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ALCOHOL DECOMPOSITION ON BASIC/ACID LIGNIN-DERIVED SUBMICRON DIAMETER CARBON FIBERS

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Introduction

The use of lignin, the second most abundant polymer in nature, along with a simple and versatile technique, electrospinning, represents an advantageous and promising approach for the preparation of carbon fibers. In previous studies[1], we demonstrated that the incorporation of H_3PO_4 to the initial lignin solution allows for shortening the carbon fibers preparation process time and carbon fibers with high porosity development, high oxidation resistance and surface acidity were obtained. All these properties make carbon fibers with phosphorus-containing surface groups of great interest for heterogeneous catalysis. In this work, the influence of the surface acidity on the dehydration of ethanol over the carbon fibers with P-containing surface groups has been studied.

Materials and Methods

Different carbon fibers catalysts were prepared by electropinning of Alcell lignin solutions in the absence or presence of H_3PO_4 (weight ratio H_3PO_4/lignin = 0 and 0.3, respectively)) in a coaxial configuration[2]. The as spun lignin fibers were stabilized at 200 ºC in an oxidative atmosphere (air) before being carbonized at 500 and 900 ºC. Carbon fibers prepared at 900 ºC were also treated at 1200 and 1600 ºC. Carbon fibers were characterized by adsorption-desorption of N_2 at 77 K, adsorption of CO_2 at 293 K, temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) under air atmosphere and scanning electron microscopy (SEM). Gas phase decomposition of alcohols was studied in a fixed bed microreactor with an alcohol partial pressure of 0.0185 atm, in inert or air atmosphere.

Results and Discussion

Table 1. Porous texture and chemical surface composition by XPS

Carbon fiber catalysts	A_{BET}^{N2} m^2/g	A_{DR}^{CO2} m^2/g	Chemical weight composition by XPS C %	O %	P %
CF-500	328	458	84.3	15.1	--
CF-900	851	1002	95.9	4.1	--
CF-900-TT1200	628	739	97.8	2.0	--
CF-900-TT1600	150	517	98.0	1.9	--
PCF-500	749	794	86.0	12.3	1.0
PCF-900	1155	950	90.5	7.3	2.2
PCF-900-TT1200	938	870	89.6	6.9	3.1
PCF-900-TT1600	823	686	97.9	1.8	0.2

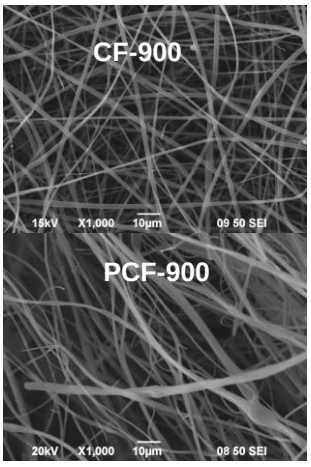

Figure 1. SEM images of CF-900 and PCF-900

The used preparation method allows for preparing carbon fibers with a high variety of porosity and surface chemistry. The incorporation of H_3PO_4 produces a widening of the microporosity. The maximum porosity development was obtained at an activation temperature of 900 ºC (**Table 1**). The further thermal treatment at 1200 and 1600 ºC produces an important shrinkage of the porous structure, minimized in case of phosphorus containing carbon fibers. **Figure 1** shows the SEM

images of carbon fibers with and without phosphorus, PCF and CF, respectively, prepared at 900 ºC. The carbon fiber diameter for all the carbon fibers was between 0.5 to 3 μm.

Figure 2 shows the isopropanol conversion and selectivity on carbon fibers with and without phosphorus. The isopropanol decomposition was used as a catalytic test to study the acid or basic character of the samples. Carbon fibers without phosphorus surface groups generate acetone as the main product of the isopropanol decomposition reaction, from 400 to 600 ºC, suggesting the basic character of these catalysts. On the contrary, phosphorus-containing carbon fibers show high acid character, producing a selectivity to propylene of 100 % at temperatures between 250 and 350 ºC. The influence of oxygen in the gas phase was studied for the most active phosphorus-carbon catalyst, improving the catalytic behaviour. The decomposition of ethanol was also studied with the most acid catalyst. In the absence of oxygen, a significant deactivation of the catalyst is produced, while a total ethanol conversion with a high selectivity to ethylene is obtained when air is used.

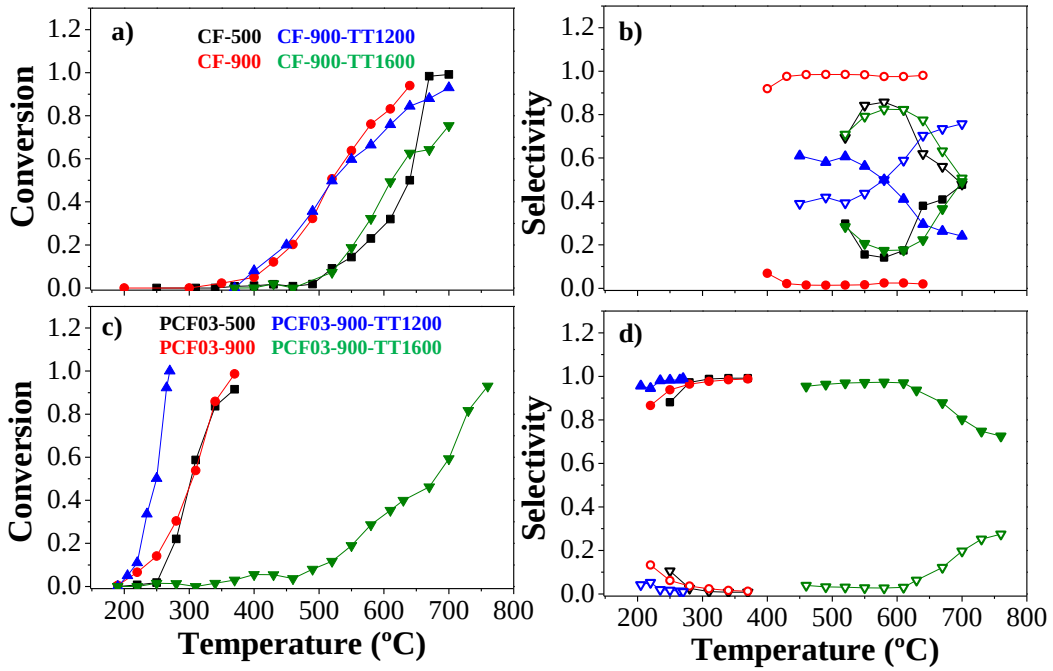

Figure 2. Isopropanol conversion (a and c) of different carbon fibers catalysts and selectivity (b and d) to propylene (filled mark) and acetone (hollow mark).

Conclusions

Basic and acid carbon fibers have been obtained by electrospinning of H_3PO_4/Alcell lignin/ethanol solutions. Carbon fibers prepared in the absence of phosphoric acid presented a basic character, yielding mainly acetone as the reaction product for the isopropanol decomposition reaction. P-containing carbon fibers showed acid character, producing propylene as the main product.

Acknowledgment

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References

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