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KILLING TWO BIRDS WITH ONE STONE: CATALYSTS PREPARED FROM BIOMASS WASTE TO BE USED FOR TRANSFORMATION OF BIOMASS WASTE

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The preparation procedure of activated carbons with acid or basic properties has been optimized in order to prepare acid/basic solids with a high number of strong acid-basic active sites on the surface of the carbon material. These solids have been prepared by chemical activation of biomass waste (olive stone) with different activation agents (NaOH or H_3PO_4) and present appropriate porous structure for being used as heterogeneous catalysts. The acid/basic properties of the surface of the carbons have been analyzed by pH titrations. These carbon materials with acid or basic surface sites can be used for a wide range of biomass waste transformation processes.

Keywords: biomass waste, chemical activation, activated carbon, catalyst

INTRODUCTION

Nowadays there is a need for developing acid and basic solid catalysts in order to replace conventional homogeneous acid and basic catalysts because of the environmental problems they cause and difficulty of operation. Twenty years ago, Tanabe and Hölderich calculated that more than three hundred solid acids and bases had been developed in the previous decades.[1]In spite of that, nowadays sulfuric acid and sodium hydroxide, among others, continue being used as catalysts for many industrial applications, as for example, for the synthesis of biodiesel. So, despite all the effort that has been done in this research direction, more studies are required in order to replace corrosive liquid strong acids and bases that are being actually used as homogeneous catalysts. On the other hand, carbon materials are quite useful in catalysis, since their surface chemistry is relatively easy to modulate in order to have acid and/or basic sites. In addition, they can be produced by low cost processes and by revalorization of biomass wastes.[2-4] In addition, they are suitable as supports of other activated phases, such as metals. Once the supported carbon catalyst is deactivated, the activated phase can be easily recovered by gasification of the carbon support, and some energy can be produced.

The present study describes the preparation and characterization of activated carbons, obtained by revalorizing a biomass waste (olive stone), with strong acid/basic surface sites. The possibility of modulating the acid/basic properties of these carbons, along with their easy removal after reaction by filtration and their possible reuse, makes carbons very attractive materials to be used as acid or basic heterogeneous catalysts in several industrial processes. In this respect, biorefineries use biomass as an abundant and renewable resource for the production of energy, biofuels and valuable chemicals through different processes that require the use of a catalyst. Thus, the use of biomass waste for the preparation of the catalytic materials necessary for biorefineries is quite beneficial for the viability of the biorefinery process.

EXPERIMENTAL

Activated carbons were prepared by chemical activation with NaOH or H_3PO_4. Olive stone waste (provided by Sociedad Cooperativa Andaluza Olivarera y Frutera, Periana) was used, in both cases, as starting material.

The olive stone waste was cleaned with deionized water, dried at 100 ºC, and ground with a roller mill to obtain samples of 400-800 μm particle size. Raw olive stone waste shows a negligible porous structure. Olive stone char was obtained by carbonization of the precursor under continuous N_2 (99.999%, Air Liquide) flow (150 cm^3 STP/min) at 500 ºC (C500). For the chemical activation process with NaOH, the char C500 was impregnated at room temperature with the activating agent, NaOH (≥95%, Sigma–Aldrich),with an impregnation ratio of 1/1 or 3/1 (NaOH/char). For the preparation of the acid carbon-based catalysts, the raw material was impregnated with concentrated commercial H_3PO_4 (85 wt%, SigmaAldrich) at 60 or 200 ºC, with a weight ratio of 3/1 (H_3PO_4/olive stone). The impregnated samples were activated at 900 ºC (those impregnated with NaOH) and 500 ºC (those impregnated with H_3PO_4) under continuous N_2 (purity 99.999%, Air Liquide) flow (150 cm^3 STP/min) in a conventional tubular furnace. The activation temperatures were reached at a heating rate of 10 °C/min and maintained for 2 h. The activated samples were cooled inside the furnace under the same N_2 flow and then washed by distilled water at 60 °C. The resulting carbon materials were dried at 100 ºC, then were ground and sieved (100-300 μm).

The porous structure of the activated carbons and supported catalysts was characterized by N_2 adsorption-desorption at -196 ºC and by CO_2 adsorption at 0 ºC, carried out in an ASAP 2020 from Micromeritics Instruments Corporation. Samples were previously outgassed during 8 hours at 150 ºC. From the N_2 adsorption/desorption isotherm, the apparent surface area (A_{BET}) was determined applying the BET equation, the micropore volume (V_t) and the external surface area (A_t) were calculated using the t-method, and the mesopore volume (V_{mes}) was determined as the difference between the adsorbed volume at a relative pressure of 0.95 and the micropore volume (V_t). The narrow micropore surface area (A_{DR}) and volume (V_{DR}) were obtained by the Dubinin-Radushkevich method applied to the CO_2 adsorption isotherm.

The pH of the carbon material suspensions was determined following the procedure described by El-Sayed and Bandosz.[6]An amount of 0.4 g of sample, previously dried overnight at 100 ºC, was added to 20 ml of water and the suspension was stirred overnight to reach equilibrium. Then the sample was filtered and the pH of the solution was measured with a Hanna pHmeter equipped with an HI 1230B electrode. In order to have information about the number and type of the acid/basic sites, potentiometric titrations were also performed. A suspension of each sample was prepared with 0.10 g of carbon and 40 ml of electrolyte (NaCl 0.01N), and kept for 24h, under stirring in nitrogen at room temperature in order to avoid CO_2 effect during the titrations, which were performed in nitrogen atmosphere. AHCl (0.1N) solution was used as titrating agent. Its concentration was exactly determined by titration with a normalized $CaCO_3$ solution. The pH was monitored during HCl additions with the pHmeter.

Table 1

Acid and basic carbon materials synthetized

Sample	Impregnation ratio	Activating agent	Activation T (ºC)
AC(60)-3-500	3:1	H_3PO_4	500
AC(200)-3-500	3:1	H_3PO_4	500
BC(C500)-1-900	1:1	NaOH	900
BC(C500)-3-900	3:1	NaOH	900

The catalytic activity of the activated carbon was studied by decomposition of ethanol in the gas phase at atmospheric pressure in a fixed bed microreactor (i.d. 4mm) placed inside a vertical furnace with temperature control, under different operating conditions. In a typical experiment, 150 mg of catalyst (100-300 μm mesh) was used. Ethanol was fed to the system in a controlled way by using a syringe pump (Cole-Parmer® 74900-00-05 model). The reaction was carried out in air atmosphere in the temperature range of 250-350 ºC and in helium atmosphere between 350-500 ºC. Ethanol partial pressure was 0.02 atm with a space time of 0.100 g·s/μmol. Reactants and reaction products were analyzed on-line by gas chromatography (Agilent 490 micro-GC equipped with PPQ, 5A molecular sieve and Wax columns).In all the cases, carbon mass balances were closed with errors lower than 5%. The ethanol conversion is defined as the molar ratio of the ethanol converted to the ethanol fed to the reactor. The selectivity is defined as $S_i=C_i/(\sum_i C_i)$, where C_i is the molar flow of i product in the outlet stream.

RESULTS AND DISCUSSION

Figure 1 presents the N_2 adsorption–desorption isotherms at -196 ºC of the carbon catalysts. Basic carbons and CA(200)-3-500 show type I isotherms characteristic of solids with a predominantly microporous structure. The isotherms of these carbons have an almost negligible hysteresis cycle, which indicates the lack of a developed mesoporosity. On the other hand, the N_2 isotherm of CA(60)-3-500 is type IV, showing a hysteresis loop, often associated to slit-shaped pores. The parameters calculated from the isotherms are shown in Table 2.The char C500 shows higher micropore volume value (DR) when $CO_2$is used instead of N_2as adsorbate gas, which indicates the presence of a narrow micropore structure (Vt).[7]

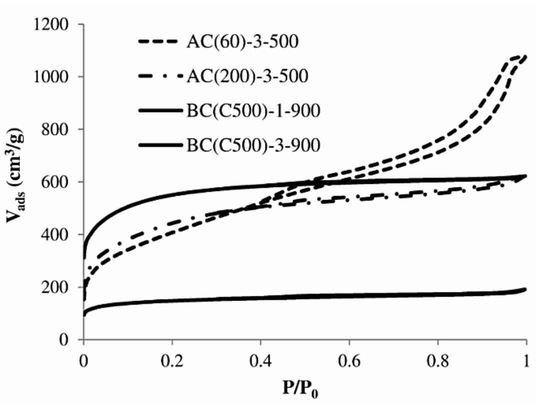

Figure 1: N_2 adsorption-desorption isotherms of activated carbons

Table 2
Porous structural parameters obtained from N_2 and CO_2 isotherms

	N_2 isotherm						CO_2 isotherm	
Sample	A_{BET} (m^2/g)	A_t (m^2/g)	V_t (cm^3/g)	V_{ads} (cm^3/g)	A_{DR} (m^2/g)	V_{mes} (cm^3/g)	A_{DR} (m^2/g)	V_{DR} (cm^3/g)
C500	5	2	0.001	0.008	7	0.007	344	0.137
AC (60)-3-500	1482	665	0.448	1.662	817	1.214	592	0.237
AC (200)-3-500	1597	227	0.653	0.964	1369	0.311	700	0.280
BC (C500)-1-900	528	49	0.217	0.295	428	0.055	528	0.212
BC (C500)-3-900	1975	106	0.844	0.962	1868	0.118	1248	0.500

Table 3
pH values of the carbon surface and titration results

Sample	pH	$meq_{HCl\ or\ NaON}/g_{sample}$	pH_{eq}	meq/m^2
AC (60)-3-500	3.2	0.090	5.03/8.09	0.0000606
AC (200)-3-500	3.9	0.010	5.74	0.0000062
BC (C500)-1-900	8.4	0.071	7.71	0.0001384
BC (C500)-3-900	7.4	0.012	7.72	0.0000063

In the case of acid carbons, the surface area and micropore volume increases when the impregnation temperature is increased, while the mesoporous volume decreases. In the case of basic carbons, when the impregnation ratio is increased (from 1 to 3), an increment in the porous structure (BET surface area and micro- and mesoporous volumes) is observed according to the data shown in Table 2.

Table 3 shows the pH of the suspensions.As expected, the samples prepared with phosporic acid present pH values below 7 and those prepared with NaOH have a pH higher than 7. The first derivatives of the titration curves are shown in Figure 2. The shape of the curves for the two acid carbons is different. The activated carbon impregnated at 60ºC (AC(60)-3-500) presents two shifts, at 5.03 and 8.09 (Table 3), clearly indicating that it possesses two types of acid sites with different strength. The one in the 4-6 pH range can be associated both with the pKa of carboxylic acids and with the one of the deprotonations of phosphoric acid. The peak near 8 corresponds to the H+ of the phosphoric system.

In the case of the AC(200)-3-500 sample, only one peak near pH 6 is detected. These data indicate that carboxyl groups can be present in both carbons and that the amount of phosphoric acid surface groups decreases when the temperature of impregnation is increased. This fact is also evidenced (Table 3) by the low amount of surface acid groups that the sample activated at higher temperature presents (0.0000062 meq/m^2 for AC(200)-3-500 vs. 0.0000606 for AC(60)-3-500).

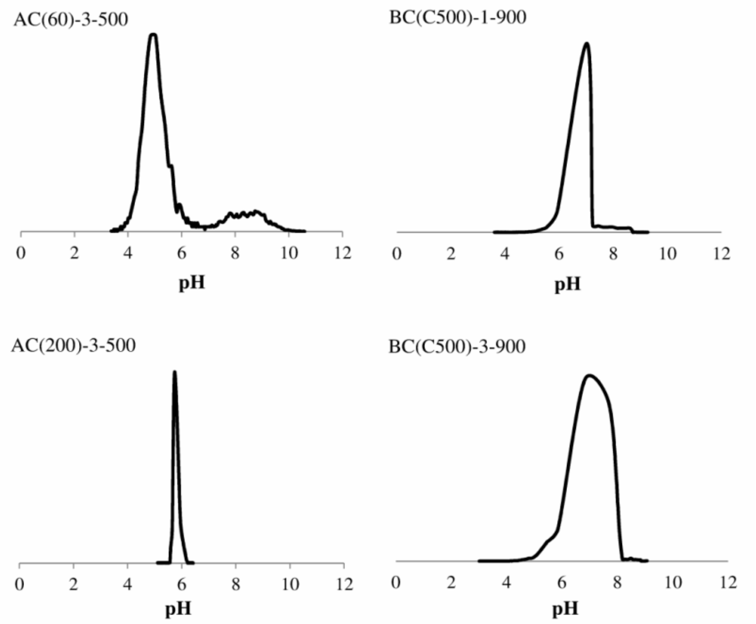

Figure 2: First derivative of titration curves

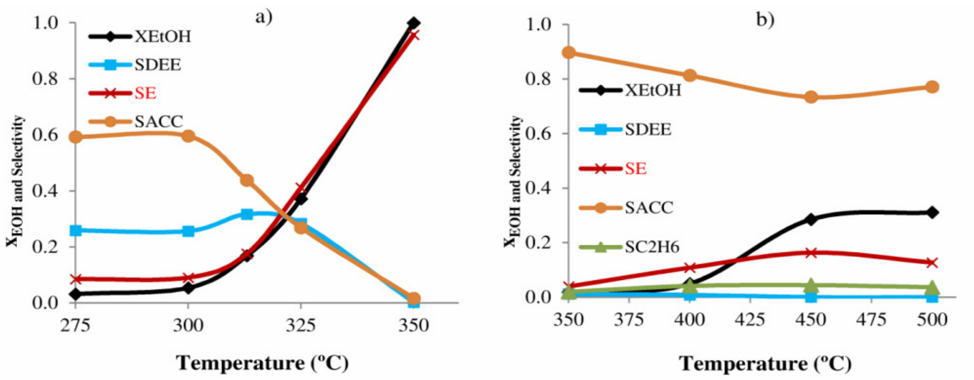

Figure 3: Ethanol conversion and selectivity to main products as a function of reaction temperature (a) in air over AC(60)-3-500 and (b) in He over CB(C500)-3-900 (PMeOH=0.02 atm, W/FMeOH=100000 g·s/mol)

Basic carbons also have different acid-basic properties. Figure 2 shows that both of them present only one peak, but the distribution is broader in the case of the carbon prepared with an impregnation ratio of 1, although both peaks are centered near 7.7, indicating that the nature of basic groups is similar in both samples. The data shown in Table 3 indicate that the amount of basic sites decreases when the impregnation ratio is increased from 1 to 3. Studies performed by DTP (not shown for patency reasons) indicated that these basic groups are associated with quinones and lactones. It has been demonstrated that basic carbonsare very promising for the lactose isomerization to produce lactulose.[8] The interest of this reaction is that lactose is a biomass waste present in milk permeate, whereas lactulose is a ketose disaccharide used in both pharmaceutical and food industries. Actually, this process is carried out using corrosive homogeneous catalysts.

The presence of stably bonded phosphorus complexes on the surface of the acid carbons is demonstrated by the titration results. In addition, the presence of C-O-PO_3 and C-PO_3 groups on the surface of phosphoric acid activated carbons has been previously reported.[9] This is due to the activation method, which produces the reaction between the acid and some organic species, forming phosphate bridges, which are responsible for connecting and crosslinking the biopolymer fragments and have been proven to remain on the carbon surface after the washing step. These phosphorus groups remain very stable at relatively high temperatures and provide the carbon a relatively high oxidation resistance and surface acid sites, which makes these acid carbon-based materials very attractive as catalysts.[10] Figure 3 shows the steady state conversion of ethanol and selectivity to different products with the reaction temperature at a space time of 0.1 g·s/ìmol and an inlet partial pressure of ethanol of 0.02 atm in air for AC(60)-3-500 (Fig. 3a) and in He for CB(C500)-3-900 (Fig.3b). Only at low temperatures and low conversion values, the selectivity to diethyl ether (DEE) and acetaldehyde (ACC) is significant over AC(60)-3-500. An increase in the reaction temperature results in higher ethylene (E) selectivity, whereas the selectivity to DEE and ACC drastically decreases. Furthermore, at 350 ºC the ethanol dehydration on AC(60)-3-500 in air shows selectivity to ethylene of about 95% under the experimental conditions used in this study. As expected, the catalytic decomposition of ethanol over the basic carbon (Fig. 3b) yields mainly acetaldehyde as main product in the whole range of temperature studied, characteristic of the dehydrogenation reaction over basic sites.

CONCLUSION

A simple and low-cost method has been demonstrated for obtaining basic and acid activated carbons by valorizing biomass waste. It has been also proven that potentiometric titrations are a simple and low-cost technique for determining the number and type of surface acid/basic sites on the surface of these materials. This is very important information directly related with the catalytic properties of these materials. The porous structure and the acid-basic properties have been related with the conditions used during the preparation of these solids. For the acid carbons, the data indicated how the amount of surface acid groups increases when the temperature of impregnation is increased. In the case of basic carbons, the amount of basic sites decreases when the impregnation ratio is increased. These basic/acid solids are useful as catalytic materials in several processes for biomass waste valorization, such as the isomerization of lactose (present in milk permeate) or the transformation of alcohols (obtained by biomass fermentation).

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