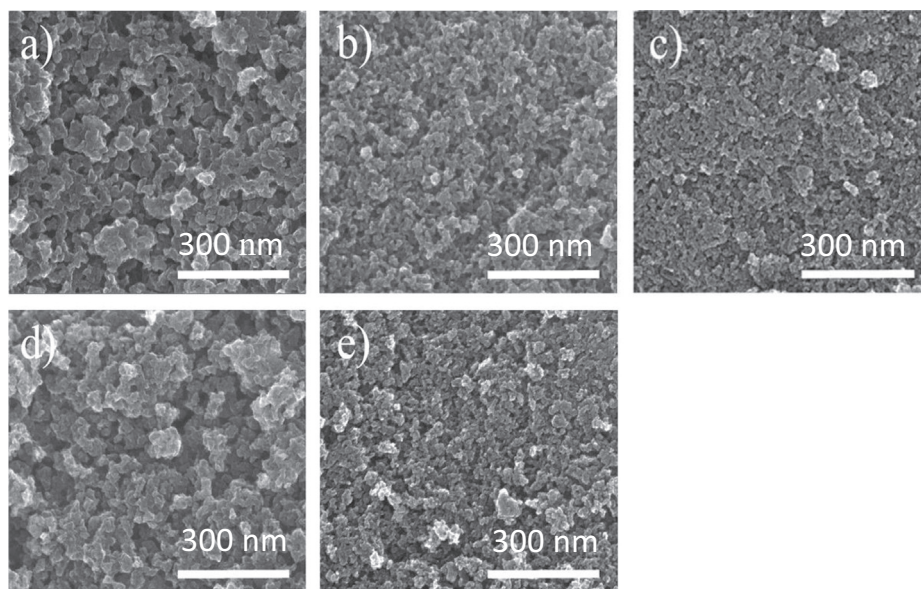
NPCs were synthesized using a molar ratio PD/R = 7 and various R/C molar ratios. The variation of the R/C molar ratios was investigated in order to determine the optimal value of R/C to produce a catalyst with the best activity. It is very well known that, varying R/C it is possible to produce carbon materials with different morphology, size pore and pore distribution. The gels obtained were dried in air and monolithic carbons are obtained by carbonization. For all of the R/C ratios the synthesis produces monolithic carbons with good stability.

### 3.2. Surface morphology and textural properties

#### 3.2.1. Scanning electron microscopy (SEM)

The influence of catalyst concentration on surface morphology of NPCs is examined by SEM. Fig. 1 shows SEM images of the external surface of the NPCs obtained at different concentration of  $\text{Na}_2\text{CO}_3$ .

The SEM images of Fig. 1 show significant differences in the materials morphology. It seems that as the R/C ratio increases, the size of the particles decreases and the carbon becomes more compact, except for R/C 400. The process of generation of porous carbon can be explained taking into account that primary particles are formed by polycondensation of resorcinol and formaldehyde during the sol-gel process. Subsequently, during the gelation stage, those particles in the



**Figure 1** SEM images of the NPCs with a R/C molar ratio of (a) 100, (b) 200, (c) 300, (d) 400 and (e) 500. All samples were synthesized at a PD/R equal to 7.

nanometer size range aggregate to form clusters, which contain micropores as a result of interparticle voids, whereas, the inter-cluster voids generate the mesoporous and/or macroporous topography. On the other hand, it is known that RF primary particles, and RF clusters, are negatively charged in basic media due to the presence of phenolic groups. The cationic polyelectrolytes can stabilize negative nanoparticles by minimizing aggregation (Studart et al., 2007). PD is positively charged and electrostatically interacts with RF negative particles, initiating self-assembly processes that result in RF-particles/PD aggregates. From the analysis of the SEM images it is possible to conclude that by changing the amount of  $\text{Na}_2\text{CO}_3$  in the synthesis, the morphology of the resulting NPCs varies significantly. As the ratio R/C is increased, the clusters are smaller producing a carbon with lower porosity, as it can be confirmed observing Table 1. It seems that at higher relative amounts of C, more primary particles are generated. In this way, the primary particles are smaller and produce pores of smaller size. These results show that it is possible to control

the surface pore size of NPCs simply by changing the amount of C used in the synthesis of carbon precursor gel.

### 3.2.2. Textural properties

Nitrogen adsorption–desorption measurements and pore size distribution of NPCs prepared with R/C ratios 100–500 are shown in Fig. 2(a) and (b), respectively. The pore size distribution and the textural properties of the different NPCs are listed in (Table 1). All samples show a type IV isotherm with a hysteresis loop, indicating the presence of mesoporous in the carbon material. All isotherms exhibit a sharp knee at low relative pressures  $P/P_0 = 0.01$ , indicating the presence of narrow micropores. Moreover, all the isotherms present an inflexion point at very high relative pressures due to condensation in the interparticle space and/or the presence of macroporosity. BJH method results show that carbon has a well-developed mesoporosity pore sizes from 4 to 21 nm. From these results we can confirm that using a molar ratio of PD/R = 7 the collapse of the pore is avoided during the appointment process of drying. We demonstrate that varying the ratio R/C it is possible to tuning the micropores and mesopores ratio. The micropores ratio and mesopores ratio present a direct influence in the surface area; consequently, more active catalytic groups will be anchored during the sulfonation process. The material PC200 exhibits the highest BET surface area ( $695 \text{ m}^2/\text{g}$ ). It seems that R/C = 200 generates a greater crosslinking of the agglomerated particles producing consequently a high surface area.

### 3.3. Determination of acidic groups

The carbon materials were sulfonated by different methods and the content of the different acids groups was determined by titration. Moreover, the amount of different acid groups was also determined in the precursor resins (PR200) of PC200 catalyst.

**Table 1** Textural properties of NPCs.

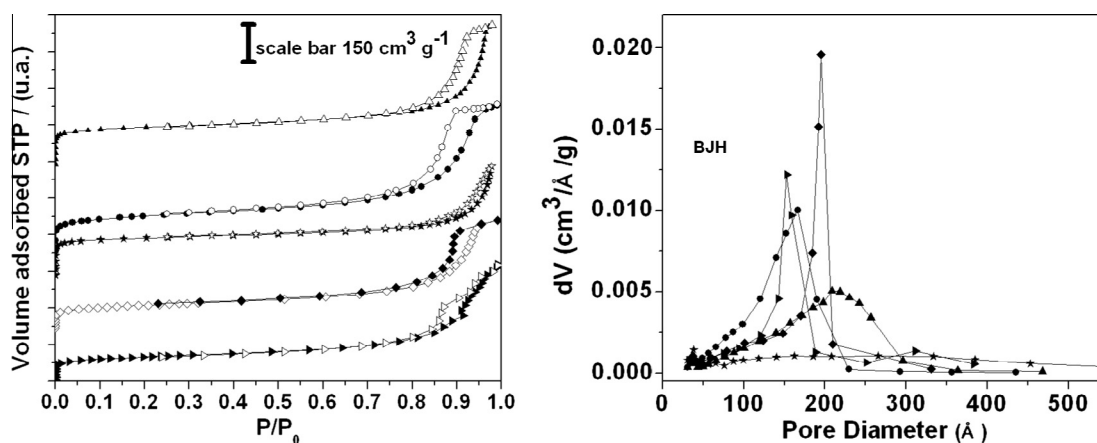
| Samples                           | $S_{\text{BET}}^{\text{a}}$<br>( $\text{m}^2/\text{g}$ ) | $V_0^{\text{b}}$<br>( $\text{cm}^3/\text{g}$ ) | $V_{\text{meso}}^{\text{c}}$<br>( $\text{cm}^3/\text{g}$ ) | $V_{\text{t}}^{\text{c}}$<br>( $\text{cm}^3/\text{g}$ ) | $D_{\text{p}}^{\text{d}}$<br>(nm) |
|-----------------------------------|--|--|--|---|-----------------------------------|
| PC100                             | 625  | 0.251  | 0.666  | 0.917   | 21                                |
| PC200                             | 695  | 0.331  | 0.669  | 1.000   | 17                                |
| PC200-<br>$\text{H}_2\text{SO}_4$ | 140  | 0.000  | 0.340  | 0.340   | 16                                |
| PC300                             | 630  | 0.274  | 0.439  | 0.713   | 4                                 |
| PC400                             | 360  | 0.141  | 0.555  | 0.696   | 20                                |
| PC500                             | 395  | 0.160  | 0.597  | 0.757   | 15                                |

<sup>a</sup> Determined from BET theory.

<sup>b</sup> Determined from Dubinin–Radushkevich.

<sup>c</sup> Volume adsorbed at  $P/P_0$  of 0.984.

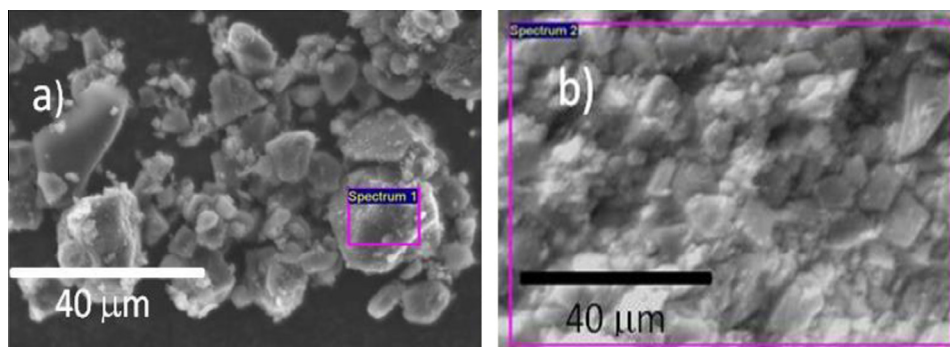
<sup>d</sup> Determined from the BJH desorption method.



**Figure 2** (a) Nitrogen adsorption–desorption isotherms of NPCs prepared with different R/C ratios, ( $\blacktriangle$ ) PC100, ( $\bullet$ ) PC200, ( $\star$ ) PC300, ( $\blacklozenge$ ) PC400 and ( $\blacktriangleright$ ) PC500. (b) Pore size distribution calculated by BJH method prepared with different R/C ratios.

**Table 2** Contents of acid groups in different stage of samples PC200 and sulfonated NPCs determined by the modified method Boehm.

| Samples   | Phenols (mmol/g) | Lactonic (mmol/g) | Carboxylic (mmol/g) | Sulfonic (mmol/g) | Total of acid sites (mmol/g) |
|---|------------------|-------------------|---------------------|-------------------|------------------------------|
| Resin PR200   | 0.34             | 0.00              | 0.48                | 0.00              | 0.82                         |
| PC200   | 0.00             | 0.00              | 0.71                | 0.00              | 0.71                         |
| Resin PR200-H <sub>2</sub> SO <sub>4</sub>              | 1.91             | 0.00              | 1.51                | 2.67              | 6.09                         |
| PC200-H <sub>2</sub> SO <sub>4</sub>                    | 0.48             | 0.00              | 0.26                | 0.39              | 1.12                         |
| PC200-H <sub>2</sub> SO <sub>4</sub> -fuming            | 0.00             | 0.00              | 0.33                | 0.45              | 0.78                         |
| PC200-ClSO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> | 0.00             | 0.00              | 0.43                | 0.58              | 1.01                         |
| PC100-H <sub>2</sub> SO <sub>4</sub>                    | 0.46             | 0.00              | 0.40                | 0.35              | 1.22                         |
| PC300-H <sub>2</sub> SO <sub>4</sub>                    | 0.00             | 0.00              | 0.61                | 0.49              | 1.10                         |
| PC400-H <sub>2</sub> SO <sub>4</sub>                    | 0.00             | 0.00              | 0.47                | 0.40              | 0.87                         |
| PC500-H <sub>2</sub> SO <sub>4</sub>                    | 0.00             | 0.00              | 0.89                | 0.38              | 1.27                         |



**Figure 3** (a) SEM Images of (a) PC200 (b) PC200-H<sub>2</sub>SO<sub>4</sub> catalysts.

### 3.3.1. Titration of acid groups in porous carbons

Table 2 shows the content of acid groups in different porous materials synthesized, for PC200 and the analysis was made before and after sulfonation and for its precursor resin.

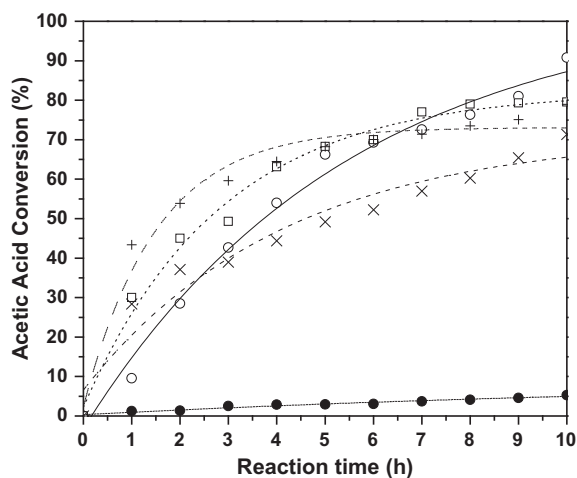
The resin only contains phenolic and carboxylic groups and the unsulfonated NPC contains only carboxylic groups. It seems that some of the phenolic groups during pyrolysis are transformed into carboxylic groups and others are lost.

The sulfonation process of PC200 and PC100 using H<sub>2</sub>SO<sub>4</sub> seems not only to generate sulfonic groups but also to increase

the amount of oxidized groups such as phenolic groups. This is likely due to the hydrolysis of sulfonic groups attached to aromatic rings in concentrated H<sub>2</sub>SO<sub>4</sub>. The other sulfonation techniques in this carbon increase the quantity of carboxylic acid probably due to the oxidative effect of the sulfonating agent (H<sub>2</sub>SO<sub>4</sub>-fuming and HClSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>). The results show that using HClSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> as sulfonating agent in PC200, the carbon incorporates a larger amount of sulfonic groups. On the other hand, the resin PR200, sulfonated with H<sub>2</sub>SO<sub>4</sub> for 8 h at a temperature of 80 °C presents the highest content of

**Table 3** Elemental analysis by EDX of PC200, PC200, PC200-H<sub>2</sub>SO<sub>4</sub> catalysts.

| Element                                  | Atomic % |
|--|----------|
| <i>PC200</i>                             |          |
| C  | 74.41    |
| O  | 24.94    |
| Na                                       | 0.08     |
| S  | 0        |
| <i>PC200-H<sub>2</sub>SO<sub>4</sub></i> |          |
| C  | 88.08    |
| O  | 9.14     |
| Na                                       | 0        |
| S  | 1.21     |

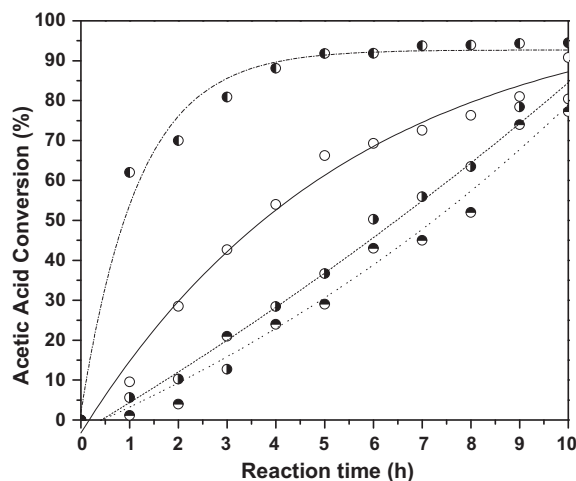
**Figure 4** Catalytic efficiency of the catalyst (○) PC200-H<sub>2</sub>SO<sub>4</sub>, (●) PC200, (□) Nafion® 117, (X) Amberlite IR-120 and (+) Vulcan-H<sub>2</sub>SO<sub>4</sub> in the esterification reaction of acetic acid and ethanol at 75 °C for 10 h.

sulfonic groups. This is reasonable since the resin is mainly composed of phenol and phenyl ether moieties which are more reactive toward sulfonation than aromatic rings in the graphitic domains of carbon (Al-Muhtaseb and Ritter, 2003; Pekala et al., 1992).

### 3.3.2. Energy dispersive X-ray analysis (EDX)

To confirm the presence of sulfonic groups in the carbon materials subjected to sulfonation, we performed EDX measurements. Fig. 3(a) and (b) shows the SEM images of PC200 and PC200-H<sub>2</sub>SO<sub>4</sub> catalysts; the square shows the mapping area used for EDX analysis. Table 3 shows the results of the elemental analysis of the samples.

The results indicate the presence of C, O and Na in PC200. These three elements are expected due to the composition of carbon, the presence of oxidized groups and the presence of Na<sub>2</sub>CO<sub>3</sub> used during the synthesis which is retained to counterbalance the anionic groups. The sodium disappears in the sulfonated material since all acid groups are converted from sodium salt form into acid form by the concentrated sulfuric acid. In the catalyst PC200-H<sub>2</sub>SO<sub>4</sub>, the EDX shows the presence of S confirming the success of the sulfonation process.

**Figure 5** Acetic acid conversion versus time of (●) PR200-H<sub>2</sub>SO<sub>4</sub>, (○) PC200-H<sub>2</sub>SO<sub>4</sub>, (●) PC200-H<sub>2</sub>SO<sub>4</sub> fuming, (○) PC200-HClSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. Esterification of acid acetic with ethanol at 75 °C molar ratio (1:10) using 0.2 g of catalyst, for 10 h.

The amount of S for PC200-H<sub>2</sub>SO<sub>4</sub> measured using EDX renders a value of meq/g (3.12) which is larger than the value measured by titration, and it seems that not all the sulfur containing groups are accessible for titration.

### 3.4. Catalytic activity evaluation

#### 3.4.1. Fischer esterification of acetic acid with ethanol

The catalytic activity of PC200-H<sub>2</sub>SO<sub>4</sub> and PC200 for the esterification reaction of acetic acid with ethanol is compared to determine whether sulfonic groups are necessary to catalyze the reaction. The results are shown in Fig. 4. Only 5% of conversion is obtained using the pristine carbon (PC200), indicating that the phenolic and carboxylic groups are not effective to catalyze this reaction. On the other hand, using sulfonated PC200 it is possible to obtain up to 90% of conversion using the same conditions. For comparison, the catalytic activity of other acid catalysts: (i) a cation exchange resin (Amberlite IR-120) and (ii) a copolymeric fluoropolymer bearing sulfonic groups (Nafion®) is tested. Additionally, a commercial porous carbon (Vulcan XC-72®) is sulfonated using concentrated sulfuric acid and tested. As it can be seen (Fig. 4), all the sulfonated materials show conversion of acetic acid to ethyl acetate, but PC200-H<sub>2</sub>SO<sub>4</sub> shows the highest conversion value at 10 h of reaction. Nafion® 117, Amberlite IR-120 and sulfonated Vulcan® show lower conversions in comparison with PC200-H<sub>2</sub>SO<sub>4</sub>.

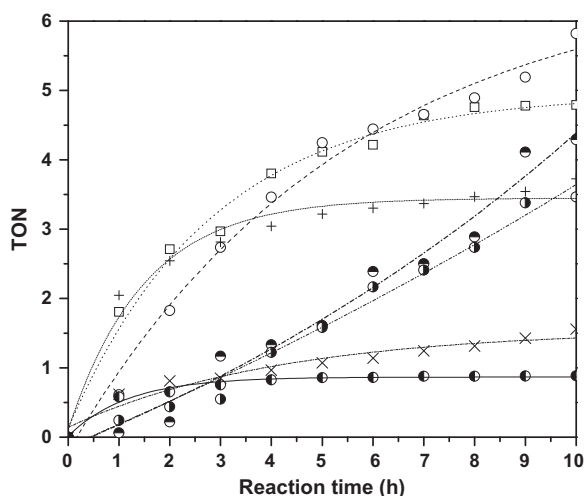
Then, we compare the different sulfonation methods, and Fig. 5 shows the percentage of conversion of acetic acid catalyzed by, PC200-H<sub>2</sub>SO<sub>4</sub>, PC200-H<sub>2</sub>SO<sub>4</sub> fuming, and PC200-HClSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. Additionally, the sulfonated resin PR200-H<sub>2</sub>SO<sub>4</sub> is also tested. As expected, the sulfonated PR200 resin shows the best conversion rate, because of the largest amount of sulfonic groups. On the other hand, PC200-H<sub>2</sub>SO<sub>4</sub> reaches the same conversion at 10 h of reaction. It is noteworthy that PC200-HClSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> and PC200-H<sub>2</sub>SO<sub>4</sub> fuming, despite having a higher content of sulfonic groups than other carbons, achieve a lower percentage of conversion at all times of reac-

tion. This behavior could be caused by formation of a surface where the sulfonic groups generated are unstable and thus they are deactivated during reaction or by the poor internal diffusion of the reactants to the active sites. The result of this analysis indicates that the sulfonation process using  $\text{H}_2\text{SO}_4$  at  $80^\circ\text{C}$  produces a better catalyst for acetic acid esterification. In this experiment, it seems likely that an accessible structure of micropores and mesopores produces better internal diffusion and more efficiency of the active catalytic groups.

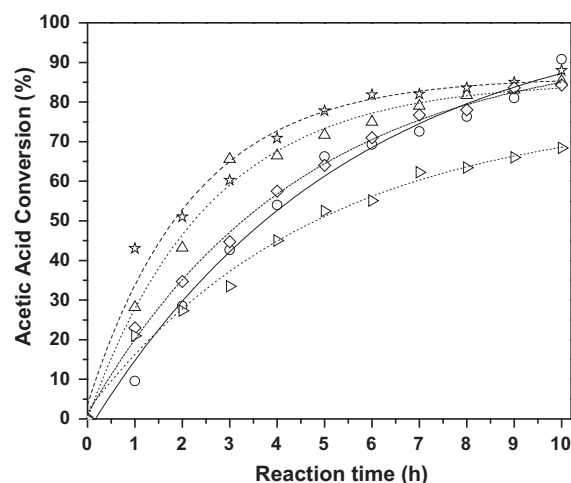
Moreover, if the conversion values are divided by the amount of sulfonic groups in the materials, the Turnover Number (TON) is obtained. In Fig. 6, it can be seen that catalytic activity of each group in  $\text{PC200-H}_2\text{SO}_4$  is larger than in the other materials except for Nafion®117 and Vulcan- $\text{H}_2\text{SO}_4$ . However the TON number at more than 6 h  $\text{PC200-H}_2\text{SO}_4$  is larger than the other material. It is noteworthy that the TON of the sulfonated resin ( $\text{PR200-H}_2\text{SO}_4$ ) is quite low, suggesting that the more hydrophobic nature of the carbon matrix, compared with the phenolic resin, helps in the interaction of the sulfonic group with the reactants or products increasing the turnover number.

Another parameter which can affect the catalytic activity is the textural properties (porosity, pore size, etc.) of the sulfonated NPCs, which, as it was shown above, can be controlled by the relative amount of catalyst concentration in the resin synthesis. The catalytic activity for the esterification of acetic acid with ethanol of the sulfonated NPCs synthesized with R/C from 100 to 500, is shown in Fig. 7. All carbons were sulfonated using  $\text{H}_2\text{SO}_4$  at  $80^\circ\text{C}$  for 8 h.

As it can be seen  $\text{PC200-H}_2\text{SO}_4$  shows a higher conversion rate, while the content of sulfonic acid groups of all the catalysts is nearly the same, Fig. 7. This behavior indicates that the reactants are less inhibited and they access easily by the active sites in this catalyst. This result is consistent with the specific surface area calculated by the BET method since the  $\text{PC200}$  shows the highest BET value and when this material is sulfonated achieves the larger conversion rate. The electrophilic sulfonation of aromatic rings is a reversible reaction



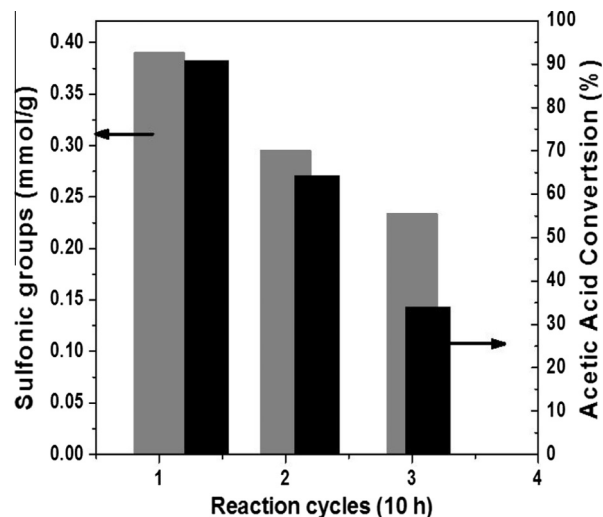
**Figure 6** Turnover number for the esterification of acetic acid with ethanol vs. the time of reaction. In all cases, using 0.2 g of catalyst of: (●)  $\text{PR200-H}_2\text{SO}_4$ , (○)  $\text{PC200-H}_2\text{SO}_4$ , (◐)  $\text{PC200-H}_2\text{SO}_4$  fuming, (◑)  $\text{PC200-HClSO}_3/\text{H}_2\text{SO}_4$ , (□) Nafion® 117, (X) Amberlite IR-120 and (+) Vulcan- $\text{H}_2\text{SO}_4$ .



**Figure 7** Acetic acid conversion versus time of (Δ)  $\text{PC100-H}_2\text{SO}_4$ , (○)  $\text{PC200-H}_2\text{SO}_4$ , (☆)  $\text{PC300-H}_2\text{SO}_4$ , (◇)  $\text{PC400-H}_2\text{SO}_4$  and (▷)  $\text{PC500-H}_2\text{SO}_4$ . Esterification of acid acetic with ethanol at  $75^\circ\text{C}$  molar ratio (1:10) using 0.2 g of catalyst, for 10 h.

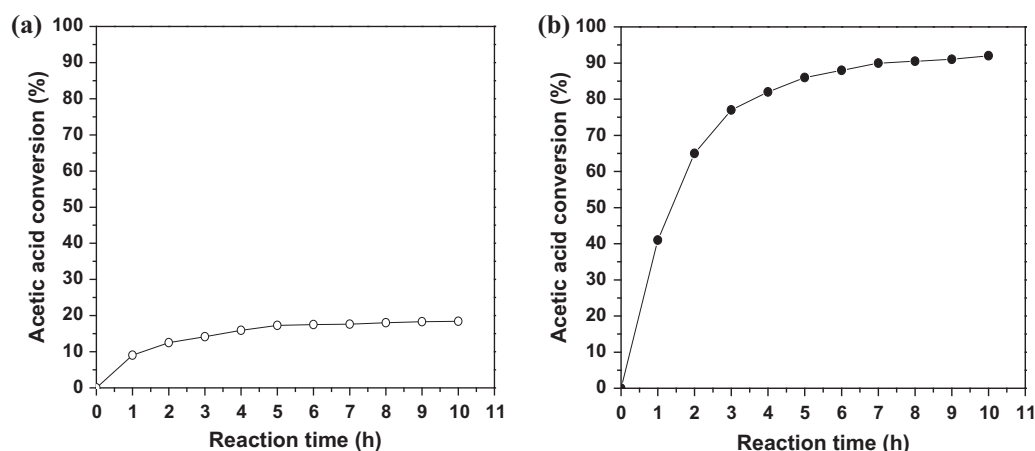
(Katritzky et al., 2009). Therefore, all sulfonated aromatic materials including graphitic domains of carbon, could lose the sulfonic groups by hydrolysis. In order to study the stability of sulfonic acid groups and the possibility to reuse the catalyst,  $\text{PC200-H}_2\text{SO}_4$  was recovered from the reaction mixture after 10 h of reaction, by filtration. The catalyst is then washed with water, ethanol and hexane. After that it was dried and incorporated to a kinetic measurement of Fischer esterification. Before each cycle of use, the content of sulfonic groups was determined by titration.

The experimental results indicate that the conversion decreases to 64.3% in the second reaction cycle, and the content of sulfonic groups also decreases by approximately 24.3%, while in the third cycle conversion rate reaches a value of 34% and the content of sulfonic groups decreases by 40% from original value, Fig. 8. Similar behavior has been found

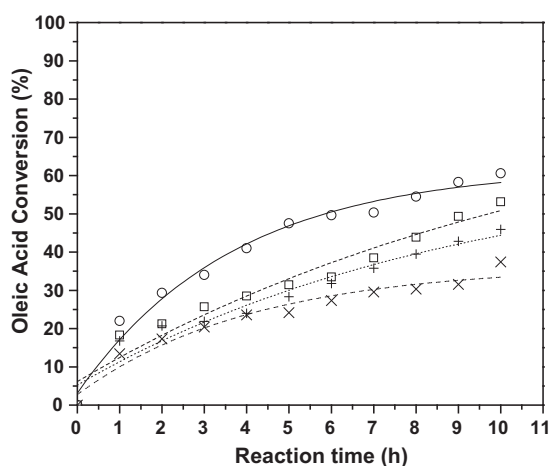


**Figure 8** Acetic Acid conversion (black box) and sulfonic group (gray box) content of  $\text{PC200-H}_2\text{SO}_4$  vs. number of reaction cycles of 10 h of esterification each one.





**Figure 9** (a) Acid acetic conversion, of the reaction mix after the first cycle with removal of the catalyst. (b) Homogeneous esterification reaction using the amount of 10 mmol of H<sub>2</sub>SO<sub>4</sub>.



**Figure 10** Catalytic efficiency (○) PC200-7-H<sub>2</sub>SO<sub>4</sub>, (□) Nafion® 117 and (X) Amberlite IR-120 and (+) Vulcan-H<sub>2</sub>SO<sub>4</sub> for the esterification reaction of oleic acid with ethanol at 75 °C for 10 h.

in Starbons-300 sulfonated, and this catalyst showed a decrease of 28% in the catalytic activity during the second cycle and a decrease of 30% in the amount of mmols SO<sub>3</sub>H/g (Aldana-Pérez et al., 2012). The catalyst after the first cycle presented 1.6 mmol SO<sub>3</sub>H/g corresponding to 70% of active sites. The low catalytic activity and the decrease in the sulfonic group content can be attributed to deactivation or leaching of the active sites. However, in the third cycle the decrease of conversion is larger than the decrease of sulfonic groups present in the carbon, suggesting that some other mechanisms, such as site poisoning, could be operative. The leached sulfonic groups could act as homogeneous catalyst for the esterification. In order to verify this, a test was carried out by removing the catalyst after 1 h reaction. Then the reaction allows continuing until 10 h. Further the esterification reaction of acetic acid was studied using an amount of about 10 mmol of H<sub>2</sub>SO<sub>4</sub>. This quantity is choice because it is the same acid groups quantity that the catalyst loss between the

first cycle and the second cycle (Fig. 9(a and b)). The results of Fig. 9(a) show no catalytic activity after removing the heterogeneous catalyst. The maximum conversion value reached 10% supports the theory of the deactivation of sulfonic acid groups on the catalyst surface. Moreover, the percentage of conversion of acetic acid obtained with 10 mmol/g of H<sub>2</sub>SO<sub>4</sub> at 1 h of reaction is c.a. 41% (Fig. 9(b)) indicating that the leaching of the acid groups is negligible in comparison with its deactivation.

### 3.4.2. Fischer esterification of oleic acid with ethanol

A more relevant reaction for biodiesel synthesis involves long chain fatty acids, such as those present in natural oils and fats. Therefore, the catalytic efficiency of PC200-H<sub>2</sub>SO<sub>4</sub> was tested for the esterification of oleic acid with ethanol. The material was compared with commercial catalysts: Nafion® 117 and Amberlite IR-120 (Fig. 10).

As it can be seen in Fig. 10, PC200-H<sub>2</sub>SO<sub>4</sub> produces a 60.6% conversion at 10 h of reaction. This value is higher than for Nafion® 117 (53.0%), Amberlite IR-120 (37.4%) and Vulcan-H<sub>2</sub>SO<sub>4</sub> (45.9%). However, the conversion achieved by the catalyst PC200-H<sub>2</sub>SO<sub>4</sub> in the esterification reaction with oleic acid is lower than that obtained in the esterification of acetic acid. This result is expected due to the more difficult mass transport for viscous solutions of long chain acids. The results suggest that the catalytic activity for the esterification of large molecules of long chain acids depends not only on the content of sulfonic acid groups, but also on the properties of the catalyst surface, such as BET surface area and pore diameter. The conversion value obtained is comparable and even superior to values obtained in other published works (Lee et al., 2014), for example CMK-5-SO<sub>3</sub>H obtained 80% of conversion at 6 h of reaction (Wang et al., 2007), and Mo et al. obtained 40% of conversion in 1 h (Mo et al., 2008).

### 3.4.3. Conversion efficiency of sulfonated NPCs

Table 4 summarizes the catalytic efficiency and shows the values of sulfonic groups and catalytic activity of the catalysts analyzed for esterification reactions. As it can be seen, the sulfonated carbon shows higher conversion values than

**Table 4** Sulfonic groups and catalytic activity of the catalysts analyzed for esterification reactions.

| Samples   | Acetic Acid conversion (%) (10 h) | Oleic acid conversion (%) (10 h) |
|---|-----------------------------------|----------------------------------|
| PC200-H <sub>2</sub> SO <sub>4</sub>                    | 90.8                              | 60.6                             |
| PC200-H <sub>2</sub> SO <sub>4</sub> -fuming            | 77.3                              | –                                |
| PC200-ClSO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> | 80.4                              | –                                |
| PC100-H <sub>2</sub> SO <sub>4</sub>                    | 85.3                              | –                                |
| PC300-H <sub>2</sub> SO <sub>4</sub>                    | 88.0                              | –                                |
| PC400-H <sub>2</sub> SO <sub>4</sub>                    | 84.3                              | –                                |
| PC500-H <sub>2</sub> SO <sub>4</sub>                    | 68.4                              | –                                |
| Nafion® 117   | 79.5                              | 53.0                             |
| Amberlyst IR-120  | 71.3                              | 37.4                             |
| Vulcan-H <sub>2</sub> SO <sub>4</sub>                   | 78.9                              | 45.9                             |

commercial solid catalysts. Since the commercial catalysts are more expensive and show lower activity, the PC200-H<sub>2</sub>SO<sub>4</sub> would be an excellent candidate for industrial application.

#### 4. Conclusions

An easy approach to obtain heterogeneous acid catalysts for Fischer esterification making this process more environmentally friendly is shown. The catalysts were obtained from porous carbons, synthesized by pyrolysis of resorcinol/formaldehyde resins. The use of PD as pore stabilizer produces porous carbons. The relative amount of catalyst (sodium carbonate) allows controlling the textural properties of the dry precursor resin and the final nanoporous carbon. All the sulfonation methods employed are successful. However we conclude that using concentrated sulfuric acid in the procedure makes the most active sulfonic groups. Also we showed that the Boehm modified technique is an excellent tool for determining the content of acidic groups of the catalysts including sulfonic groups. The results suggest that the porosity of the material plays an important role to anchor the sulfonic groups. The carbons that have a high  $S_{\text{BET}}$  volume with connected meso and micropores facilitate the incorporation of such groups. The material with better properties is obtained using (R/C) molar ratio to 200 and (PD/R) to 7. The PC200-H<sub>2</sub>SO<sub>4</sub> catalyst achieves the highest catalyst activity for esterification of acetic acid (90.8%) and oleic acid (60.6%) with ethanol after 10 h of reaction, and such values are better than the ones achieved with other solid commercial catalysts. The conversion of acetic acid and the content of sulfonic groups decrease along several reaction cycles; this is likely due to the deactivation or leaching of active sites. Because of their easy synthesis, separation and low cost compared to other acidic heterogeneous catalysts, the sulfonated NPCs are promising materials for the synthesis of biodiesel.

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