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# Preparation of carbon aerogel supported platinum catalysts for the selective hydrogenation of cinnamaldehyde

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# ABSTRACT

The selective hydrogenation of cinnamaldehyde is investigated using platinum catalysts supported on carbon aerogels with different textural and chemical properties. Despite the large amount of oxygenated surface groups introduced after the oxidation step, the original porosity of the carbon aerogels is maintained. The oxidation treatments performed on the materials are found to strongly influence the surface chemistry which in turn affects the Pt dispersion, yielding larger metal particles after the chemical modifications and the H<sub>2</sub> pre-treatment. The presence of mesopores and the increase of the acidic character in the carbon aerogels lead to a higher catalytic activity and selectivity towards cinnamyl alcohol when compared with that obtained for the untreated materials. A thermal treatment at 973 K is found to favor the hydrogenation of the olefinic bond when using carbon aerogels, due to the remaining oxygenated surface groups, at variance with other previously reported carbon supports (xerogels and nanotubes).

# 1. Introduction

Following the first synthesis of carbon aerogels reported by Pekala [1] other types of carbon gels have been reported based on the use of different solvent removal steps in the synthetic route [2]: (i) aerogels, when supercritical  $CO_2$  is used, (ii) xerogels, when the removal takes place under ambient temperature and pressure conditions, and (iii) cryogels, in the case of using a freeze-drying method. Carbon aerogels usually have surface areas between 400 and 1000 m<sup>2</sup> g<sup>-1</sup> and are promising materials for applications such as adsorbents, catalysts or capacitors [3–8]. Their potential is based on their unique properties: purity, homogeneity and above all, controllable porosity. Different precursors and methods have been developed over the years to produce highly porous carbon aerogels. The porous texture of carbon aerogels, and consequently their applications, depend strongly on several experimental conditions. The most important is the polymerization step, since it defines the

\*\* Corresponding author at: Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Campus Fuentenueva s/n, 18071 Granada, Spain. Tel.: +34 958 243 235: fax: +34 958 248 526. structure and consequently the porous texture of the organic aerogels. In this context, meso- or macroporous carbon aerogels can be developed by simply modifying the polymerization catalyst, while maintaining constant the other synthesis parameters [9].

Because the support plays an important role in catalyst design, in order to optimize the dichotomy between metal and support, the use of a material whose properties can be finely tuned is highly desirable. Furthermore, due to the importance of the oxygenated surface groups in the design of efficient catalysts it is advantageous to have the possibility of easily modifying the surface chemistry of the support materials to incorporate those groups [10,11]. Thus, polymer-based carbon materials are an important category of materials suitable to produce noble metal supported catalysts [5]. This type of catalyst is extremely useful in heterogeneously catalyzed reactions, namely for fuel cell applications [12,13] and selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes (acrolein, crotonaldehyde, cinnamaldehyde, etc.) [14-17]. The latter is a key process for the production of important intermediates in the preparation of fine chemicals for fragrance, pharmaceutical and agrochemical industries [18,19]. Unfortunately, there are some thermodynamic and kinetic constrictions that limit the selectivity towards the unsaturated alcohol formation [20], commonly the most valuable intermediate compound. In spite of these drawbacks, the selectivity to unsaturated alcohols using heterogeneous catalysts can be improved by careful design of the catalyst. Several

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works in the literature indicate that an increase of the metal particle size favors the selectivity towards the unsaturated alcohol, either due to steric or electronic effect between the molecule and metal surface or due to the distribution of crystal surfaces and the presence of certain edges and corners [17,21]. Another possibility to control the selectivity and activity of hydrogenation is the design of the catalyst support, i.e., by changing its porous texture, chemical properties or by making thermal treatments that modify these characteristics, or influence the state and particle size of the metal [15,22]. In our previous works [14,16], mesoporous carbon xerogels demonstrated to be excellent supports for noble metals (Pt, Ru and Ir) in the selective hydrogenation of cinnamaldehyde. In a similar context, Job et al. [23] prepared carbon xerogels with different porous textures: micro- and macroporous and micro- and mesoporous, which were used as supports of Pt catalyst and tested in the hydrogenation of benzene. They concluded that these supported catalysts were more active than others on active carbon and the most active catalyst was prepared on a carbon xerogel with microand mesopores, which also presented the highest Pt dispersion.

The hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes is a structuresensitive reaction, i.e., the activity and selectivity of the catalyst are influenced by the metal particle size and orientation [17]. Therefore, a comprehensive study on how the porous texture and surface chemistry influences the activity and selectivity of carbon aerogel supported Pt catalysts in the liquid-phase hydrogenation of cinnamaldehyde is described in this work. In addition, a high temperature thermal activation of the materials was also carried out in order to determine its influence on the catalytic performance of the supported catalysts.

# 2. Experimental

## 2.1. Support preparation

Carbon aerogels were obtained by carbonization (at 1173 K) of the corresponding organic aerogels, which were synthesized by polymerization of resorcinol with formaldehyde in aqueous solution using alkali carbonates ( $M_2CO_3$ ; M = Li or Cs) as polymerization catalysts, according to a methodology described elsewhere [9]. These samples will be referred as CA-Li and CA-Cs indicating the alkaline metal used in their synthesis.

Samples of CA-Li were further oxidized (1g carbon/10 mL of solution) with concentrated hydrogen peroxide (9.8 M) and with a saturated solution of ammonium peroxydisulfate in sulfuric acid (1 M) for 48 h at ambient temperature [24]. After oxidation, the samples were washed with distilled water and dried at 393 K in an oven during 24 h. The samples oxidized with  $H_2O_2$  and  $(NH_4)_2S_2O_8$  will be referred as CA-LiH and CA-LiS, respectively.

## 2.2. Catalyst preparation

The materials described in the previous section were used as supports to prepare 1 wt.% Pt catalysts. Incipient wetness impregnation was used to deposit  $Pt(NH_3)_4(NO_3)_2$  over the different carbon aerogels, being the metal precursor previously dissolved in an aqueous solution. Prior to reaction, the resulting catalysts (Pt/CA-Li, Pt/CA-LiH, Pt/CA-LiS and Pt/CA-Cs) were treated in N<sub>2</sub> during 4 h and reduced in H<sub>2</sub> during 3 h at 573 K. A post-reduction treatment (PRT, 2 h, N<sub>2</sub>) was performed at 973 K to remove part of the surface groups (Pt/CA-Li973, Pt/CA-LiH973, Pt/CA-LiS973 and Pt/CA-Cs973).

## 2.3. Catalyst characterization

The surface morphology of the aerogels was studied by scanning electron microscopy (SEM) using a LEO (Carl Zeiss) GEMINI-1530 microscope. Textural characterization of the supports and the catalysts was carried out using N<sub>2</sub> physical adsorption at 77 K (Quantachrome Autosorb-1). The BET equation [25] and *t*-method [26] were used for the analysis of the corresponding adsorption isotherms, from which the BET surface area ( $S_{\text{BET}}$ ), the external porous surface area ( $S_{\text{EXT}}$ ) and the micropore volume ( $V_{\text{MIC}}$ ) were obtained. The BJH method [27] was applied to the desorption branch of the N<sub>2</sub> adsorption isotherms to obtain the pore size distributions curves in the case of mesoporous samples, while for macroporous ones the Hg porosimetry (Quantachrome Autoscan 60) was used.

The surface chemistry of the carbon aerogels was characterized by temperature programmed desorption (TPD) and  $pH_{PZC}$  (point of zero charge) measurements, accordingly to a previously reported procedure [28]. The  $pH_{PZC}$  values correspond to the equilibrium pH of 250 mg of carbon dispersed in 4 mL of H<sub>2</sub>O at 298 K. TPD experiments were carried out by heating the samples to 1273 K in He flow (60 cm<sup>3</sup> min<sup>-1</sup>) at a heating rate of 50 K min<sup>-1</sup>. The amount of evolved gases was recorded as a function of temperature using a quadrupole mass spectrometer (Balzers, model Thermocube), as described elsewhere [29]. The oxygen content was calculated from the amounts of CO and CO<sub>2</sub> released during the TPD experiments.

Pt dispersion ( $D_{Pt}$ ) was obtained by H<sub>2</sub> chemisorption measurements performed at 298 K. In addition, assuming the formation of spherical particles and a H:Pt = 1:1 stoichiometry it was possible to calculate the Pt average particle size, using  $d_{Pt} = 1.08/D_{Pt}$  (nm). Pt particle size was also determined by high-resolution transmission electron microscopy (TEM). TEM experiments were carried out using a Phillips CM-20 microscope equipped with an EDAX microanalysis system.

#### 2.4. Catalytic hydrogenation

The liquid-phase hydrogenation of cinnamaldehyde was performed according to a procedure described elsewhere [30]. Briefly, the reaction mixture containing heptane, 0.14 g cinnamaldehyde, decane (as internal standard for gas chromatography) and 0.20 g of catalyst was bubbled with nitrogen several times to remove traces of dissolved oxygen before being purged with hydrogen. The temperature was set at 363 K and the reactor pressurized with hydrogen to the desired 10 bar immediately before starting the reaction.

The results of the reaction runs were analyzed in terms of cinnamaldehyde (CAL) conversion (Eq. (1)) and product selectivity (Eq. (2)), measured at 50% conversion:

$$X_{\text{CAL}} = \frac{C_{\text{CAL},0} - C_{\text{CAL}}}{C_{\text{CAL},0}} \tag{1}$$

$$S_i = \frac{C_i}{C_{\text{CAL},0} - C_{\text{CAL}}} \tag{2}$$

where  $C_i$  represents the concentration of cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL).

To compare the activity exhibited by the catalysts, the turn-over frequency (TOF) was calculated based on CAL disappearance:

$$TOF = \frac{mol_{CAL} \text{ converted}}{time(m_{cat}y_{Pt}/M_{Pt})D_{Pt}}$$
(3)

where  $m_{\text{cat}}$ ,  $y_{\text{Pt}}$ , and  $M_{\text{Pt}}$  represent the catalyst mass, Pt load and molar mass, respectively.  $D_{\text{Pt}}$  was determined based on TEM analysis.

Table 1	1
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Surface oxidation in terms of evolved CO and CO<sub>2</sub> (µmol g<sup>-1</sup>), oxygen content (O<sub>TPD</sub>, wt.%) and acidity pH<sub>PZC</sub> of the original and treated at 573 K and 973 K carbon aerogels.

Sample	$\begin{array}{c} \text{CO} \\ (\pm 20\mu\text{mol}\text{g}^{-1}) \end{array}$	$CO_2 \ (\pm 20 \mu mol  g^{-1})$	O <sub>TPD</sub> (±0.1 wt.%)	CO/CO <sub>2</sub>	pH <sub>PZC</sub> (±0.1)
CA-Li	420	61	0.9	7	10.2
CA-Li573	419	50	0.8	8	n.d.
CA-Li973	314	5	0.5	64	n.d.
CA-LiH	1110	335	2.9	3	4.9
CA-LiH573	1102	270	2.9	4	n.d.
CA-LiH973	735	28	1.3	26	n.d.
CA-LiS	2846	1621	9.7	2	3.2
CA-LiS573	2818	1330	8.9	2	n.d.
CA-LiS973	1734	112	3.1	16	n.d.
CA-Cs	534	59	1.0	9	10.3
CA-Cs573	532	44	1.0	12	n.d.
CA-Cs973	410	3	0.7	137	n.d.

n.d., not determined.

# 3. Results and discussion

## 3.1. Support functionalization

The surface chemistry of carbon materials is mainly determined by the acidic and basic character of their surface, which can be modified by treating the material with different oxidizing agents [24,31] and by submitting it to thermal treatments under inert atmosphere. It is commonly accepted that the oxygenated surface groups that contribute to the acidic character of a carbon material are carboxylic acids, anhydrides, lactones and phenols [32]. Regarding the basic groups some restraints arise concerning the strength and extent of their contribution to the overall carbon basicity. Nevertheless, groups such as chromene structures, quinone, pyrone-like groups and  $\pi$ -electrons of the carbon basal planes have been suggested [32].

The changes in the surface chemistry of the carbon aerogel induced by oxidation treatments with H<sub>2</sub>O<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were followed by TPD (Fig. 1 and Table 1), and resulted in the formation of different oxygenated surface groups. Carboxylic acids (CAc, released as CO<sub>2</sub> at 550 K), carbonyls/quinones situated in different energetically sites (CQ, released as CO at 1163-1253 K), ethers (Eth, released as CO at 1073 K), lactones (Lac, released as CO<sub>2</sub> at 923 K), carboxylic anhydrides (CAn, released as CO and as CO<sub>2</sub> at 773 K) and phenol groups (Ph, released as CO at 973 K) were introduced with both treatments [33,34], although higher amounts of more acidic groups (evolved as  $CO_2$ ) were obtained with the  $(NH_4)_2S_2O_8$ treatment, i.e., the CO/CO2 ratio decreased as follows: CA-Li < CA-LiH < CA-LiS. The amount of oxygenated surface groups evolved as CO, increased from 420  $\mu$ mol g<sup>-1</sup> for CA-Li (non-oxidized) to 2846  $\mu$ mol g<sup>-1</sup> for CA-LiS (oxidized with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), which corresponds to an increase of ca. 85%; an increase of ca. 96% was observed for the oxygenated surface groups evolved as CO<sub>2</sub>. In the case of CA-LiH (oxidized with H<sub>2</sub>O<sub>2</sub>), an increase of ca. 62% and 82% for CO and CO<sub>2</sub>, respectively, was observed. Similar results were reported with identical oxidation procedures using an activated carbon [24,31], and the enhanced acidity using  $(NH_4)_2S_2O_8$  is attributed to the creation of stronger carboxylic groups close to other groups, such as carbonyls and phenols (electron-withdrawing groups), which enhance their acidity due to a negative inductive effect [24].

The surface chemistry of the carbon aerogels was also studied by TPD after thermal treatment with N<sub>2</sub> at 573 K and 973 K (Table 1), which are the temperatures used in order to reduce the Pt particles and to remove some oxygenated surface groups in the supported Pt catalysts. For all materials, a decrease of these groups was reached, being more effective for those evolved as  $CO_2$  (mainly acid groups) during TPD experiments. CA-LiS treated at different temperatures presented always a lower  $CO/CO_2$  ratio (2 and 16 for CA-LiS573 and CA-LiS973, respectively) than CA-LiH (4 and 26 for CA-LiH573 and CA-LiH973, respectively), due to their higher oxygen content (9.7 wt.% in comparison with 2.9 wt.% for CA-LiH) and the presence of stronger acid surface groups. Therefore, a less acidic surface is also obtained for carbon aerogel oxidized with  $H_2O_2$  and treated at 573 K or 973 K. The surface acidity of the materials was also seriously affected by the oxidation procedure. The acid character of the samples, determined by  $pH_{PZC}$  measurements (Table 1), was found to increase in the following order: CA-LiS (3.2) > CA-LiH (4.9) > CA-Li  $\approx$  CA-Cs (10.2). In addition, the surface oxygen content determined by TPD was found to increase with decreasing  $pH_{PZC}$ , i.e., CA-LiS (9.7 wt.%) > CA-LiH (2.9 wt.%) > CA-Li  $\approx$  CA-Cs (1 wt.%).

The introduction of these oxygenated surface groups was achieved without any significant changes of the initial textural properties of the carbon aerogels synthesized with  $Li_2CO_3$ : a decrease of only ca. 4% was observed in both  $S_{BET}$  and  $S_{EXT}$  values (Table 2), while the micropore volume and the pore size distribution ( $d_{pore}$ ) remained practically unchanged. The difference in porous texture between CA-Li and CA-Cs (meso- and macroporous materials, respectively), is explained in terms of the polarizing power of the alkaline cation during the polymerization of resorcinol and formaldehyde [9].

## 3.2. Catalyst characterization

In general, BET, external surface areas and micropore volumes (Table 3) decreased for Pt catalysts in comparison to the corresponding supports. This is thought to be related to a partial blockage of porosity induced by the Pt particles deposition. An increase of BET surface area was also observed for all Pt catalysts treated at 973 K. In addition, the percentage of increase is different and increases with the oxygen surface content of the support. BET surface area increased 18 and 42% for Pt/CA-LiH973 and Pt/CA-LiS973, respectively, while only a 10% increase was observed for Pt/CA-Li973. This can be explained in terms of pore opening, produced as a consequence of the release of surface groups during the N<sub>2</sub> treatment at 973 K and confirmed by the decrease on the surface oxygen (O<sub>TPD</sub>, Table 1) of the treated carbon aerogels. In

Table 2

Textural characterization of the different carbon aerogels. BET ( $S_{\text{BET}}$ , m<sup>2</sup> g<sup>-1</sup>) and external ( $S_{\text{EXT}}$ , m<sup>2</sup> g<sup>-1</sup>) surface areas, micropore volumes ( $V_{\text{MIC}}$ , cm<sup>3</sup> g<sup>-1</sup>) and pore dimension ( $d_{\text{pore}}$ , nm).

Sample	$S_{BET} \ (\pm 5 \ m^2 \ g^{-1})$	$S_{\text{EXT}} \ (\pm 5 \text{ m}^2 \text{ g}^{-1})$	$V_{ m MIC} \ (\pm 0.01  { m cm}^3  { m g}^{-1})$	$d_{ m pore}$ (±0.5 nm)
CA-Li	902	284	0.25	22
CA-LiH	863	275	0.24	23
CA-LiS	861	269	0.24	22
CA-Cs	758	94	0.27	90.0 <sup>a</sup>

<sup>a</sup> Determined by Hg porosimetry.



Fig. 1. TPD spectra for the carbon aerogel CA-Li before and after oxidation with hydrogen peroxide (CA-LiH) and ammonium peroxydisulfate (CA-LiS): (a) CO and (b) CO<sub>2</sub> desorption profiles.

fact, increases in the average pore size (23–27 nm) and in the external surface area were also observed for these Pt catalysts.

Platinum dispersions and particle sizes of the carbon aerogel supported catalysts are given in Table 4. Excellent Pt dispersions over the untreated aerogels (Pt/CA-Li and Pt/CA-Cs) were observed,

but somewhat lower values were detected when using the oxidized supports (Pt/CA-LiH and Pt/CA-LiS).

Comparing the Pt particle size obtained by  $H_2$  chemisorption with that obtained by TEM, it can be observed that there is a general agreement between these two techniques.

There are two main factors that can affect the metal dispersion over a support: (i) the available surface area and (ii) the interaction between the surface and the precursor solution. The textural

# Table 3

Textural characterization of the Pt catalysts. BET ( $S_{\text{BET}}$ , m <sup>2</sup> g <sup>-1</sup> ) and external ( $S_{\text{EX}}$	т,
$m^2 g^{-1}$ ) surface areas, micropore volumes ( $V_{MIC}$ , $cm^3 g^{-1}$ ) and pore dimension ( $d_{por}$	e,
nm).	

Catalyst	$S_{\text{BET}} \ (\pm 5  \text{m}^2  \text{g}^{-1})$	$S_{EXT} (\pm 5  m^2  g^{-1})$	$V_{\rm MIC} \ (\pm 0.01  { m cm}^3  { m g}^{-1})$	$d_{ m pore}$ (±0.5 nm)
Pt/CA-Li	882	275	0.25	23
Pt/CA-Li973	967	289	0.27	26
Pt/CA-LiH	908	274	0.26	23
Pt/CA-LiH973	1069	313	0.31	27
Pt/CA-LiS	801	242	0.23	23
Pt/CA-LiS973	1141	324	0.33	27
Pt/CA-Cs	720	90	0.25	n.d.
Pt/CA-Cs973	832	104	0.30	n.d.

n.d., not determined

#### Table 4

Pt dispersion ( $D_{Pt}$ , in %) and particle size (in nm) determined by H<sub>2</sub> chemisorption ( $d_{Pt}$ ) and TEM analysis ( $d_{Pt}^{\dagger}$ ).

Catalyst	D <sub>Pt</sub> (±0.1%)	$d_{ m Pt}$ (±0.1 nm)	${d_{ m Pt}}^{\dagger}_{(\pm 0.1~ m nm)}$
Pt/CA-Li	74.1	1.5	1.4
Pt/CA-Li973	38.1	2.8	2.8
Pt/CA-LiH	46.1	2.3	2.5
Pt/CA-LiH973	30.5	3.5	2.6
Pt/CA-LiS	44.4	2.4	2.1
Pt/CA-LiS973	28.7	3.8	2.2
Pt/CA-Cs	87.3	1.2	1.5
Pt/CA-Cs973	42.5	2.5	2.4



Fig. 2. TEM micrographs of Pt/CA-Li and Pt/CA-LiH catalyst: (a and b) before and (c and d) after a post-reduction treatment at 973 K, respectively.

properties of the supports were not significantly changed by the oxidation treatments, as already shown, but the presence of oxygenated surface groups increased the hydrophilic character of the surface. Taking into consideration that the surface is negatively charged (pH<sub>PZC</sub> < 10.5, pH of precursor solution) and the cationic nature of the precursor ( $[Pt(NH_3)_4]^{2+}$ ), an improved metal dispersion should be expected when using the oxidized supports, in comparison with the catalysts prepared using the untreated supports. However this is not the case. The explanation could rely on the oxygenated surface groups, which act as anchoring sites, retaining the Pt-precursor molecules at the entrance of the pores and preventing the diffusion of Pt through the porous structure. Furthermore, during the reduction treatment, the less stable oxygen surface complexes (carboxylic acids groups) may be removed, promoting the mobility of the platinum particles, thus favoring their agglomeration [35]. The different porous texture observed for

Pt/CA-Li and Pt/CA-Cs does not appear to have a marked influence over the Pt particle size, since both Pt catalysts presented similar particle sizes (1.5 and 1.2 nm for Pt/CA-Li and Pt/CA-Cs, respectively). Therefore, the low external surface area of Pt/CA-Cs (with respect to Pt/CA-Li) seems to be sufficient to obtain very small and accessible Pt particles.

When a post-reduction treatment is carried out in N<sub>2</sub> at 973 K, the experimental conditions are severe enough to induce sintering of the Pt particles [14]. This effect was particularly more intense in the catalysts with higher dispersion. After the thermal treatment, all materials (independently of their surface chemistry) show Pt particles with sizes between 2.2 and 2.8 nm (values determined by TEM analysis). In addition to sintering related with the temperature effect, particle sizes could also be influenced by the surface chemistry of the support materials, as the Pt particles supported in untreated aerogels increased ca. 2 times (Fig. 2a and c), while for



Fig. 3. Reaction network for the selective hydrogenation of cinnamaldehyde with carbon aerogel supported catalysts.



**Fig. 4.** Product distribution for the selective hydrogenation of cinnamaldehyde using (a) CA-Li, (b) CA-LiH, (c) CA-LiS and (d) CA-Cs. Full and open symbols: before and after thermal treatment in N<sub>2</sub> at 973 K, respectively (*C*<sub>CAL0</sub>  $\approx$  12 mM, *T* = 363 K and *P* = 10 bar).

the oxidized supports no sintering effect was observed (Fig. 2b and d) once the less stable oxygenated surface groups were removed. As previously reported for multi-walled carbon nanotubes [30], surface groups can act as anchoring sites and increase the thermal stability of the catalysts while providing a stronger interaction between the metal and the surface, resulting in improved catalytic properties at the metal–support interface. Oxidized carbon aerogels could, thus, present a similar behavior.

Besides the sintering effect, the treatment at 973 K is able to purge most of the CO<sub>2</sub>-releasing groups, but only a part of the oxygenated surface groups evolving as CO are removed as previously indicated. Hence, groups like ethers, carbonyls or quinones, which are only released at higher temperatures due to their stability [36], should remain to some extent on the surface.

# 3.3. Selective hydrogenation

The network of reactions observed for the selective hydrogenation of cinnamaldehyde in heptane is shown in Fig. 3. The thermodynamically preferred route goes through the hydrogenation of the C=C bond yielding the saturated aldehyde (HCAL). Selective hydrogenation of the C=O bond yields the unsaturated alcohol (COL). Both COL and HCAL can be further hydrogenated to produce the fully saturated alcohol (HCOL). Side-products involving the loss of the hydroxyl group, like  $\beta$ -methylstyrene (MS) and 1-propylbenzene (PB) were also detected in different amounts, indicating a strong adsorption of the substrate over the metal sites and a possible poisoning effect. The reaction kinetics at 363 K and 10 bar (total pressure) are represented in Fig. 4 in terms of conversion of CAL and selectivity to COL, HCAL and HCOL with time of reaction. In Table 5 it is given the turn-over frequency (TOF), the time required to reach 50% conversion of CAL ( $t_{50\%}$ ), as well as the selectivities towards COL ( $S_{COL}$ ), HCAL ( $S_{HCAL}$ ), HCOL ( $S_{HCOL}$ ) and other by-products ( $S_{OTHERS}$ ), at 50% conversion of CAL.

There are two effects, generally attributed to the support, which can have a significant influence on the hydrogenation reaction: steric and electronic interactions [37]. These effects can be related with the different modes of adsorption/repulsion of cinnamaldehyde on the metal and/or the support surface. Taking into account the kind of porosity of the materials tested and the experimental conditions used in the hydrogenation of cinnamaldehyde, the

#### Table 5

Turn-over frequency (TOF), time required to reach 50% conversion of CAL ( $t_{50\%}$ ), and selectivities towards COL, HCAL, HCOL and other products (measured at 50% conversion of CAL).

Catalyst	$TOF$ $(s^{-1})$	t <sub>50%</sub> (min)	S <sub>COL</sub> (%)	S <sub>HCAL</sub> (%)	S <sub>HCOL</sub> (%)	S <sub>OTHERS</sub> (%)
Pt/CA-Li	1.6	64.1	11	54	20	15
Pt/CA-Li973	3.4	27.3	12	54	25	9
Pt/CA-LiH	1.6	36.2	53	18	20	9
Pt/CA-LiH973	3.5	26.8	21	41	28	10
Pt/CA-LiS	2.3	30.2	36	23	25	16
Pt/CA-LiS973	4.4	19.5	21	44	27	8
Pt/CA-Cs	0.9	102	24	34	35	7
Pt/CA-Cs973	2.8	42.0	12	54	19	15

 $C_{\text{CAL},0} \approx 12 \text{ mM}, T = 363 \text{ K} \text{ and } P = 10 \text{ bar}.$ 

absence of internal mass transfer limitations during the reaction could be expected. Since the support surface chemistry and the Pt particle size were similar for both Pt/CA-Li and Pt/CA-Cs, the higher activity (TOF) exhibited by Pt/CA-Li should be related to its textural characteristics.

Another way of monitoring the activity of the catalysts is to measure the time required to reach 50% conversion of cinnamaldehyde  $(t_{50\%})$ . If one compares these values against those obtained for the TOF, a general correspondence can be observed: higher TOF values produce lower  $t_{50\%}$ . In this context, a much lower  $t_{50\%}$  was observed for Pt/CA-Li (64.1 min) when compared to Pt/CA-Cs (102 min). Thus, Pt/CA-Li not only leads to a higher conversion of cinnamaldehyde but also is able to do so in a shorter period of time, indicating that the material porous texture could be playing an important role in the activity of the Pt catalyst.

Because both catalysts presented a similar micropore volume, the different activity observed could be related to the presence of mesopores and, consequently, to the higher external surface area in the case of Pt/CA-Li. Thus, the porous texture formed by micro- and mesopores of Pt/CA-Li should increase the interactions between the cinnamaldehyde molecules and the Pt particles located throughout the mesopores.

Selectivity results also appear to be somewhat affected by the porous texture, as the hydrogenation of both C=O and C=C bonds are favored for Pt/CA-Cs, while the formation of HCAL was favored when Pt/CA-Li was used. In accordance with the adsorption/repulsion model, the Pt particle size affects the selectivity, leading to the hydrogenation of C=C and C=O, or C=O bonds, preferably when small or large Pt particles are used, respectively [22]. In our case, both catalysts presented a similar Pt particle size around 1.5 nm and thus, the different selectivity detected should be due to the different porous texture. Therefore, when the surface chemistry and the metal particle size of the Pt catalysts are similar, the mesoporous catalyst provides a higher selectivity towards the hydrogenation of only the C=C bond, when compared to the macroporous one.

Oxidation of the carbon aerogel was found to have a marked effect over the activity and the selectivity towards COL (Fig. 5). Activity values increased when Pt particles were deposited on oxidized carbon aerogels of similar porous texture, where slightly larger Pt particles were obtained. This correlation between Pt-dispersion and catalytic activity was previously observed by Teddy et al. [38]. Comparing the catalytic performance of Pt/CA-LiH and Pt/CA-LiS, which have similar Pt particle sizes (2.3 and 2.4 nm, respectively) it is clear that additional effects (namely the surface chemistry changes) should be taken into account. Selectivity to the hydrogenation of the C=O bond increased by a factor of 4.8



**Fig. 5.** Effect of the oxidation and post-reduction treatment of CA-Li on the selectivity towards cinnamyl alcohol ( $C_{CAL,0} \approx 12$  mM, T = 363 K and P = 10 bar).

for Pt/CA-LiH (53% at 50% conversion of cinnamaldehyde) and 3.3 for Pt/CA-LiS (36%), compared with the catalyst prepared using the untreated support (11%).

This result is in line with the work published by Coloma et al. [39] on the gas-phase hydrogenation of crotonaldehyde over carbon black supported Pt catalysts. They reported that the selectivity towards the desired unsaturated alcohol increased when the support was previously oxidized with hydrogen peroxide. This behavior, which was not related to the metal particle size, was said to be associated to the decomposition of the oxygenated surface groups upon the thermal treatments in hydrogen. In our work, the oxidation treatments carried out on the materials produce an increase in the catalytic activity and selectivity towards the hydrogenation of the C=O bond, which improves when  $H_2O_2$  is used.

As previously reported for other carbon materials [14,30,40], high-temperature treatments at 973 K in N<sub>2</sub> do enhance both the activity and the selectivity (towards hydrogenation of the C=O bond) of the catalysts. This same result was also corroborated by Guo et al. [41] and Vu et al. [42] regarding both activity and selectivity to cinnamyl alcohol, using Pt/CNT catalysts treated at different calcination temperatures to eliminate oxygen from the CNT surface. According to them, the enriched electron density surrounding the metallic nanoparticles reduces the probability of C=C bond coordination to Pt active sites due to the electronic repulsion, thereby increasing the selectivity towards cinnamyl alcohol.

In the present work, the same thermal treatment was found to increase the TOF for all tested materials by a factor up to 3, but shifted selectivity to the C=C bond (Fig. 5), due to the amount



**Fig. 6.** Influence of the porous texture, surface chemistry and Pt particle size on the activity and selectivity to COL for the Pt catalysts not treated at 973 K ( $C_{CAL,0} \approx 12$  mM, T = 363 K and P = 10 bar).

and kind remaining oxygenated surface groups after treatment, since both catalysts (Pt/CA-LiH973 and Pt/CA-LiS973) presented similar Pt particle size and porosity. Thus, selectivity towards the hydrogenation of the olefinic bond in carbon aerogel supported Pt catalysts appears to be enhanced by the presence of certain amount of stable oxygenated groups (such as ether and quinone groups), on the material surface. Upon oxidation treatment with HNO<sub>3</sub>, carbon xerogels and nanotubes [14,30,40] were found to possess a strong acidic surface, which decreased after a thermal treatment at 973 K. Similarly to these materials, after an identical thermal treatment, carbon aerogels also lost part of its acidic character, although not to the extent of the other reported carbon materials, since they conserved a higher amount of surface groups. This fact could explain the selectivity towards olefinic bond for the carbon aerogels. Hence, for carbon aerogels, an acidic surface favors the interaction with the carbonyl group (i.e., carbon aerogels oxidized with  $H_2O_2$  or  $(NH_4)_2S_2O_8$  while a less acidic surface (e.g., after PRT) favors the reduction of the olefinic bond.

Another possible interpretation could be associated to the polarity of the surface. Toebes et al. [43] related an increased activity and selectivity towards the olefinic bond, in the non-polar surface of Pt/CNF catalysts, upon surface group removal. They suggested that the hydrogenation of the C=C bond was assisted by adsorption of the cinnamaldehyde aromatic ring on the non-polar CNF support surface, thus increasing the selectivity towards hydrocinnamaldehyde.

To have an overall idea of catalyst performance both textural and chemical characteristics had to be taken in account simultaneously (Fig. 6).

Comparison of both CA supports (CA-Li and CA-Cs) allow to estimate the influence of the porous texture, because both oxygen contents ( $O_{TPD}$ ) and the particle sizes of their corresponding Pt catalysts are similar. The effect of the surface chemistry on the activity and selectivity can be discussed by comparing Pt/CA-LiH to Pt/CA-LiS, both catalysts with similar porous textures and Pt particle sizes. As referred earlier, it is noteworthy that the activity can be favored by the increase of the Pt particle size and oxygen content, while the high  $S_{COL}$  obtained for Pt/CA-LiH seems be related with some specific oxygen surface groups.

#### 4. Conclusions

Oxidation treatments with  $H_2O_2$  and  $(NH_4)_2S_2O_8$  allow the porous structure to remain relatively unchanged while introducing significant amounts of oxygenated groups.

The main acidic character of the fixed oxygenated groups leads to a strong decrease of the  $pH_{PZC}$  of the carbon support, which strongly influence the Pt dispersion over the carbon aerogels, decreasing in all cases after oxidation treatments.

When the surface chemistry and Pt particle size are similar, mesoporous Pt catalysts exhibit a higher activity and selectivity to the C=C bond than macroporous ones in the hydrogenation of cinnamaldehyde.

In the case of similar porous texture and Pt particle size, the increased acidity of the Pt/CA-LiH and Pt/CA-LiS supports leads to a higher activity and selectivity towards cinnamyl alcohol, especially in the case of carbon aerogels oxidized with  $H_2O_2$ , which could be related with a lower content of stronger acid surface groups.

At variance with other carbon supported Pt catalysts, a thermal treatment at 973 K favors the activity and hydrogenation of the C=C bond when using carbon aerogels as supports, due to the kind and amount of remaining stable oxygenated groups.

Finally, the improvement of catalytic performance and selectivity towards the desired product using supported Pt catalysts can be carried out by designing carbon aerogels with tailored porous texture and surface chemistry.

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