

# OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE TO STYRENE ON ACTIVATED CARBONS DERIVED FROM A NATIVE WOOD AS CATALYST

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**Abstract**— Activated carbons were developed by phosphoric acid activation of a native wood (*Prosopis ruscifolia*) under a self-generated atmosphere or flowing air. Their potentiality as catalyst for oxidative dehydrogenation of ethylbenzene to styrene was examined at pre-established operating conditions. The carbons developed in the self-generated atmosphere showed specific surface area of 2281 m<sup>2</sup>/g and total pore volume of 1.7 cm<sup>3</sup>/g, whereas values of 1638 m<sup>2</sup>/g and 1.3 cm<sup>3</sup>/g, respectively, characterized those obtained in air. A commercial activated carbon (1200 m<sup>2</sup>/g and 0.7 cm<sup>3</sup>/g) was also used for comparison. Both wood-derived carbons resulted potentially suitable as catalyst for ethylbenzene oxidative dehydrogenation. Nevertheless, those developed in the self-generated atmosphere showed a better catalytic performance than the carbons obtained in air and the commercial sample. The behaviour could be due to its lower microporosity compared with the commercial sample, and to the formation of oxidative condensation products during the oxidative dehydrogenation of ethylbenzene with greater content of carbonyl groups than for the sample activated under flowing air. Chemical and textural characterization of the used carbons conclusively evidenced the presence of oxidative condensation products pointing to formation of new active surfaces.

**Keywords**— ethylbenzene, styrene, oxidative dehydrogenation, activated carbons, catalyst.

## I. INTRODUCTION

Styrene (ST) is one of the most important basic chemical species. It is mainly used as the monomer of synthetic polymers. It is commercially produced by the dehydrogenation of ethylbenzene (EB) on iron oxide catalyst at 873-973K. However, the dehydrogenation of EB is thermodynamically limited and a very energy consuming process because of the excessive requirement of superheated steam. As an alternative, the oxidative dehydrogenation (ODH) of EB has been proposed as it is free from thermodynamic limitations regarding conversion, and it operates at lower temperatures involving exothermic reactions. Most of the work on EB has been devoted to the selection of suitable catalysts and appropriate reaction conditions to improve the styrene yield and selectivity (Morales and Lunsford, 1989; Swaan *et al.*, 1992; Chang *et al.*, 1993; Sulikowski *et al.*, 1994).

It has been reported that high activities and selectivity can be obtained at relatively low temperature using activated carbon as catalyst (Pereira *et al.*, 1999; Pereira *et al.*, 2000). In previous works (Iwasawa *et al.*, 1973; Schraut *et al.*, 1987; Cadus *et al.*, 1990), it has been concluded that oxygenated functional groups on catalyst surface, especially quinone-like structures, enhance the catalytic performance. Considering that the textural properties and surface functional groups of activated carbons (ACs) depend on the precursor used, as well as on the strategy and preparation conditions (Patrick, 1995), we have studied the feasibility of developing ACs with specific characteristics for their use as catalyst in ODH (de Celis, 2003).

In the present work, activated carbons have been developed from *Prosopis ruscifolia* wood as a precursor through the chemical activation process with phosphoric acid solution as the activating agent for two different activation atmospheres and pre-established experimental conditions. In this sense, the aim of this paper is to study the influence of the activation atmosphere on textural properties, chemical characteristics and catalytic behaviour of the resulting ACs in EB oxidative dehydrogenation. For the sake of comparison, a commercial activated carbon (CAC) was also characterized and catalytically evaluated.

## II. MATERIALS AND METHODS

### A. Preparation of the Activated Carbons (ACs)

*Prosopis ruscifolia* is a species of tree indigenous to south of South America. It grows very rapidly in Chaco region, the vast plain in Argentina, Paraguay, and Bolivia. Until a few years ago, it was considered as a plague due to its ability to fast invade degraded lands turning them unproductive. A recent programme has been launched in order to control the spread of this species, and *Prosopis* wood has been introduced in the market for furniture manufacture and the timber industry.

A piece of *Prosopis ruscifolia* wood without bark kindly provided by GESER (Facultad Ciencias Exactas y Naturales, Universidad de Buenos Aires) was used for ACs preparation. It was crushed, milled, and screen-sieved. Fractions of average particle diameter of 0.75 mm were employed to obtain the ACs.

Briefly, the sawdust was impregnated with a H<sub>3</sub>PO<sub>4</sub> acid aqueous solution (50 % wt), using an acid/precursor weight ratio of 2. Each impregnated sample was placed

in a stainless steel tubular reactor (220 x 100 mm) externally heated by an electric furnace. The impregnated samples were heated at 3 °C/min from room temperature to 450 °C. The samples were thermally treated at this final temperature for 0.5 h. Further details of the equipment and procedure used have been reported earlier for other precursors (Castro *et al.*, 2000; Vernersson *et al.*, 2002; Basso *et al.*, 2002; Basso and Cukierman, 2005). Thermal treatment of the impregnated sawdust was carried out under either in the air enclosed with the sample in the reactor upon insertion, namely an oxygen self-generated atmosphere or under a flow of air (99.999 % v/v; 0.1 m<sup>3</sup>/h). Air flowed through the reactor throughout the thermal treatment and further cooling of the samples. In order to remove the acid, the so-obtained ACs were subsequently rinsed with distilled hot water until neutral pH in the wash water was attained. Afterwards, they were dried in an oven to constant weight. Yields were evaluated from weight differences.

The activated carbons developed under the self-generated atmosphere and flowing air are denoted as ACS and ACF, respectively. Similar yields (≈ 40 %) were attained for both atmospheres. For the sake of comparison, a commercial activated carbon (CAC) was also used and characterized by the same methods applied to the ACs developed from *Prosopis* wood.

### B. Chemical, Textural and Thermal Characterization of the ACs

Chemical characteristics of the precursor, the ACs developed in the two activation atmospheres, and the CAC were determined by standard methods. Proximate analyses of the samples were performed according to ASTM (American Society of Testing and Materials) standards. An elemental analyzer (Carlo Erba model EA 1108) was used to assess their elemental compositions.

The total and individual amounts of acidic/polar oxygen functional groups (OFG) on the surface of the derived ACs and the commercial sample were determined following a modified procedure based on Boehm's method (Toles *et al.*, 1999; Basso *et al.*, 2002; Basso and Cukierman, 2005). It enables to quantify carbonyls, phenols, lactones, and carboxyl groups by titration with a series of bases of different strength. Sodium ethoxide was used to determine the total amount of oxygen groups. Phenols, lactones, and carboxyls were quantitatively ascertained by titration with sodium hydroxide, whereas sodium bicarbonate allowed quantification of only carboxyl groups. Carbonyls were estimated by subtraction of NaOH-titrable groups from the total amount of OFG, as determined by titration with sodium ethoxide. In turn, the quantity of phenols and lactones was evaluated by subtracting carboxyl groups from NaOH-titrable groups.

A total of 0.5 g of each sample was suspended in 50 mL of a 0.05 N solution of sodium ethoxide, sodium hydroxide, or sodium bicarbonate. The slurries were stirred for 24 h and afterward filtered. A 10 mL aliquot of the resulting solutions was added to 15 mL of a 0.05 N HCl acid solution. The solutions were subsequently

back-titrated with 0.05 N NaOH. Values are expressed as milliequivalents per gram of sample.

Besides, identification of surface functionalities of the ACs was complementary conducted by Fourier Transform Infrared (FT-IR) spectroscopy.

The spectra were recorded using a Nicolet Magna IR 550 spectrometer within the wavenumber range of 400-4000 cm<sup>-1</sup>. Each sample was mixed with KBr and then ground in an agate mortar at an approximate ratio of 1:100 for preparation of the pellets. The resulting mixture was finally pressed. The background obtained from a scan of pure KBr was automatically subtracted from the sample spectra.

N<sub>2</sub> adsorption isotherms at (-196 °C) for the precursor and derived ACs were determined with a Micromeritics Gemini 2360 Surface Area Analyzer (Micromeritics, Norcross, GA, USA). Nitrogen adsorption experiments were conducted to determine the specific surface area and pore volume of the activated carbons. The BET model was applied to fit nitrogen adsorption isotherms and evaluate the specific surface area ( $S_{\text{BET}}$ ) of the samples. Total pore volumes ( $V_{\text{T}}$ ) were estimated from the amount of nitrogen adsorbed at the highest relative pressure ( $p/p_0 = 0.98$ ). The mean pore radius was estimated from  $r_{\text{m}} = 2V_{\text{T}}/S_{\text{BET}}$ , assuming the pores to be parallel and cylindrical. Micropore volumes ( $V_{\text{micro}}$ ) were calculated from the nitrogen adsorption isotherms using the Dubinin-Radushkevich (D-R) equation. Textural properties were assessed from the isotherms, according to conventional procedures detailed earlier (Castro *et al.*, 2000; Basso *et al.*, 2002; Basso and Cukierman, 2005).

### C. Catalytic tests

Catalytic tests were carried out in a conventional fixed-bed flow reactor, operated isothermally at atmospheric pressure. The reactor was made of a Pyrex glass tube of 13 mm inner diameter (length of catalyst bed = 1 cm) and heated with an electric oven equipped with temperature controller. A diagram of the equipment used is shown in Fig. 1.

Since oxidation reactions are highly exothermic and in order to keep away from undesirable thermal effects, the catalyst bed was diluted (1:5) with glass particles, of the same diameter. The EB was fed by means of an airstream carrier diluted with N<sub>2</sub> flowing through a saturator in order to avoid adverse thermal effects. The feed EB/air molar ratio was controlled by adjusting both the saturator temperature and the N<sub>2</sub> flow rate. The reaction temperature was measured with a sliding thermocouple placed inside the bed.

Composition of the feed and the effluent was analysed using an on-line gas chromatograph HP 6890, equipped with a FID detector and HP INNOWAX 30m/320µm/0.25µm Polyethylenglicol column. Catalytic tests were performed under the conditions detailed in Table 1. Preliminary catalytic tests were performed in order to ensure that, at the selected operating conditions, contribution of homogeneous oxidative dehydrogenation of ethylbenzene, as well as internal and external diffusion effects were negligible.

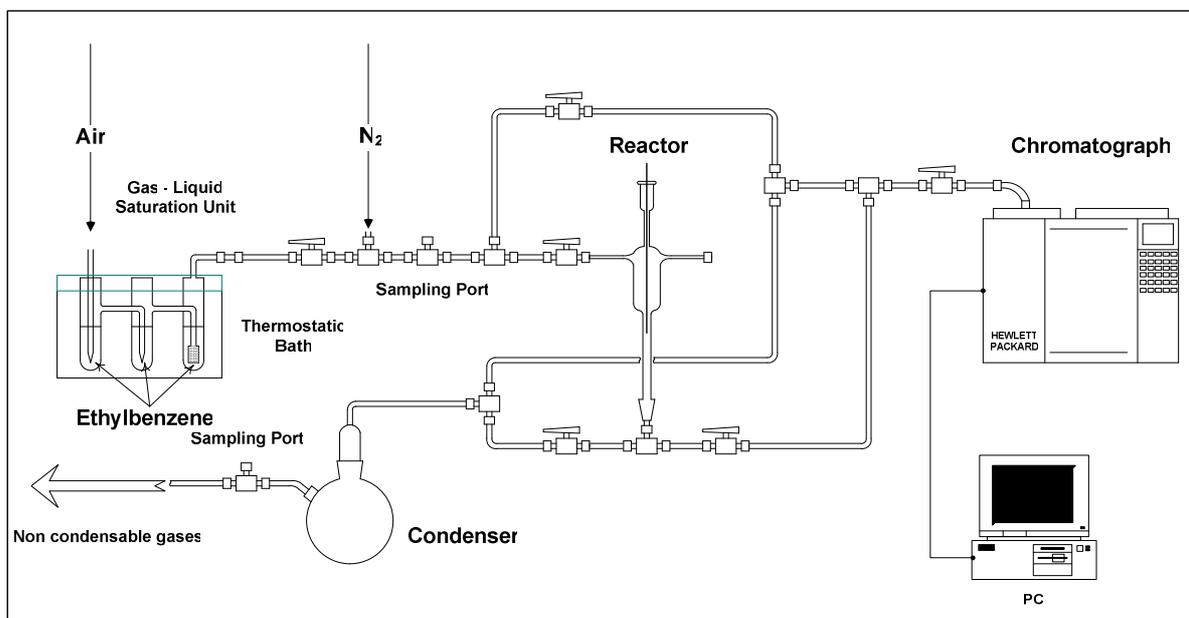


Figure 1. Scheme of the experimental apparatus.

The main products obtained were styrene (ST), carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) and traces of toluene and benzaldehyde.

The EB conversion and the ST yield were calculated, respectively, as:

$$X = (F_{EB}^i - F_{EB}^o) / F_{EB}^i, \quad (1)$$

$$R = F_{ST} / F_{EB}^i, \quad (2)$$

where  $F_{EB}^i$  is the EB molar flux in the feed,  $F_{EB}^o$ , the EB molar flux in the output stream, and  $F_{ST}$ , the ST molar flux in the product stream.

### III. RESULTS AND DISCUSSION

The results obtained from proximate and elemental analyses of the precursor are presented in Table 2. The elemental analyses of the developed activated carbons (ACS and ACF) and the commercial sample (CAC) are detailed in Table 3.

As it can be seen, the ACS and ACF activated carbons have no S, whereas contents of C and N are lower than those determined for the commercial sample.

The hydrogen content for the derived ACs is similar, even though it is higher than that for the CAC. The activation under flowing air should be responsible for the higher contents of oxygen and ash for the ACF sample.

Comparison of results in Tables 2 and 3 reveals that the carbon precursor has lower content of C and higher proportions of hydrogen and oxygen; this means that the activation process promotes the dehydration and devolatilization of the precursor, thus leading to ACs enriched with C.

In Table 4 the compositions of the AC samples after being used as catalyst in the ODH reaction (ACS1, ACF1) are presented. Although an increment of the oxygen content in both samples is observed, this trend is even more evident for ACS1. Besides, the carbon content shows a slight diminution for both samples.

Table 1. Operating Conditions Used in the Standard Catalytic Test.

Mass of activated carbon	0.45 - 0.78 g
Particle diameter	≤ 600 μm
Total gas flow	350 - 600 ml/min
Molar fraction of EB	0.01
Concentration of O <sub>2</sub>	1.0 % v/v
Reaction temperature	350 °C
Contact time [τ]	0.001g min / ml

Table 2. Proximate and Ultimate Analyses of the *Prosopis Ruscifolia* Wood Used as Precursor.

Proximate Analysis	(wt %, dry basis)	Ultimate Analysis	(wt %, ash and moisture free)
Volatile matter	75.4	C	47.1
Ash	2.4	H	6.2
Fixed carbon*	22.2	N	0.4
		O*	46.3

\*Estimated by difference.

Table 3. Ash Contents and Ultimate Analyses of the Developed ACs (ACS and ACF) and the Commercial Sample (CAC).

Parameter	ACS	ACF	CAC
Ash (%)	3.0	8.0	6.0
%C	88.0	81.1	89.4
%H	2.4	2.1	0.6
%N	0.2	0.3	0.6
%O*	9.4	16.5	8.9
%S	0.0	0.0	0.5

Table 4. Ultimate Analyses of the Developed ACs After Being Used in ODH Reaction (ACS1 and ACF1).

Parameter	ACS1	ACF1
%C	83.0	77.8
%H	2.1	2.2
%N	0.2	0.4
%O*	14.6	19.6
%S	0.0	0.0

The individual amounts of acidic/polar oxygen functional groups (OFG) on the surface of the derived ACs and of the commercial sample are shown in Fig. 2. These results show that the ACS has 12% less total oxygen functional groups than the CAC, while total OFG of the ACF is at least 50% greater than the corresponding amount of CAC. As observed in Fig. 2, the activation atmosphere pronouncedly affected the development of oxygen functionalities on the activated carbons' surface. The ACF obtained under severe oxidation conditions exhibited a larger total content of oxygen functional groups than the ACS developed with a limited supply of oxygen. The trend agrees with the elemental oxygen content of these samples, as assessed by elemental analysis (Table 3).

For ACF, the contribution of phenols and lactones groups is far larger (2.5 times) than the corresponding proportion obtained for the ACS and CAC samples. On the other hand, the content of carbonyl groups is similar for the ACF and CAC, being slightly lower for ACS. The carboxylic group for the ACF is twice the value for the ACS and the CAC.

In Fig. 3 the amount of oxygen functional groups for the used ACs are shown. The results indicate that total functional groups diminished for ACF1 and CAC1 samples, whereas a slight increase is observed for ACS1. The distribution of oxygen functional groups for ACS1 and ACF1 indicates that phenols and lactones increase while the carbonyl groups decrease. Therefore, an increase of the amount of carboxylic groups for the ACS1 sample is verified. The CAC1 has a different behaviour due to the diminution of phenols, lactones and carboxylic groups after the reaction. Likewise, a dimi-

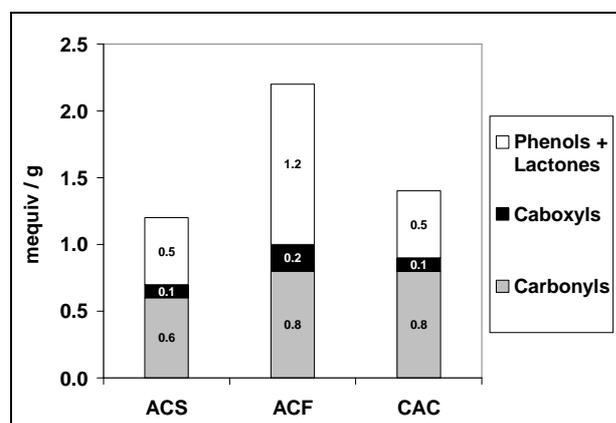


Figure 2. Effect of the Activation Atmosphere on the Content of Surface Oxygen Functional Groups of the ACs Derived Under the Self-Generated Atmosphere (ACS), Flowing Air (ACF) and the Commercial Activated Carbon (CAC).

nution of carbonyl groups is observed in all the samples after the reaction.

For the sake of comparison, the textural characterization of the materials, before and after the reaction (fresh and used), are presented in Table 5. The results reveal that the samples prepared from *Prosopis* wood have higher specific surface area and total pore volume than the commercial one. Particularly, the highest specific surface area is observed for the ACS sample. They

also evidence that the stronger oxidation conditions generated by the air flow induced a reduction in the porous structures development in comparison with the results obtained for the ACS.

This might be due to an enhanced development of porosity at the outer surface of the precursor's particle and/or to pore blockage occasioned by the larger formation of ash (Table 3), in turn resulting from carbon oxidation because of the greater presence of oxygen in the thermal treatment stage.

On the other hand, the three samples (ACS, ACF and CAC) present predominantly microporous structures, but the CAC sample exhibits the highest proportion of micropores (< 2 nm).

After the reaction, for all the used samples, a pronounced diminution of the specific surface area and total pore volume take place. The contribution of mesopores increases for the three ACs, although in a greater extent for ACF1. The cause of the changes is almost certainly the deposition of oxidative condensation products (OCP) during the catalytic tests (Lisovskii and Aharoni, 1994).

The results obtained by Fourier transform infrared spectroscopy (FT-IR) are presented in Fig. 4 for the fresh samples. The spectra corresponding to the developed ACs show an intense band at 950-1500  $\text{cm}^{-1}$  usually found in ACs obtained with phosphoric acid (Jagtøyen *et al.*, 1992; Toles *et al.*, 1996; Puziy *et al.*, 2002). Absorption in this region is usually attributed to compounds containing P(V) in their structure (Jagtøyen *et al.*, 1992) and to oxygen functional groups. The broad

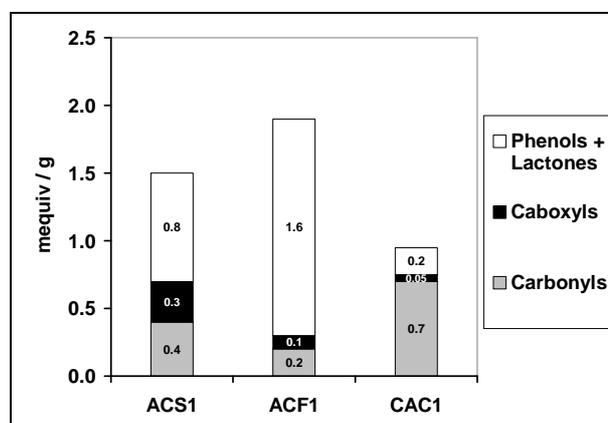


Figure 3. Content of Surface Oxygen Functional Groups of the ACs Derived Under the Self-Generated Atmosphere (ACS1), Flowing Air (ACF1) and the Commercial Activated Carbon (CAC1) After Being Used in ODH Reaction.

Table 5. Textural Characteristics of the ACs Developed Under the Self-Generated Atmosphere (ACS) and Flowing Air (ACF), the Commercial Carbon (CAC), and of the Same Samples after Being Used in ODH reaction (ACS1, ACF1, CAC1).

Parameter	ACS	ACF	CAC	ACS1	ACF1	CAC1
$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	2280	1640	1200	930	910	1010
$V_{\text{T}}$ ( $\text{cm}^3/\text{g}$ )	1.73	1.28	0.66	0.75	0.78	0.57
$r_{\text{m}}$ (nm)	1.5	1.6	1.1	1.6	1.7	1.1
$V_{\text{micro}}$ (%)	67	71	93	65	66	91
$V_{\text{meso}}$ (%)	33	29	7	35	34	9

bands at 1000-1300  $\text{cm}^{-1}$  have been assigned to CO single bonds such as those in ethers, phenols, acids and esters (Fanning and Vannice, 1993; Puziy *et al.*, 2002).

In addition, the band between 1400 and 1750  $\text{cm}^{-1}$  can be assigned to carboxyl groups, quinones, ketones, lactones, diketone and keto-ester, and keto-enol (Fanning and Vannice, 1993; Biniak *et al.*, 1997; Puziy *et al.*, 2002).

The latter band is more pronounced for ACF, whereas the relation of intensities is slightly opposite for the ACS.

For the CAC sample, an important absorption band appears at 900 and 1300  $\text{cm}^{-1}$  resulting from phenol or ether-like structures.

The absorption band at 500 and 850  $\text{cm}^{-1}$ , assigned to aromatics substituted by aliphatic groups, appears in the spectra of the ACS and ACF but it is absent in the one corresponding to the CAC sample. This behavior might be related with the lower content of hydrogen determined for the CAC sample (Table 3) compared to that for the developed ACs.

The ACS and ACF present an intense band at 1550 and 1650  $\text{cm}^{-1}$  resulting from C=C stretching vibrations in aromatic rings enhanced by polar functional groups (Fanning and Vannice, 1993; Puziy *et al.*, 2002). Nevertheless, this band has a lower intensity for the CAC spectrum.

Only for the ACs prepared from *Prosopis* wood (ACS and ACF), the presence of a band at around 1690  $\text{cm}^{-1}$  is observed. It may be due to the stretching vibrations of C=O moieties in carboxylic acid groups, esters, lactones and quinones (Fanning and Vannice, 1993; Biniak *et al.*, 1997).

The FTIR spectra of the carbons developed by phosphoric acid activation show absorption bands at 2300 and 2900  $\text{cm}^{-1}$ . The peaks at 2380  $\text{cm}^{-1}$  for the ACF and at 2364  $\text{cm}^{-1}$  for the ACS, may be assigned to carbon-oxygen bonds in ketene groups (Fanning and Vannice, 1993). The peak at 2890  $\text{cm}^{-1}$  could be originated from C-H stretching in  $\text{CH}_2$  groups (Fanning and Vannice, 1993; Puziy *et al.*, 2002). These bands are absent in the FTIR spectrum of the CAC.

In addition, the OH bond corresponding to alcohols, phenols and water chemisorbed is in the range between 3600 and 3200  $\text{cm}^{-1}$ . This band is more intense for the CAC than for the ACS and ACF.

The FTIR spectra corresponding to the used samples (ACS1 and ACF1) are shown in Fig. 5. For ACS1 and ACF1 samples, the absorption bands are similar but differences in the relative intensities are noticeable.

The ACF1 and ACS1 spectra show an absorption band at 760  $\text{cm}^{-1}$  due to aliphatic groups (Puziy *et al.*, 2002). Both samples also present a broad band around 1230  $\text{cm}^{-1}$ . It may be assigned to CO vibration and OH bending modes (Biniak *et al.*, 1997).

The band centred at 1576  $\text{cm}^{-1}$  for ACF1 and at 1566  $\text{cm}^{-1}$  for ACS1, may be associated to C=O stretching from quinone and conjugated groups as diketone, keto-ester, and keto-enol (Fanning and Vannice, 1993;

Biniak *et al.*, 1997; Puziy *et al.*, 2002). The C=O stretching due to carboxylic groups is observed at 1700  $\text{cm}^{-1}$  for the ACS1 and ACF1 samples.

The absorption bands between 2300  $\text{cm}^{-1}$  and 2900  $\text{cm}^{-1}$  observed in the fresh samples do not appear in the spectra for the used ones. The bands centred at 3700  $\text{cm}^{-1}$  can be assigned to the OH bond from alcohol and phenol groups (Fanning and Vannice, 1993; Puziy *et al.*, 2002).

The catalytic evaluation of the different ACs is presented in Fig. 6 and Fig. 7.

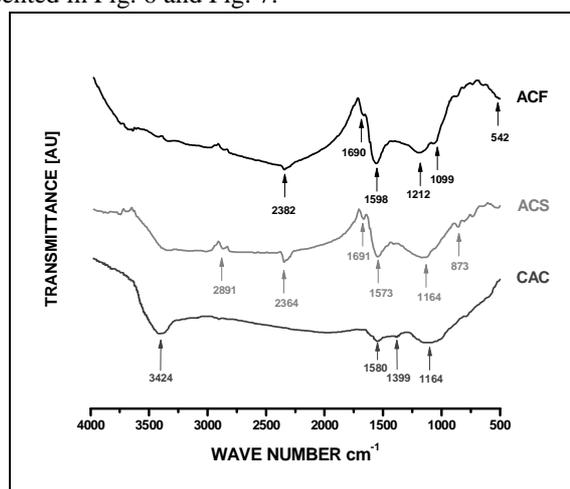


Figure 4. Transmission FTIR Spectra of the Activated Carbons Developed from Vinal Under the Self-Generated Atmosphere (ACS), Flowing Air (ACF) and the Commercial Activated Carbon (CAC).

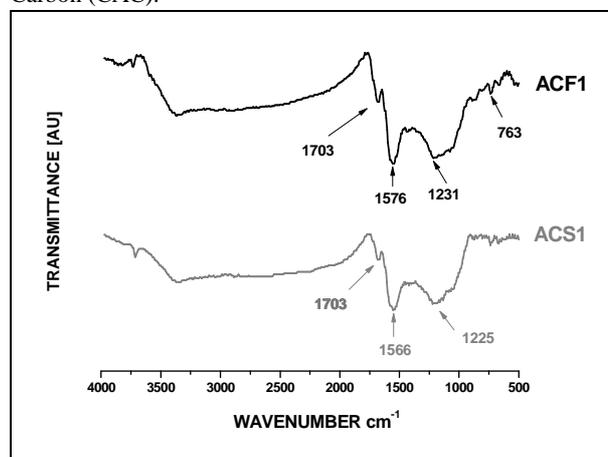


Figure 5. Transmission FTIR Spectra of the Activated Carbons Developed Under the Self-Generated Atmosphere (ACS1) and Flowing Air (ACF1) After Being Used in ODH Reaction.

The activities are similar for all the samples, being the obtained conversions around 35%. The behavior of ACS and CAC as catalyst was stable, while conversion obtained using the ACF sample diminished slightly during the reaction time. Nevertheless, since the ST yield determines the ACs behavior as catalyst, it may be inferred that the ACS sample presents a better performance. Moreover, the higher ST yield attained by the ACS with respect to the CAC at isoconversion implies that ACS sample has higher selectivity to styrene.

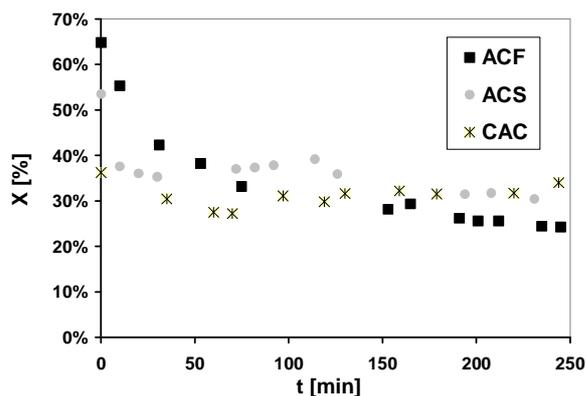


Figure 6. Evolution of Conversion as a Function of Reaction Time for the ACs Developed Under the Self-Generated Atmosphere (ACS), Flowing Air (ACF) and the Commercial Activated Carbon (CAC).

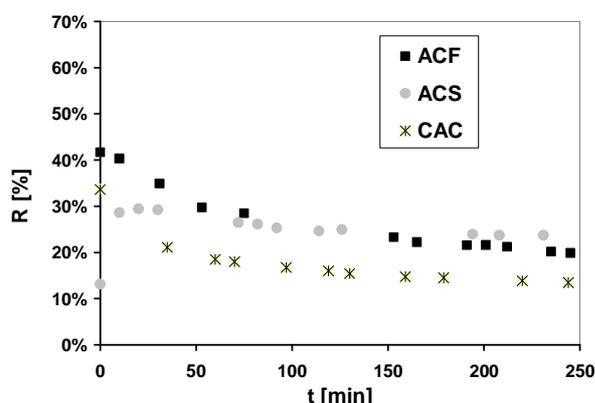


Figure 7. Styrene Yields Obtained as a Function of Reaction Time for the ACs Developed Under the Self-Generated Atmosphere (ACS), Flowing Air (ACF) and the Commercial Activated Carbon (CAC).

This performance could be attributed to a higher diffusion rate of the ST compound through a porous structure with larger pore radius (Table 5), avoiding ST oxidation to  $\text{CO}_2$ . During the initial transient period, an increase of ST yield is verified for the ACS sample indicating a possible surface activation. It was reported (Alkhazov and Lisovskii, 1976; Cadus *et al.*, 1988; Lisovskii and Aharoni, 1994) that the deposition of carbonaceous products (oxidative condensations products; OCP) promoted the formation of new active surface on the catalyst.

### III. CONCLUSIONS

The ACs developed from *Prosopis* wood under the two different atmospheres, ACS and ACF, resulted potentially adequate as catalysts for ODH of EB to produce ST. The activated carbon developed under the self-generated atmosphere, ACS, increased ST production more than the commercial sample, CAC, and was more stable than the carbon developed in air (ACF).

At the initial reaction period, the deposition of carbonaceous products (OCP) seems to promote the formation of a new active surface on the catalyst. The IR spectra showed conclusively the presence of OCP on the used catalyst, and the textural and chemical analyses revealed the same trend.

The ACS exhibited a better catalytic performance than the CAC, probably because it has less microporosity than the latter, which could facilitate the access of EB to active sites and ST diffusion out of the carbon particles. Finally, the greater content of carbonyls groups for the ACS1 with respect to the ACF1 samples, observed after being used, could be responsible for the higher catalytic activity verified for the ACS sample.

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