Preparation of submicron carbon fibers from lignocellulosic waste for energy and environmental applications

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Objective and Novelty

The objective of this PhD Thesis was the preparation of advanced fibrous carbon materials to be used in energy and environmental applications. For this purpose, coaxial electrospinning technique, a simple and versatile method, was used to prepare submicron diameter fibers. Alcell lignin was used as carbon precursor for the preparation of carbon fibers. In this Thesis work, the incorporation of phosphoric acid to the initial lignin/ethanol solutions was investigated with the objective to study its effect on the stabilization of the lignin fibers during an oxidative treatment at low temperature and on the textural and surface chemistry properties of the final carbon fibers obtained after a thermal treatment at high temperature. The presence of high thermally stable surface phosphorus group improved the development of porosity, surface acid character and oxidation and electro-oxidation resistance of the obtained carbon fibers. The incorporation of metal precursor to the lignin solutions was also studied in order to obtain carbon fibers doped with metal nanoparticles in a simple way. These carbon materials presented very interesting properties to be used in different applications of the chemical industry, confirming that electrospinning is a powerful tool for maximizing the value of lignin as carbon precursor.

Results

The third and fourth chapters of the PhD Thesis were focused on the study of lignin fibers stabilization step. Lignin, which has a low glass transition temperature, requires for long times to be stabilized, making crucial the stabilization step for the preparation of carbon fibers. Figure 1 shows the effect of the heating rate on the lignin and P-containing lignin fibers stabilization. Pure lignin fibers were obtained by the electrospinning of lignin/ethanol solutions (mass ratio of lignin/ethanol of 1/1). The stabilization stage required the use of a low heating rate (0.08 ºC/min) up to 200 ºC, then, this temperature is kept for 60 hours. Therefore, the total duration of the step necessary to stabilize the pure lignin fibers is 90 hours. This long stabilization time is necessary to get the crosslinking of the lignin structure.

The incorporation of small amount of H_3PO_4 to the initial lignin/ethanol solutions (0.3/1/1 H_3PO_4/lignin/ethanol) produces the generation of phosphates (and/or polyphosphates) groups in the lignin structure, improving the cross-linking of lignin structure and making faster the air stabilization step of P-lignin fibers. These lignin fibers can be stabilized at heating rates as high as 3-5 ºC/min and only maintained at 200 ºC for 1 hour. The comparison of stabilized lignin fibers at 1 ºC/min showed the melting of pure lignin fibers, meanwhile P-containing lignin fibers kept completely their morphology (Figure 1). The incorporation of low amounts of H_3PO_4 to the lignin solutions allows to stabilize fibers 50 times faster. In addition, the use of phosphoric acid also improved the development of the carbon fibers porosity, acid character and oxidation and electro-oxidation resistance of the resulting carbon fibers that make these carbon materials very interesting for different chemical engineering applications.

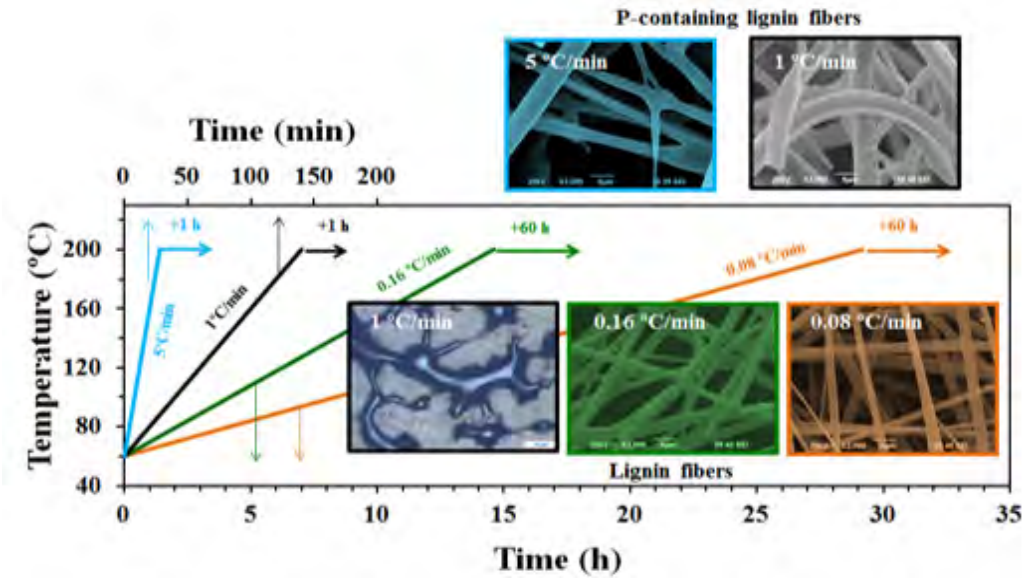

Figure 1. Effect of stabilization heating rates and times on lignin and P-lignin fibers

In the fifth chapter, the adsorbent characteristics of these microporous carbon fibers for phenol removal in liquid phase, with adsorption capacities as high as 180 mg/g at an equilibrium concentration of 25 mg/L and 25 ºC, was reported. The small carbon fibers diameters facilitate the diffusion of the pollutant to the surface of microporosity, making the adsorption process faster and, simultaneously, very low pressure drops are achieved when submicron diameter carbon fibers are used as adsorbent in a column adsorption. Furthermore, the incorporation of H_3PO_4 to the initial lignin solutions produces a widening of the carbon fibers porosity, improving the kinetic of the adsorption process. Equilibrium and kinetic adsorption experiments were carried out at different temperatures. A mathematical model was used to predict the breakthrough profiles in fixed-bed columns by using equilibrium and kinetics adsorption parameters obtained from the batch experiments. Figure 2 a) shows the experimental breakthrough profile for phenol adsorption (dots) on P-carbon fibers and the predicted values (lines) obtained from the mathematical model. The regeneration of the phenol saturated carbon fibers with a water stream at 25ºC was also studied and a regeneration yield of 55 and 14 % for P-containing and pure carbon fibers, respectively, was obtained.

In the sixth chapter, the preparation of P-containing carbon fibers at different temperatures and their use as acid catalysts for alcohol decomposition in a fixed bed reactor were reported. In this sense, isopropanol decomposition reaction was used as a test to characterize the surface acidity or basicity of the carbon fiber materials. The selectivity for isopropanol decomposition was 100 % to propylene, demonstrating the acid character of these materials. In Figure 2 b) a steady state conversion values of isopropanol on P-containing carbon fibers prepared at 900 ºC are reported. A relationship between the amount of P and the activity for isopropanol decomposition was found and conversions similar to those observed for a commercial acid catalyst (γ-Al_2O_3) were observed for the carbon fiber containing higher amount of surface P. The thermal stability of carbon catalysts is very important in applications under oxidizing conditions. The P-containing carbon fibers present high oxidation resistance, starting to gasify at temperatures as high as 525-550 ºC in the presence of air. Phosphorus surface groups are the responsible for this high oxidation resistance. Ethanol and methanol decomposition were also studied on P-containing carbon fibers in the presence of air. High selectivity to ethylene and dimethyl ether was observed for ethanol and methanol decomposition, respectively.

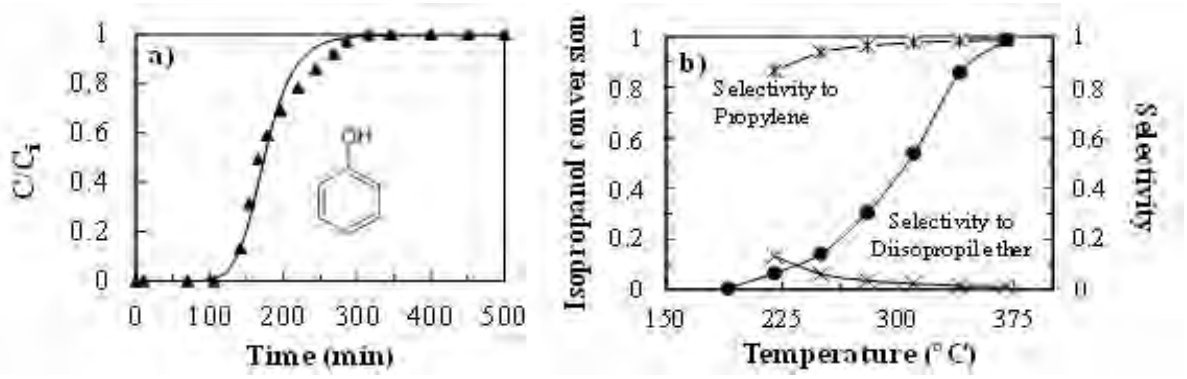

Figure 2. Breakthrough profile of phenol adsorption at 25 ºC on carbon fibers (a) and steady state conversion of isopropanol and selectivity on acid carbon fibers (b).

In the two last chapters, the use of the carbon fibers as carbon electrodes for energy storage and conversion was reported. Figure 3 shows some results about the utilization of carbon fibers in these applications. Interconnected carbon fibers obtained by electrospinning of lignin solutions were evaluated as binderless and flexible electrodes in supercapacitors, without using any type of conductive promoter. The interconnection of carbon electrodes (CF-I) improves the electrical conductivity with respect to the linear carbon electrodes (CF-L), enhancing the electrochemical behavior at higher scan rates (Figure 3). A symmetric two-electrode supercapacitor was constructed in aqueous electrolyte (H_2SO_4, 1M) showing 60 kW/kg of maximum power density and energy density of 10 Wh/kg. This supercapacitor was stable during 100000 cycles operating at 1.3 V and 5 A/g.

The preparation of electrospun Pt supported lignin-based carbon fibers was also evaluated as electrocatalyst for alcohol electro-oxidation. The effect of Pt and H_3PO_4 loadings on the physicochemical properties and activity of the catalyst was analyzed. A higher Pt content produces a development of the mesoporosity in carbon fibers. Differently, the presence of H_3PO_4 only delivers a slight increase in the specific surface area, even at the highest Pt loading, while Pt particle sizes decrease from 9.6 nm to 2.1 nm. The absence of Pt in the carbon electrode does not present electro-activity for alcohol electro-oxidation. On the contrary, when carbon electrodes with Pt were used an outstanding MOR and EOR is produced with a current density as high of 495 A/g_{Pt} (Figure 3). These carbon fibers showed promising results as anodes for the direct alcohol fuel cells for methanol (MOR) and ethanol (EOR) electro-oxidation, due to the well-dispersed Pt nanoparticles, their physicochemical properties and their adequate conformation in fuel cell devices.

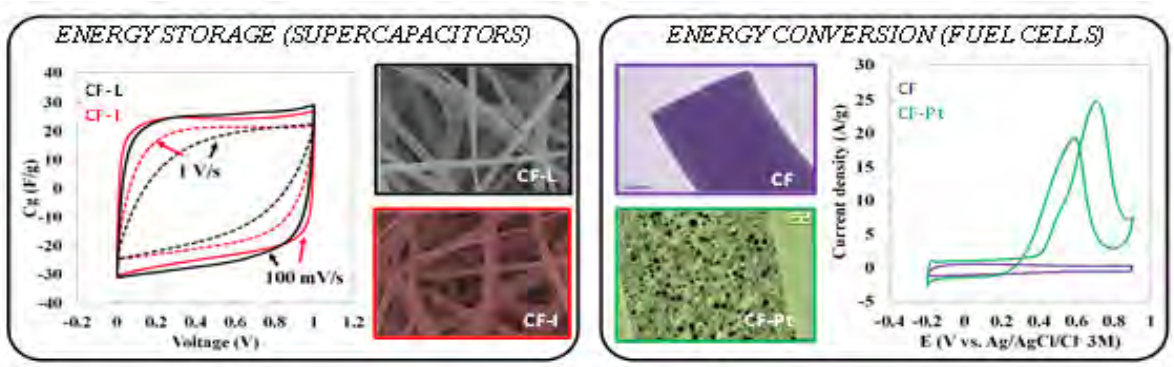

Figure 3. Steady state CVs from symmetric 2-electrode supercapacitors and from carbon electrodes in fuel cells in presence of methanol.

Conclusions

The advantages of electrospinning of Alcell lignin/ethanol solutions to produce carbon fibers have been presented in this PhD work. All combinations of physico-chemical, metal dispersion, electrical conductivity and mechanical properties make these carbon fibers excellent porous materials as catalysts, electrocatalysts, electrodes, and adsorbents.

Related Publications

[1] Berenguer R., García-Mateos, F.J. Rodríguez-Mirasol, J., Cordero, T. Partículas y materiales carbonosos con propiedades optimizadas, procedimientos para su obtención, y aplicaciones de los mismo.ES2531462B2, 2016

[2] García-Mateos, F.J., Ruiz-Rosas, R., Rosas, J.M., Rodríguez-Mirasol, J., Cordero, T. Controlling the composition, morphology, porosity, and surface chemistry of lignin-based electrospun carbon materials. Front. Mater. 2019; 6:114

[3] García-Mateos, F.J., Berenguer, R., Valero-Romero, M.J., Rodríguez-Mirasol, J., Cordero, T. Phosphorus functionalization for the rapid preparation of highly nanoporous submicron-diameter carbon fibers by electrospinning of lignin solutions. J. Mater. Chem. A 2018; 6(3): 1219-1233

[4] García-Mateos, F.J., Cordero-Lanzac, T., Berenguer, R., Morallón, E., Cazorla-Amorós, D., Rodríguez-Mirasol, J., Cordero, T. Lignin-derived Pt supported carbon (submicron) fiber electrocatalysts for alcohol electro-oxidation. App. Catal. B: Environ 2017; 211 18-30

[5] Berenguer, R., García-Mateos, F.J., Ruiz-Rosas, R., Morallón, E., Cazorla-Amorós, D., Rodríguez-Mirasol, J., Cordero, T. Biomass-derived binderless fibrous carbon electrodes for ultrafast energy storage. Green Chem. 2016; 18(6): 1506-1515

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