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Preparation of Pt catalysts supported on activated carbon felts (ACF)

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Abstract

Activated carbon felts (ACFs) have been used as supports for Pt catalysts. The preparation was carried out by the impregnation method using chloroplatinic acid as metal precursor. The effect of impregnation time and surface chemistry of the support on the catalytic properties and the characteristics of the metallic phase have been investigated. Nitrobenzene (Nbz) hydrogenation in liquid phase at 25 °C and cyclohexane (CH) dehydrogenation in gas phase at 300 °C were used as catalytic tests. The state of platinum in reduced catalysts (at 100 and 350 °C) was studied by TPR and XPS. Oxygen surface groups only produce a slight effect on the catalytic properties. The use of low impregnation times (30 min) during the preparation of Pt/ACF leads to catalysts with Pt mainly deposited in the outer shell of the fibers, while at higher impregnation times, the metallic atoms seem to be deposited inside the pores. Pt(0) species appear in catalysts reduced at 100 °C by effect of the reducing properties of the carbon fiber exhibiting a considerable catalytic activity for Nbz hydrogenation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Activated carbon felts; Metallic supported catalysts; Nitrobenzene hydrogenation; Catalyst characterization

1. Introduction

Activated carbons as catalyst supports have an increasing interest due to their industrial application in different processes in liquid phase [1–3]. New forms of activated carbons, such as activated carbon felts (ACFs) and activated carbon clothes (ACC), represent promising supports due to the excellent characteristics and properties of these materials [4]. The surface area of these activated carbons is very high, and the porous network is mainly formed by deep pores in a narrow range of sizes, especially micropores [5]. These new forms of activated carbon have important advantages with respect to the conventional granular activated carbons, such as, uniform distribution of microporosity, faster adsorption–desorption rate, faster equilibrium rate and high fluid permeability [4,6–9].

The applications of these new materials are related with adsorption of gases [4,6,10,11], retention of pollutants, bacteria or metal ions [8,9,12–15], electrodes manufacture [8], and catalyst supports [16–20].

It must be noted that the literature has reported few papers about the use of these carbonaceous materials as supports of catalysts. In this sense, Macías Perez et al. [20] investigated the use of activated carbon

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clothes (ACC) as a support of Pt catalysts. They observed that the metallic catalysts supported on these materials are easily reduced and that these Pt/ACC catalysts can be used in processes at low and high reaction temperatures.

From numerous studies on granular activated carbon as a support of metals, it was found that the catalytic properties of the metals are defined not only by the textural properties of the support but also by the surface chemistry, which can be modified by different pre-treatments (functionalization and oxidation treatments) [3,21]. Also, the dispersion and location of metallic particles are important factors in the catalytic activity [22]. These characteristics can depend both on the conditioning treatment of the support and on the deposition conditions of the metallic precursors.

Taking into account the scarce literature about activated carbon fibers, felts and clothes as catalyst support, an study about the effect of impregnation time and surface chemistry on the catalytic properties and the characteristics of the metallic phase of an ACF is developed in this paper. In this sense, we investigated the incidence of both parameters on the catalytic activity for nitrobenzene (Nbz) hydrogenation and cyclohexane (CH) dehydrogenation. The former, a liquid phase reaction performed at low temperature (25 °C) and the second one is a gas phase reaction carried out at 300 °C. In addition, the state of platinum in catalysts has been investigated by TPR and XPS.

2. Experimental

A commercial activated carbon felt ACN-210-15-AC (phenol derived from GUN EI Chemical Industry Co. Ltd.) with a specific surface area of 1661 $m^2\,g^{-1}$, pore volume of 0.59 $cm^3\,g^{-1}$ (obtained from N_2 adsorption) and a content of impurities equal to 1.5 wt.% (Mg: 0.06; Ca: 0.30; K: 0.435; Si: 0.165; P: 0.075; Cr: 0.024; Al: 0.0375; S: 0.0508; Ti: 0.018; Cl: 0.165; Fe + Sn + Zn balance), was used as a support. This material was purified (elimination of inorganic impurities) by successive treatments with aqueous solutions (10 wt.%) of HCl, HNO_3 and HF, respectively, at room temperature during 48 h. After HCl and HNO_3 treatments, the carbon felt was repeatedly washed with deionized water up to a final pH = 4. After the HF treatment, the carbon was washed with deionized water up to the final pH of this water and then it was dried at 120 °C. In order to eliminate sulfur compounds, the acid-treated felts were submitted to a thermal treatment under a hydrogen flow of 5 ml H_2 $min^{-1}\,g^{-1}$ at 850 °C during 8 h. After the purification and hydrogen treatments, the impurities content decreased to 0.028% Ca, 0.032% K, 0.059% P, 0.023% Al, 0.029% S, 0.116% Cl, Mg: n.d. The analysis of the impurities was carried out by X-ray fluorescence (Phillips PW1480). This purified sample was labeled as ACF-P, and two fractions of this carbon were subsequently submitted to functionalization treatments with aqueous solutions of HNO_3 (ACF-P-N) and H_2O_2 (ACF-P-H) at 25 °C during 48 h. The concentrations of both solutions were 10 wt.%. The functionalized carbons were dried at 120 °C during 24 h.

The characterization of the porous texture of the ACF was carried out by N_2 and CO_2 adsorption at −196 and 0 °C, respectively, in an automatic volumetric system Autosorb-6 from Quantachrome. The surface area obtained from CO_2 adsorption (S_{CO_2}) was calculated by using the DR equation and it corresponds to the narrow micropore contribution (pore size smaller than 0.8 nm), the difference $S_{N_2} - S_{CO_2}$ (both obtained from the DR equation) gives the supermicropore one (from 0.8 to 2.0 nm) and finally the mesopore (from 2.0 to 7.5 nm) contribution has been estimated from the N_2 isotherm (obtained from BET equation) in the relative pressure range between 0.2 and 0.7 [23].

The surface chemistry of the different samples of ACF was determined by temperature programmed desorption (TPD) experiments, which were carried out in a differential flow reactor coupled to a mass spectrometer VG Quadrupoles, for gas analysis. Approximately, 200 mg of sample were heated in an electric furnace at 50 °C min^{-1} up to 900 °C. During the TPD experiments, He was passed through the reactor with a flow rate equal to 60 $cm^3\,min^{-1}$.

The preparation of the Pt catalysts was carried out by impregnation of the different felts with an aqueous solution of chloroplatinic acid (H_2PtCl_6) at 25 °C. In all cases, the Pt amount used for the impregnation was the appropriate to obtain a Pt content of 1 wt.%. The conditions to carry out a correct impregnation of the small portions of the activated carbon felt with the metallic precursor were intensively studied with regards to the difficulties to obtain an homogeneous wetting of these materials and the importance of obtaining an uniform deposition of the metallic precursor in all the sample fibers. From previous experiments, it was found that an uniform and simultaneous wetting of all portions of the felt was obtained by means of a degasification treatment under high vacuum (10^{-4} Torr) at room temperature, followed by the addition of the solvent (water in our case). Once the support was completely wet, the solution of the metallic precursor was introduced. In order to obtain an uniform contact between the solid and the impregnating solution, a stirring rate of 1400 rpm was used for an impregnating volume/support weight ratio of 50 ml/g. After the impregnation, catalysts were dried at 120 °C during 12 h. These conditions were used to analyze the effect of the impregnation time of the different samples.

Temperature programmed reduction (TPR) experiments were carried out in a differential flow reactor coupled to a thermal conductivity detector. A mixture of 5% H_2 in He, with a flow rate of 60 $cm^3\,min^{-1}$ was used.

The X-ray photoelectron spectra (XPS) have been obtained with a VG-Microtech Multilab electron spectrometer, by using the Mg Kα (1253.6 eV) radiation of twin anode in the constant analyzer energy mode with pass energy of 50 eV. The pressure of the analysis chamber was maintained at 4×10^{-10} Torr. The binding energy and the Auger kinetic energy scale were regulated by setting the C 1s transition at 284.6 eV. The BE and KE values were obtained by using the Peak-fit Program implemented in the control software of the spectrometer. XPS measurements were carried out on 1 h-impregnation samples, previously treated "in situ" with H_2 at 100 or 350 °C for 2 h.

The CH dehydrogenation test reaction was carried out at 300 °C and at atmospheric pressure in a differential flow reactor by using a H_2–CH gaseous mixture (H_2/CH molar ratio = 26) and a CH volumetric flow of 6 $cm^3\,h^{-1}$. The sample weight in the experiments was the appropriate one to obtain a CH conversion lower than 5%. The reaction product (only benzene) and the remaining CH were analyzed by using a gas chromatographic system. The catalysts were previously treated at 350 °C in H_2 for 3 h.

The Nbz hydrogenation reaction was carried out in a discontinuous reactor at 25 °C and atmospheric pressure, using ethanol as a solvent (25 ml). The catalyst weight was 0.02 g and the volume of nitrobenzene was 250 μl. Previous to the reaction, catalysts were reduced at 100 °C during 3 h. The reaction rate was calculated by the measurement of the consumed H_2.

3. Results and discussion

3.1. Characterization of the supports

Table 1 shows the values of the textural characteristics of the different supports after purification and functionalization treatments. It can be observed that the functionalization treatments both with HNO_3 and with H_2O_2 do not produce important modifications with respect to the textural properties of the purified support since the total specific surface area (S_{N_2}), micro and mesopores surfaces areas (estimated from N_2 and CO_2 adsorption isotherms, as described in Section 2) remains practically constant. The pore size distribution is similar for the three felts, thus displaying mainly a narrow distribution of micropores below 0.8 nm (S_{CO_2}). Besides, it can also be observed supermicropores with sizes between 0.8 and 2 nm, which represent approximately 25% of the total porosity ($S_{N_2} - S_{CO_2}$) and a small proportion of mesopores ($S_{mesopores}$).

The oxidation treatments of ACF lead to the formation of different oxygen surface groups. These are strong acid ones (like carboxylic and anhydride groups) and weak acid ones (like lactone, phenol and carbonyl groups) [24]. TPD desorption experiments can be used to characterize the surface oxygen groups of the different activated carbons felts. During TPD experiments, the stronger acid groups lead to a CO_2-desorption at low temperatures, while the weaker acid ones produce a CO-desorption zone at high temperatures [25]. Fig. 1 shows the CO_2- and CO-TPD profiles of the purified felt (ACF-P) and

Table 1
Textural properties of purified (ACF-P), HNO_3-functionalized (ACF-P-N) and H_2O_2-functionalized (ACF-P-H) activated carbon felts

Sample	S_{N_2} ($m^2\,g^{-1}$)	S_{CO_2} ($m^2\,g^{-1}$)	$S_{mesopores}$ ($m^2\,g^{-1}$)
ACF-P	1442	997	60
ACF-P-N	1390	952	45
ACF-P-H	1405	988	54

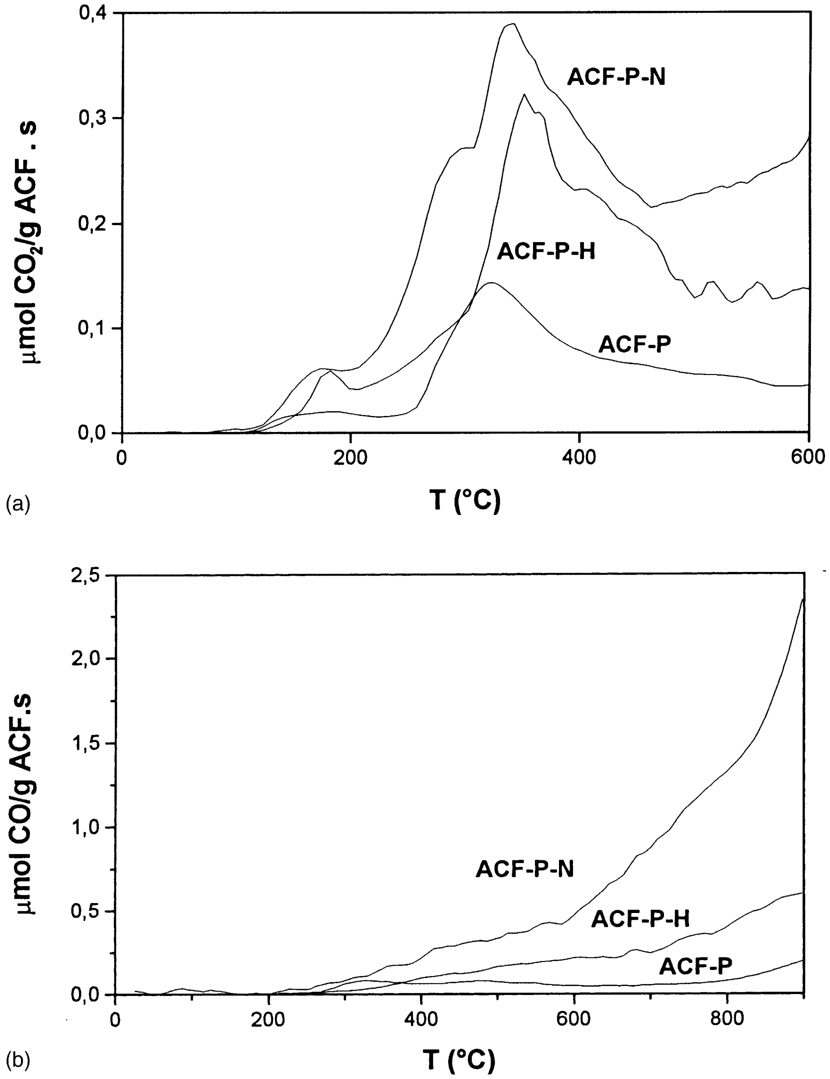

Fig. 1. (a) TPD of CO_2 for different felts; and (b) TPD of CO for different felts.

the functionalized felts (ACF-P-N and ACF-P-H). The CO_2-TPD profiles (Fig. 1a) show broad peaks beginning at approximately 150 °C and with a maximum at approximately 350 °C, while the CO-TPD profiles (Fig. 1b) are increasing functions which begin at 300 °C for all the felts. These TPD profiles are qualitatively similar to those obtained for the corresponding purified and functionalized granular activated carbons [21]. The results clearly show that the functionalization treatments of the felts (mainly with HNO_3) produce the development of important amounts of strong and weak acid groups. In fact, Table 2 summarizes the amounts of both desorbed compounds (calculated by integration of the corresponding profiles). The purified felt (ACF-P) shows very low amounts of desorbed CO and CO_2, since this support had been submitted to a treatment with H_2 at 850 °C (before the TPD experiment). The

Table 2
Amounts of desorbed CO_2 (CO_2-D) and CO (CO-D) from the different felts during TPD experiments

Sample	CO_2-D (μmol g^{-1})	CO-D (μmol g^{-1})
ACF-P	48.2	59.6
ACF-P-N	235.6	543.1
ACF-P-H	150.3	321.2

total amounts of desorbed CO and CO_2 increase with the functionalization treatment, following the tendency:

ACF-P < ACF-P-H < ACF-P-N

From these results, it can be concluded that the functionalization treatment with H_2O_2 produces a moderate increase of strong and weak acid groups, while this phenomenon is much more pronounced for the support functionalized with HNO_3, which produces a higher oxidation of the felt surface.

3.2. Catalytic activity

The reaction conditions for nitrobenzene hydrogenation in liquid phase were set in order to minimize gas–liquid and liquid–solid diffusional resistances: catalyst weight = 20 mg, solvent volume = 25 ml, nitrobenzene volume = 250 μl. Fig. 2 shows the effect of the stirring rate on the Nbz hydrogenation rate at 25 °C. At stirring rates higher than 1200 rpm, the reaction rate is maintained practically constant, thus minimizing the diffusional limitations. Therefore, the selected stirring rate was 1400 rpm. It must be noted that after the reduction treatment of the sample and before adding the reactant (Nbz), a degassing step of the Pt/ACF catalysts under vacuum and at the reaction temperature, followed by a wetting with ethanol (under stirring), are experimental details which must be taken into account in order to obtain a good reproducibility of the results.

3.2.1. Effect of impregnation time

The impregnation time is an important factor to be considered in the deposition process of the metallic precursor because, at low impregnation times the chloroplatinic acid could be deposited peripherally at the outer shell of the felt fibers without reaching the inside of the pores, while at high impregnation times, Pt could diffuse reaching the inner pores of the felt. That is the reason why metallic phases with different dispersions and different accessibilities to the reactants could be obtained. The catalysts prepared by the impregnation technique described in Section 2 and at different impregnation times were tested in the nitrobenzene hydrogenation reaction in liquid phase.

Fig. 3 shows the effect of the impregnation time over the activity in nitrobenzene hydrogenation reaction for catalysts prepared on ACF functionalized

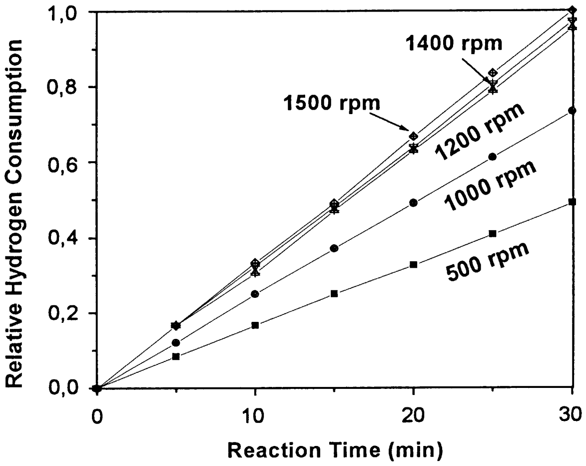

Fig. 2. Effect of the stirring rate on the relative hydrogen consumption during the nitrobenzene hydrogenation reaction.

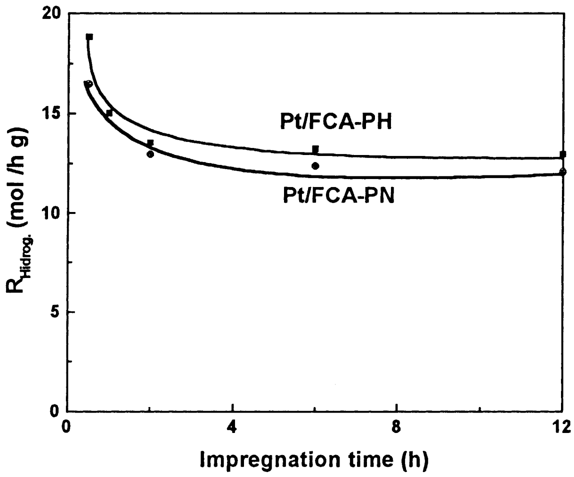

Fig. 3. Influence of the impregnation time on the nitrobenzene hydrogenation activity for different catalysts.

with HNO_3 and H_2O_2. A decrease in activity can be observed with the impregnation time, this effect being more pronounced at a low time. In this sense, for an impregnation time of 30 min, the catalytic activity is c.a. 30% higher than that corresponding to 2 h of impregnation. At higher impregnation times (6 and 12 h), the catalytic activity remains practically constant. This modification in the catalytic activity with the impregnation time cannot be related to the amount of Pt deposited on the felt. In fact, the amount of deposited Pt (determined by chemical analysis) with respect to the amount of Pt initially present in the impregnating solution, showed values higher than 97% at 30 min of impregnation time and values very close to 100% at higher impregnation times.

A second catalytic test has been performed, the CH dehydrogenation reaction in gas phase (structure-insensitive reaction which can be considered as an indirect measure of the metallic dispersion). As already mentioned in Section 2, the catalysts were previously reduced in H_2 at 350 °C and the reaction temperature was 300 °C. Fig. 4 displays the reaction rate as a function of the impregnation time. For each series, results do not show important changes in the values of the CH dehydrogenation rate and hence in the metallic dispersion, with the impregnation time.

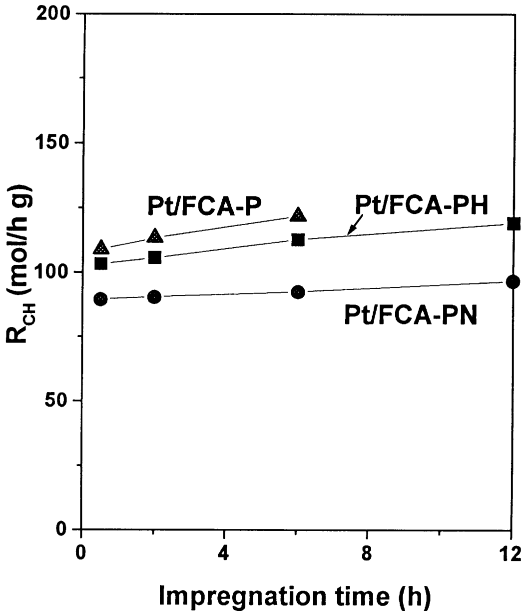

Fig. 4. Influence of the impregnation time on the CH dehydrogenation rate for different catalysts.

In conclusion, we observed a maximum value of activity at low impregnation times (30 min) for Nbz hydrogenation, but not for CH dehydrogenation, whose activity slightly changes at different impregnation times. This different behavior could be explained taking into account:

1. the higher diffusivity value of CH in gas phase ($\cong 3.5 \times 10^{-3}$ cm^2 s^{-1}, according to the Knudsen equation) than that of Nbz in liquid phase ($\cong 1 \times 10^{-6}$ cm^2 s^{-1}, according to the Wilke–Chang equation).
2. the higher size of the molecule of nitrobenzene (6.2 Å) with respect to that of CH (4.9 Å).
3. the different conditions of the reduction treatment performed in the catalyst before each reaction. This point will be discussed later.

Hence, at low impregnation times, Pt would be mainly adsorbed in the outer shell of the felts, while at higher impregnation times the metallic atoms seem to be deposited in the inside of the pores, thus leading to an inaccessibility of a fraction of the metal for a larger molecule such as nitrobenzene.

3.2.2. Effect of surface chemistry on the catalytic activity

Figs. 3 and 4 show a very little effect of the surface chemistry over the catalytic activity. However, the Pt catalysts supported on the felt functionalized with H_2O_2 shows activities in both reactions that are slightly higher than those observed for Pt supported on the felt functionalized with HNO_3. This distinctive behavior was also observed in granular activated carbons [26], though in this case, the differences in the catalytic activities between Pt/C functionalized with H_2O_2 and Pt/C functionalized with HNO_3 were higher. Results can be interpreted considering that highly acidic carbons, such as those obtained by HNO_3-functionalization, have a low isoelectric point, thus unfavouring the $PtCl_6^{=}$ adsorption strength [26,27]. On the other hand, less acidic carbons (such as those obtained by functionalization with H_2O_2), whose isoelectric point is higher, display a stronger adsorption of the metallic complex. This behavior will affect the Pt distribution as it will be shown next.

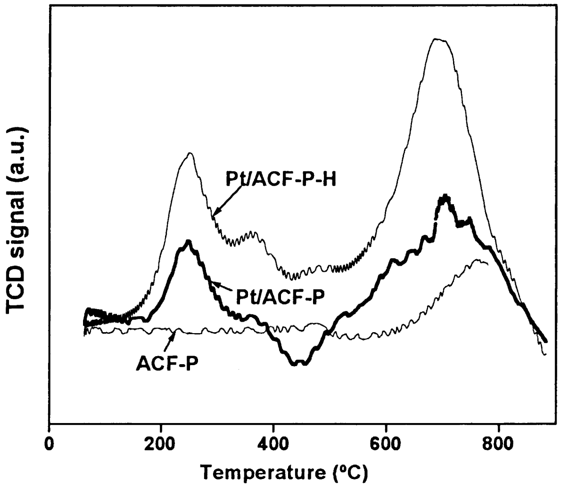

Fig. 5. TPR profiles of Pt/ACF-P-H and Pt/ACF-P catalysts and of the ACF-P support.

It must be noted that these Pt catalysts supported on ACF display a higher activity for nitrobenzene hydrogenation than similar Pt (1 wt.%) catalysts supported on granular activated carbons [26].

3.3. Characterization of the metallic phase by TPR and XPS

Fig. 5 shows the TPR profiles of the purified felt (ACF-P) and those corresponding to Pt catalysts supported on the purified and on the H_2O_2-functionalized felt. The support displays only one H_2 consumption zone at temperatures above 650 °C, which is coincident with the zone of CO desorption in TPD experiments (Fig. 1b). Hence, the CO desorption would leave reactive sites on the support surface which could interact with hydrogen at high temperatures, thus producing a H_2 consumption peak.

Both catalysts display three peaks or H_2 consumption zones: one peak at approximately 230–250 °C, a shoulder at 360–380 °C and another peak at high temperatures (between 500 and 900 °C).

The first and second reduction TPR peaks would be due to the existence of two different effects:

(a) the reduction of the deposited metal complex to a zerovalent state (first peak), in a similar way as observed in TPR profiles of Pt catalysts supported on granular activated carbons [26,28].

(b) the interaction of H_2 with the reactive sites created after the CO_2-desorption at low temperatures (TPD of different ACF^- Fig. 1a). This effect does not appear in the TPR profile of the support, thus indicating that the presence of reduced Pt is necessary for the H_2 dissociation into H atoms which could react with those sites producing the second reduction peak.

The third TPR peak, observed in Fig. 5, appears at high temperatures (>500 °C) for both catalysts and is also observed in the TPR profile of the ACF-P. Hence, this H_2 consumption zone would be related to the decomposition of functional groups of the support, which release CO (Fig. 1b, TPD results) developing new unsaturated reactive surface sites able to consume hydrogen. However, this peak in the carbon felt is small and it appears at higher temperatures than in the catalysts, thus indicating that the presence of Pt would produce a catalytic effect on the decomposition of these functional groups.

In consequence, the thermal treatment with H_2 of these Pt catalysts produces several phenomena, which involves not only reduction of metallic phase to a zerovalent state but also the decomposition of functional groups of the felt and the interaction of H_2 with the reactive sites originated after the decomposition of those strong and weak acidic groups.

It is interesting to point out that no consumption of hydrogen at temperatures lower than 150 °C is observed for the catalysts (Fig. 5). However, the catalysts reduced isothermally at 100 °C during 3 h present good activities for the nitrobenzene hydrogenation. This phenomenon will be explained with the XPS results.

Catalysts reduced at 100 and 350 °C were characterized by X-ray photoelectron spectroscopy (XPS). Figs. 6 and 7 display the Pt4f XPS spectra. From the deconvolution of the Pt4f XPS spectra of catalysts reduced at 100 °C (Fig. 6), two doublets were obtained: one at a low binding energy, which can be assigned to metallic platinum, and a second one at a higher binding energy, corresponding to Pt(II) chlorinated species [29,30]. The appearance of Pt(II) and Pt(0) species in these Pt/ACF samples reduced at low temperatures could be due to a reducing effect of the carbon fiber during the impregnation step, such as happened with Pt catalysts supported on granular carbons [3]. It must

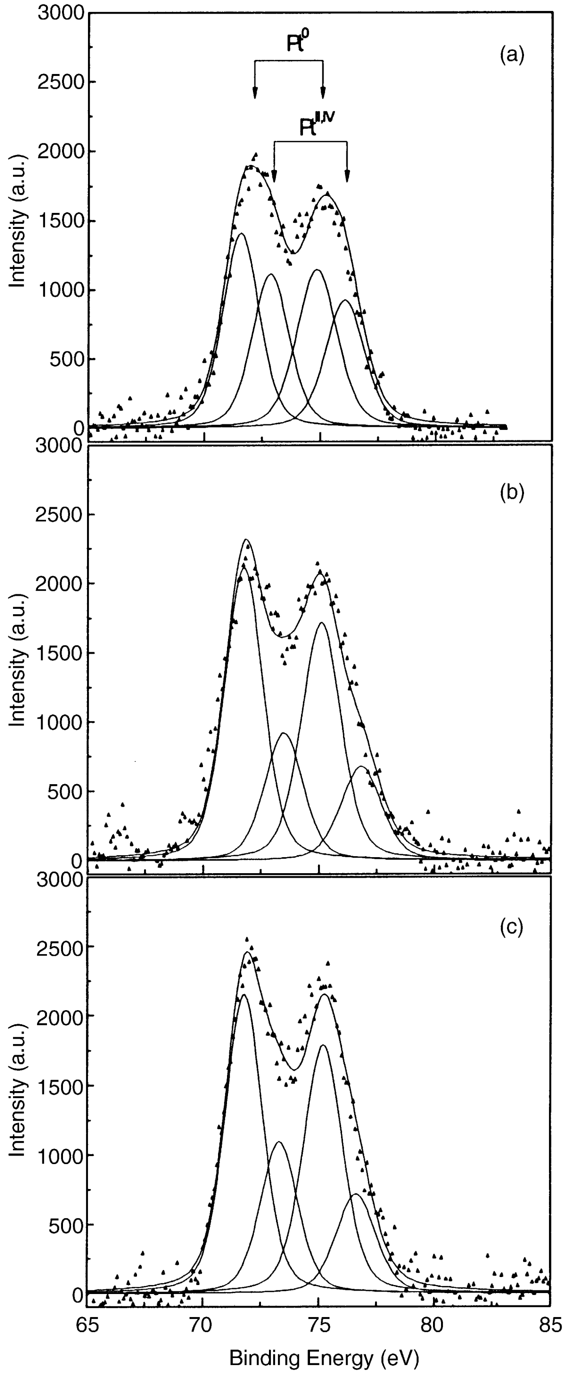

Fig. 6. Pt4f XPS spectra of catalyst reduced at 100 °C: (a) Pt/ACF-P; (b)Pt/ACF-P-N; and (c) Pt/ACF-P-H.

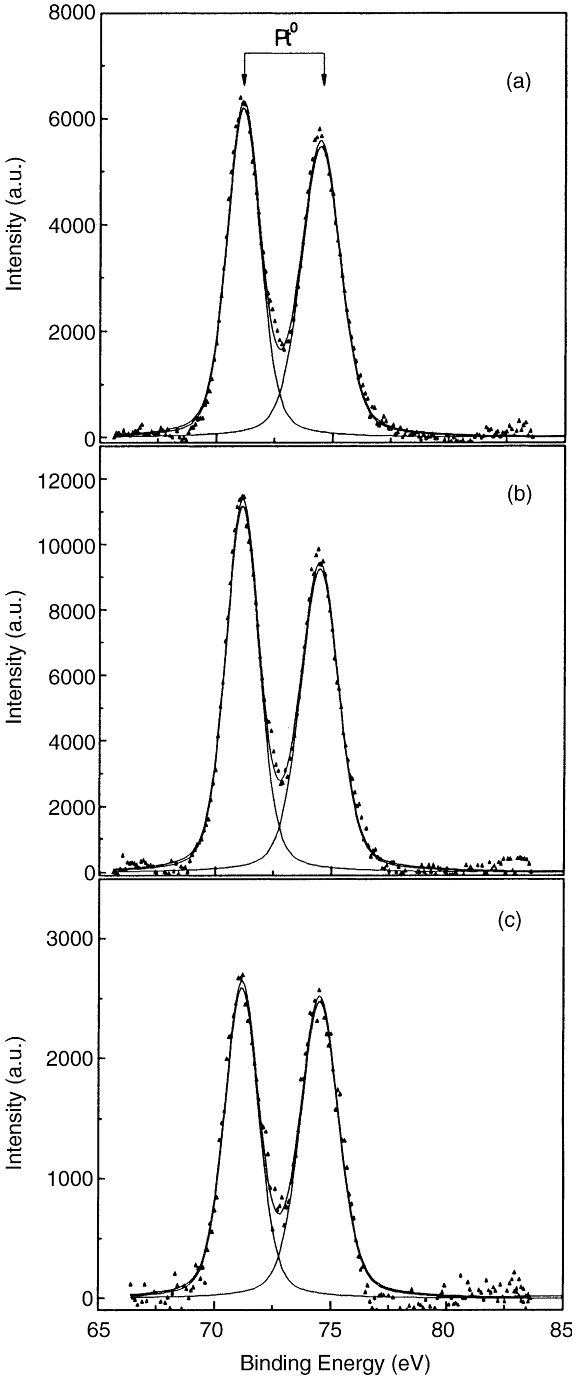

Fig. 7. Pt4f XPS spectra of catalysts reduced at 350 °C: (a)Pt/ACF-P; (b) Pt/ACF-P-N; and (c) Pt/ACF-P-H.

Table 3
Binding energies of the Pt4f$_{7/2}$ XPS level for the three monometallic Pt catalysts supported on ACF-P, ACF-P-H and ACF-P-N, both after reduction step with H_2 at 100 and 350 °C

Catalyst	Reduced at 100 °C			Reduced at 350 °C	
	BE (eV)		I_{Pt}/I_C	BE (eV)	I_{Pt}/I_C
Pt/ACF-P	71.6 (56%)	72.9 (44%)	8.7×10^{-4}	71.2 (100%)	1.17×10^{-3}
Pt/ACF-P-H	71.7 (70%)	73.5 (30%)	1.41×10^{-3}	71.1 (100%)	1.34×10^{-3}
Pt/ACF-P-N	71.8 (63%)	73.3 (33%)	1.41×10^{-3}	71.2 (100%)	4.3×10^{-4}

Values in brackets represent the percentages of each species. I_{Pt}/I_C: values of surface atomic ratios.

be reminded that no hydrogen consumption was observed at 100 °C in the TPR experiment. On the other hand, XPS spectra of the three Pt catalysts reduced at 350 °C (Fig. 7) show a unique doublet at 71.1–71.2 eV (first peak), which indicates that Pt is completely reduced to zerovalent state [29,30].

Table 3 shows the binding energies of the Pt4f$_{7/2}$ level for the three Pt catalysts supported on ACF-P, ACF-P-H and ACF-P-N, both after reduction step with H_2 at 100 and 350 °C. The percentage of Pt(0) and Pt(II) are included in brackets. As already mentioned, a partial reduction of Pt probably occurs during impregnation of the ACF with the platinum precursor. This process appears to be affected by the surface chemistry of the support, since the percentage of reduction is different for the three catalysts. A deeper analysis of the phenomenon is currently being conducted.

Table 3 also displays the values of surface atomic ratios for Pt with respect to C (I_{Pt}/I_C). This ratio, considered as a measurement of the exposed platinum, is similar for Pt/ACF-P-H and Pt/ACF-P-N catalysts reduced at 100 °C, thus explaining the activity results for the nitrobenzene hydrogenation. However, for catalysts reduced at 350 °C the differences in I_{Pt}/I_c display the following tendency:

$$\mathrm{Pt/ACF\text{-}P\text{-}H} \cong \mathrm{Pt/ACF\text{-}P} > \mathrm{Pt/ACF\text{-}P\text{-}N}$$

These results are in agreement with the activity order found for the CH dehydrogenation. Besides, a sintering or migration of platinum atoms in Pt/ACF-P-N could be other additional effects during reduction in H_2 at 350 °C (Table 3). However, these effects could not be considered for the explanation of I_{Pt}/I_C ratios observed for the other catalysts.

4. Conclusions

The functionalization treatment of the activated carbon fiber with H_2O_2 or HNO_3 produces a moderate increase of strong and weak acid groups of the carbon fiber. However, a slight effect of these oxygen surface groups in the catalytic properties was observed.

The use of low impregnation times (30 min) during the preparation of Pt/ACF leads to catalysts with a higher activity for nitrobenzene hydrogenation. At low impregnation times, Pt would be mainly deposited in the outer shell of the fibers, while at higher impregnation times, the metallic atoms seem to be deposited in the inside of the pores.

Pt is completely reduced to zerovalent state after a treatment with H_2 at 350 °C. Besides, the thermal treatment with H_2 at 350 °C produces not only reduction of metallic phase to a zerovalent state but also the decomposition of surface functional groups of the felt and the interaction of H_2 with the reactive sites originated after the decomposition of those groups. During this process, platinum atoms on the most oxidized support (ACF-P-N) would suffer a sintering or migration on the particle surface.

Catalysts reduced at 100 °C show a considerable catalytic activity for the nitrobenzene hydrogenation. The appearance of Pt(0) species, detected by XPS in the Pt/ACF catalysts reduced at 100 °C, explains such behavior. These reduced Pt species could be produced by a reducing effect of the carbon fiber, since no hydrogen consumption was observed in TPR experiments at that temperature.

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