Study of the performance of Pt catalysts supported on activated carbon felt and granular carbon for nitrobenzene hydrogenation

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Abstract

The catalytic behavior of the Pt (1 wt%) catalysts supported on purified activated carbon felt (ACF) and powder carbon (C) has been studied in the nitrobenzene (NBZ) hydrogenation reaction in liquid phase after activation under a H_2 atmosphere between 298 and 623 K. Hydrogen chemisorption measurements, temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) were used to characterize the metallic phase of the catalysts. For Pt/ACF catalysts, the catalytic activity in nitrobenzene hydrogenation after reduction at 298 K was very high and it decreased as the reduction temperature increased up to 373 K. On the other hand, the Pt/C catalyst after reduction at 298 K was inactive. The activity of the Pt/C catalysts increased in a moderate way when the reduction temperature increases up to 373 K. Between 373 and 623 K of reduction temperature, the hydrogenation rate was modified in a minor proportion for both catalysts. The Pt/ACF catalyst previously reduced at 298 K showed a lag step before the reaction ignition. This effect could be attributed to the tendency the metallic centers have to conform the proper arrangement to hydrogenate the nitrobenzene molecule.
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1. Introduction

The use of granular carbon (C) as a catalyst support of noble metals (Pt, Pd, Ru) has been widely reported in the literature [1–5]. Nevertheless, there are other carbonaceous materials such as activated carbon felts (ACF) and fibers whose use as catalyst supports has been investigated in a minor extension. The surface area of these types of activated carbons (felts and fibers) is very high, normally in the range of $1500–3000\,m^2\,g^{-1}$. These new forms of carbonaceous materials have important advantages with respect to granular carbons, derived from the uniform distribution of microporosity, faster adsorption–desorption rate, faster equilibrium rate and high fluid permeability [6,7]. The porous network of the ACF is mainly composed by pores with a narrow range of sizes, specially slit-shaped micropores [8], whereas the textural characteristics of conventional granular activated C are more complex, showing macropores (diameter > 50 nm), mesopores (2–50 nm) and micropores (0.8–2 nm).

As a consequence of their characteristics, ACF and fibers have many uses such as adsorption of gases and vapors, manufacture of electrodes, retention of pollutants, and as catalyst supports [9].

Despite the deep research carried out on the use of granular carbons as catalyst supports, few papers have been reported about the study of metallic catalysts supported on ACF and activated carbon clothes as catalyst supports [8,10].

Pt/granular C catalysts are widely used in a large variety of reactions such as hydrogenations and oxidations in liquid phase. The reduction temperature in flowing H_2 (prior to the hydrogenation reaction) could be an important variable since it can affect both the metallic dispersion and the activity. Concerning to this topic, Uhlir et al. [2] found that the activity in the nitrobenzene (NBZ) hydrogenation reaction for Pt/granular C catalysts was the highest for the samples reduced with hydrogen at low temperatures (between 343 and 373 K). Besides, Machek et al. [11], using similar catalysts, found a sintering effect at hydrogen activation temperatures close to 473 K. Another phenomenon could be influencing the catalytic activity such as the location of the metallic particles in the porous network of the support and the surface nature [12].

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With respect to the use of clothes and felts of activated carbons as a support of Pt, it should be noted that Macias Pérez et al. [10] investigated the application of activated carbon clothes as a support of Pt catalysts in the nitrobenzene hydrogenation reaction after a hydrogen reduction at 323 K and they found a good catalytic performance. Moreover, de Miguel et al. [8] also found a high activity in nitrobenzene hydrogenation of Pt/ACF catalysts reduced at 373 K with hydrogen. However, it should be noted that the literature has not explored the effect of lower reduction temperatures (like room temperature) on the characteristics of the metallic phase and its catalytic behavior in the nitrobenzene hydrogenation in liquid phase on Pt/ACF catalysts.

Taking into account these findings, the present paper studies the behavior of Pt (1 wt%) catalysts supported on commercial granular activated carbons and ACF in the nitrobenzene hydrogenation reaction in liquid phase. One relevant aspect analyzed in this paper is related to the effect of the reduction temperature on the catalytic behavior. Thus, the reduction temperature was modified between 298 (mild condition) and 623 K (severe condition). Besides, the different metallic catalysts (Pt/ACF and Pt/C) were characterized by hydrogen chemisorption, temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) in order to obtain a relationship between the catalytic behavior and the surface properties.

2. Experimental

Two different kinds of carbonaceous materials were used as supports, viz.:

(a) A commercial granular carbon derived from pit of peach (GA-160 from Carbonac) that was crushed and sieved to a final particle size between 100 and 140 mesh. Its original impurity content was 2.9 wt% with a S content of 0.03 wt%, and with the following textural properties: $S_{BET} = 987\,m^2\,g^{-1}$, $V_{pore} = 0.33\,cm^3\,g^{-1}$. This support was called "C".
(b) A commercial activated carbon felt ACN-210-15-AC (phenol derived from GUN EI Chemical Industry Co. Ltd.). Its original impurity content was 1.5 wt% with a S content of 0.0508 wt%. The textural properties were: $S_{BET} = 1661\,m^2\,g^{-1}$, $V_{pore} = 0.59\,cm^3\,g^{-1}$. It was called "ACF".

These supports were purified (elimination of inorganic impurities) by successive treatments with aqueous solutions (10 wt%) of HCl, HNO$_3$ and HF, at room temperature for 48 h without stirring. After HCl and HNO$_3$ treatments, the supports were repeatedly washed with deionized water up to a final pH 4. After the HF treatment, they were washed with deionized water up to the same pH of the water used for washing, and then were dried at 393 K. In order to eliminate sulfur compounds, the different acid-treated carbonaceous materials were submitted to a thermal treatment under flowing hydrogen (5 ml min^{-1} g^{-1}) at 1123 K for 8 h. The so-purified supports were called C–P and ACF–P. After the purification treatment, the impurity content of both granular carbon and activated carbon felts was markedly

reduced, specially the S content, as it was shown by EDX determinations [8,13]. Thus, the impurity content of the ACF was reduced from 1.5 to 0.28 wt% for ACF–P and one of the C decreased from 2.9 to 0.16 wt% for C–P. The sulphur content of purified supports was below the detection level.

The different Pt catalysts were prepared by impregnation of the supports with an aqueous solution of chloroplatinic acid (H$_2$PtCl$_6$) at 298 K. In all cases, the Pt amount used for the impregnation was such as to obtain a Pt content of 1 wt%.

The precursor of the Pt/C-P catalyst was prepared using a volume of the impregnating solution/carbon weight ratio of 30 ml g^{-1}. The carbon support was added to the aqueous solution of the metallic precursor and then the mixture was stirred at 600 rpm for 6 h.

The conditions to carry out a correct impregnation of the small square pieces (approximately 3 mm × 3 mm) of ACF–P with the metallic precursor were previously studied. It must be indicated that the main problems to be solved in order to obtain a correct impregnation of small pieces of felts are related with two factors: (i) the homogeneous wetting of this material and (ii) an uniform deposition of the metallic precursor in all the pieces of the felts [8]. In this sense, it was found that an uniform and simultaneous wetting of all pieces of the felt can be obtained by a previous outgassing treatment of the support under vacuum (10^{-4} Torr) at room temperature, followed by the addition of the solvent (in our case water) under stirring (1400 rpm). Finally, when the support was completely wet, the solution of the metallic precursor (H$_2$PtCl$_6$) was added (using a total impregnating volume/support weight ratio of 60 ml g^{-1}). In order to obtain a homogeneous contact between all the pieces of the felts and the impregnating solution, a stirring rate of 1400 rpm was used. The support was kept in contact with the solution for 2 h.

After the impregnation, the solid was separated from the liquid by filtration and then the precursors were dried at 393 K for 12 h for both catalysts.

Catalysts were characterized by XPS in 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 analysis chamber was kept at 4 × 10^{-10} Torr. The binding energy (BE) and the Auger kinetic energy (KE) scale were regulated by setting the C1s transition at 284.6 eV. The BE and KE values were obtained by using the peak-fit program of the spectrometer software. XPS measurements of the samples were carried out after a H$_2$ reduction treatment "in situ" between 298 and 623 K for 2 h for both catalysts. Besides, XPS measurements of fresh samples (without a reduction treatment) were also performed.

The H$_2$ chemisorption measurements were performed at 298 K in a volumetric equipment. The catalysts were previously reduced with H$_2$ at 298, 373 and 623 K for 3 h, then they were outgassed under vacuum (10^{-4} Torr) at the same temperature and finally cooled down to 298 K before performing the chemisorption test.

The nitrobenzene (NBZ) hydrogenation reaction was carried out in a discontinuous reactor with a magnetic stirrer, at 298 K and atmospheric pressure, using ethanol as a solvent (25 ml). The weight of the catalyst was 0.02 g, the volume of nitrobenzene was

250 µl and the stirring rate was 1400 rpm. Before the reaction, catalysts were reduced "in situ" with hydrogen at 298, 323, 373 and 623 K for 3 h. After the reduction, the samples were cooled down to 298 K, and then the solvent was added. After the solvent addition the H_2 consumption was measured (equilibrium step). Then the reagent (nitrobenzene) was injected into the reactor. The evolution of the reaction through time was followed by measuring the H_2 consumption and the reacted nitrobenzene by GC.

3. Results and discussion

3.1. Hydrogen chemisorption

Fig. 1 shows the hydrogen chemisorption values (expressed as ml H_2 STP g catalyst^{-1}) for Pt/C-P and Pt/ACF-P catalysts as a function of the reduction temperature (between 298 and 623 K). As it can be seen in Fig. 1, the Pt/C-P catalyst reduced at 298 K does not chemisorb H_2 but it does chemisorb H_2 after being reduced at 373 and 623 K. On the contrary, Pt/ACF-P catalyst reduced at 298 K highly chemisorbs hydrogen. When the reduction temperature increases from 298 to 373 K the chemisorption capacity decreases for the ACF-P supported catalyst. For higher reduction temperatures (623 K), the resulting hydrogen chemisorption capacity for the Pt/ACF-P catalyst increased again, this being higher than the chemisorption capacity of the Pt/C–P one after reduction at the same temperature.

The significant hydrogen chemisorption capacity after reduction at 298 K showed by the Pt/ACF catalyst would explain the very high activity in the nitrobenzene hydrogenation such as it would be explained below. In contrast with this behavior, the Pt/C–P sample shows a negligible H_2 chemisorption capacity and it is also inactive for NBZ hydrogenation after reduction at 298 K.

The quantity of the chemisorbed H_2 is related to the concentration of exposed Pt metallic species (at least pairs of neighboring Pt atoms) that are active for the hydrogen chemisorption [14]
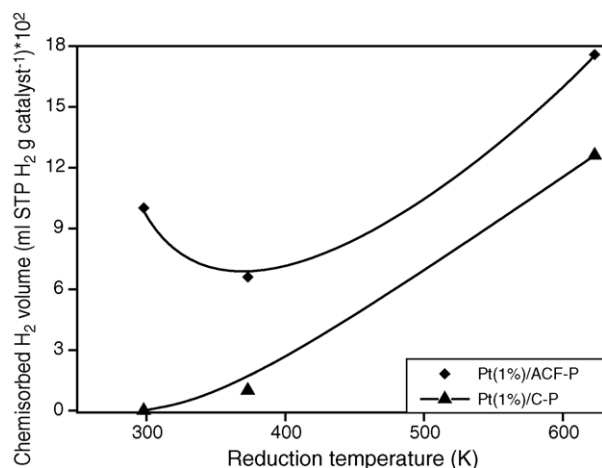
and it can be modified by the reduction temperature. It should not be omitted that the higher the reduction temperature, the higher the sintering effect even at temperatures close to 373 K [10]. In this sense, the hydrogen chemisorption capacity for the Pt/ACF-P catalyst after reduction at 373 K is lower than that observed after reduction at 298 K, this indicating that a certain sintering effect could be produced at 373 K. So, there seems to be two opposite effects coexisting during the reduction step, on the one side the formation of new metallic particles and on the other side a sintering effect. Moreover, it appears that an important sintering effect could take place on Pt/ACF–P previously reduced at 373 K [2]. At 623 K of reduction temperature, Pt is totally reduced to the metallic state and an important sintering effect would be produced according to the nitrobenzene hydrogenation results (see below).

3.2. XPS results

In order to see the effect of the reduction temperature on the oxidation state of Pt, XPS measurements were carried out. Table 1 shows the BE values obtained for the Pt4f$_{7/2}$ lines for C-P and ACF-P-based catalysts, fresh and after reduction at 298, 323, 373 and 623 K, and the percentages of Pt(0) and Pt(II) species. From the deconvolution of Pt4f$_{7/2}$ lines, two peaks were obtained, one of them at 71.1–72.0 eV, which can be assigned to metallic platinum and the other one positioned at 72.9–73.5 eV which can be due to Pt(II) [15,16]. The shifts towards higher binding energies observed for the Pt line at 71.1–72.0 eV could be due to electronic effects produced by the presence of dispersed Pt particles on the supports as it was reported by Torres et al. [13].

It is observed in Table 1 that for the two Pt-supported catalysts not only fresh but also reduced at $T \leq 373$ K, the percentages of Pt(0) and Pt(II) species are quite similar. This behavior can be explained by considering that the very low pressure (10^{-10} Torr) of the vacuum chamber could reduce an important fraction of platinum to Pt(0) both in fresh samples and for samples reduced at temperatures lower than 373 K. Hence, it is difficult to conclude about the concentration of Pt(0) species from XPS determinations for samples reduced between 298 and

Fig. 1. Hydrogen chemisorption values for Pt (1%)/ACF-P and Pt (1%)/C-P catalysts.

Table 1
Binding energies (eV) corresponding to Pt(0) and Pt(II) obtained after deconvolution of the Pt 4f$_{7/2}$ lines for the tested catalysts pre-treated at different conditions

Catalyst	Reduction temperature (K)	Pt(0) (eV)	Pt(II) (eV)
Pt (1%)/C-P	Fresh	72.0 (69.4)	73.6 (30.6)
Pt (1%)/C-P	298	71.8 (64.8)	73.0 (35.2)
Pt (1%)/C-P	323	71.8 (64.0)	72.9 (36.0)
Pt (1%)/C-P	623	71.9 (100)	(0)
Pt (1%)/ACF-P	Fresh	72.0 (58.3)	73.3 (41.7)
Pt (1%)/ACF-P	298	71.8 (55.0)	73.1 (45.0)
Pt (1%)/ACF-P	323	71.8 (54.0)	73.1 (46.0)
Pt (1%)/ACF-P	373	71.6 (50.5)	72.9 (49.5)
Pt (1%)/ACF-P	623	71.1 (100)	(0)

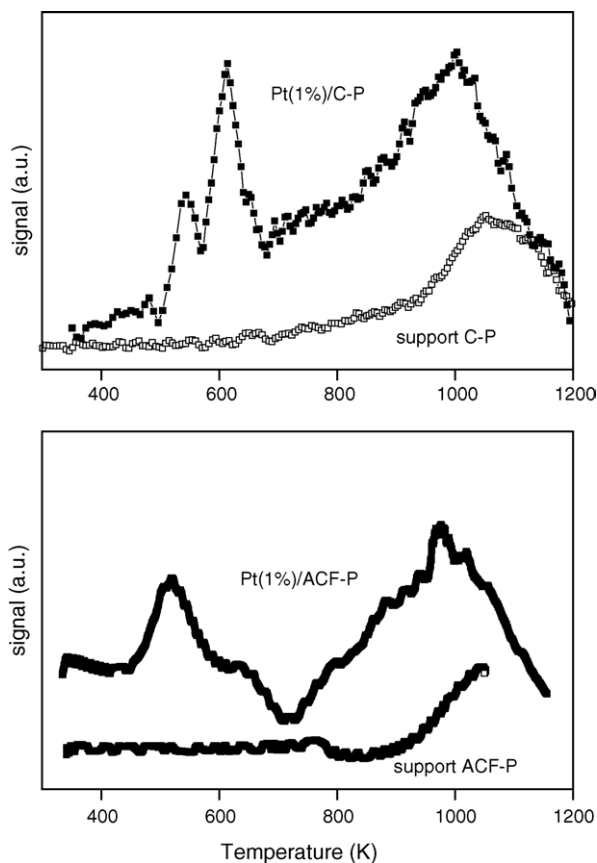The percentages of each species are indicated between parentheses.

Fig. 2. TPR profiles of Pt (1%)/ACF–P, Pt (1%)/C–P and of the C–P and ACF–P supports.
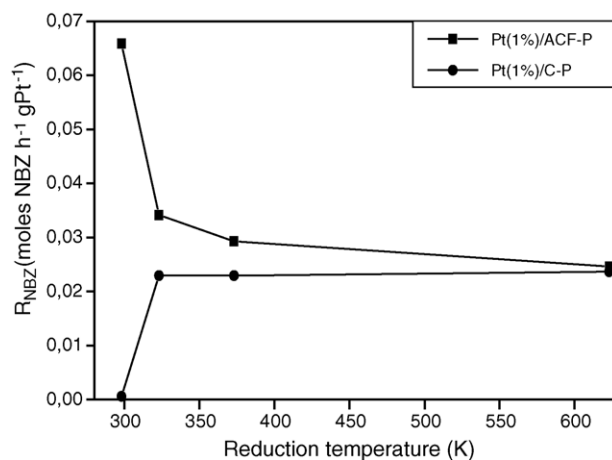

Fig. 3. Effect of the reduction temperature over the catalytic activity in the nitrobenzene hydrogenation reaction for the Pt (1%)/ACF-P and Pt (1%)/C-P catalysts.

373 K. Results of EXAFS reported in the literature for fresh Pt/C catalysts (only dried, without reduction) [16] did not show the typical Pt–Pt bonds that characterize the Pt in its metallic state. Hence, according to these results, fresh Pt/C samples displayed only oxidized Pt species in disagreement with the XPS results. On the other side, after reduction at 623 K, Pt is completely reduced to the metallic state. This agrees with TPR determinations where the first reducing peak at about 500 K corresponds to the reduction of the Pt complex as Fig. 2 shows for Pt/ACF-P catalyst. In a similar way, TPR measurements of the Pt/C-P catalyst showed that Pt complex is reduced at 550 K in catalysts supported on granular carbons. The remaining TPR peaks at higher temperature correspond to the H_2 interaction with reactive sites of the supports [17]. These TPR results would indicate a higher reducibility of the Pt/ACF-P catalyst than the Pt/C-P one.

3.3. Influence of the reduction temperature over the catalytic activity in nitrobenzene hydrogenation

The different catalysts were tested in the nitrobenzene hydrogenation reaction in liquid phase at 298 K. Fig. 3 shows the results of the catalytic activity (R_{NBZ}) expressed as mol of reacted NBZ, (mol NBZ h^{-1} g Pt^{-1}) as a function of the reduction temperature for Pt/ACF-P and Pt/C-P-based catalysts. In all cases, the NBZ consumption displayed a linear variation with

the reaction time. Hence, the R_{NBZ} was calculated as the slope of this linear function with time. It can be seen in Fig. 3 that the activity of Pt/ACF-P is very high after reduction at 298 K and then it markedly decreases when the activation temperature increases up to 373 K. When the reduction temperature increases from 373 to 623 K, the catalytic activity is slightly modified.

From Fig. 3 it can be observed that the behavior of the Pt/C-P catalyst is very different to that of Pt/ACF-P one. Thus, the catalytic activity is negligible for the Pt/C-P catalyst previously reduced at 298 K. Nevertheless, the activity of this catalyst increases when the reduction temperature increases.

Firstly, it is very interesting to analyze the behavior of the Pt/ACF-P catalyst after reduction at 298 K, since this catalyst displays the highest activity. Although the Pt reducibility to the metallic state seems to be negligible at this temperature according to TPR results (Fig. 2), the chemisorption capacity of this sample at 298 K is important. This apparent contradictory behavior can be explained taking into account that the TPR is a dynamic technique, while the reduction at 298 K in a flow equipment under isothermal conditions during 3 h could produce a partial conversion of Pt to the zerovalent state, according to the chemisorption results. The important chemisorption capacity of the Pt/ACF-P catalyst could be interpreted considering that an important fraction of pairs of contiguous zerovalent Pt atoms would be produced after reduction at 298 K and in this way, these species would chemisorb hydrogen in a dissociative way.

It should be also indicated that the nitrobenzene hydrogenation reaction carried out with the ACF-based catalyst reduced at 298 K showed a lag step at the beginning of the reaction. Fig. 4a and b show typical curves of both the catalytic activity (nitrobenzene conversion) and the H_2 consumption as a function of the reaction time for the Pt (1 wt%)/ACF-P catalyst reduced at 298 K, at two different times of the equilibrium step. It should be remembered that the equilibrium step consisted on keeping the catalyst in contact with the solvent (ethanol) under hydrogen atmosphere and stirred at 1400 rpm without the
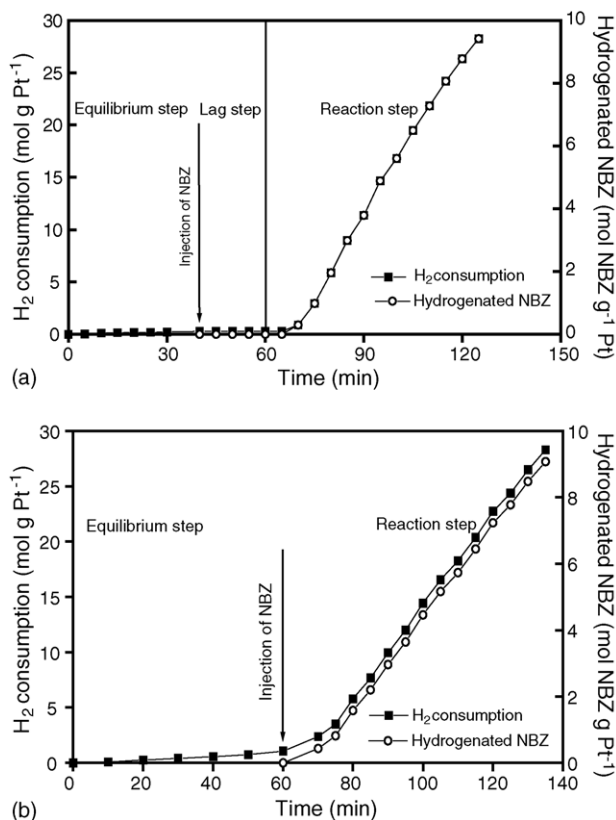
Fig. 4. (a) Catalytic activity (hydrogen consumption and amount of hydrogenated NBZ) as a function of the reaction time for the Pt (1%)/ACF-P catalyst reduced at 298 K showing the equilibrium, lag and reaction steps. (b) Catalytic activity (hydrogen consumption and amount of hydrogenated NBZ) as a function of the reaction time for the Pt (1%)/ACF-P catalyst reduced at 298 K showing the equilibrium and reaction steps.

reagent (nitrobenzene). It can be observed from Fig. 4a and b that the longer this step, the shorter the lag one (between the injection of NBZ and the ignition of the reaction). This effect was only observed for the ACF-P-based catalyst reduced at 298 K. Besides, it can be noted that the very low H_2 consumption during the equilibrium and lag steps would be responsible for the additional reduction of small amounts of Pt atoms located in the vicinity of the pairs of zerovalent Pt atoms (originated during the H_2 reduction in gas phase at 298 K), thus leading to new small ensembles of zero valent Pt atoms. The additional reduction during the equilibrium and lag steps would be favored by the H_2 spillover. In this sense, Srinivas and Kanta Rao [18] found H_2 spillover at room temperature in Pt/C catalysts. Hence, it could be inferred that during the equilibrium and lag steps, the metallic centers would reach the ensemble sizes necessary for the nitrobenzene hydrogenation. With respect to the effect of metal particle size in nitrobenzene hydrogenation, Machek et al. [11] concluded that this reaction was more structure insensitive than the 1-octene hydrogenation for Pt crystallite sizes higher than 25 Å. In a similar way, Macías Pérez et al. [10] also found a structure insensitive character of this reaction for Pt/carbon cloth catalysts with low Pt dispersions (≤20%). Furthermore, Torres et al. [13] found that the NBZ hydrogenation is a structure insensitive reaction for Pt dispersion <42%. However, it has not been

reported in the literature the behavior of this reaction for very small Pt crystallite sizes. In the light of our results, it appears that the reaction requires at least small ensembles (highly dispersed) of metallic Pt to take place for the Pt/ACF-P catalyst reduced at 298 K.

When the reduction temperature increases from 298 to 373 K, it can be observed that the chemisorption capacity for the Pt/ACF-P catalyst decreases about 35%. However, from Fig. 3 it can be observed an important decrease (56%) of the nitrobenzene hydrogenation rate for the Pt/ACF-P catalyst when the reduction temperature of this sample increases from 298 to 373 K. Hence, it is observed that there is not a linear relationship between the decrease of the chemisorption capacity and the hydrogenation rate in this range of reduction temperature. First, it is not expected a much higher reduction degree at 373 K with respect to 298 K, according to TPR results. In consequence, the catalytic behavior could be related to different factors, mainly the sintering of the metallic phase and the location of the metallic particles. In fact, when the reduction temperature increases from 298 to 373 K, a sintering effect appears to be produced leading to a decrease in the hydrogen chemisorption for the Pt/ACF-P sample, but a fraction of these metallic particles of larger size appears to be located into the inner porous structure of the carbon material being less accessible to large molecules like nitrobenzene than to small molecules like hydrogen.

It is worth saying that from the chemisorption determinations done in the range of 298–373 K of reduction temperature, the hydrogen chemisorbed should not be related with platinum dispersion values because in these conditions Pt is not completely reduced such as XPS and TPR determinations show.

Analyzing the results of H_2 chemisorption, XPS and the catalytic activity in NBZ hydrogenation for the Pt/ACF-P-based catalyst, it could be concluded that when the reduction temperature increases from 373 to 623 K, though the Pt is completely reduced to the metallic state at 623 K, a sintering of the metallic particles would simultaneously occur, thus leading to a slight decrease of the catalytic activity.

From the above comments, it could be concluded that the NBZ hydrogenation would be a structure-sensitive reaction for high dispersions (at low reduction temperatures) and it would be a structure-insensitive one for low dispersions. In this sense, Cinneide and Clarke reported that certain reactions show a positive intrinsic factor for high dispersions and then a structure-insensitive behavior for low ones [19].

As it was mentioned before, the Pt/C-P catalyst showed an opposite behavior respect to the ACF-based one at low reduction temperatures (298 K). In this condition the concentration of metallic centers active not only for chemisorption but also for nitrobenzene hydrogenation are negligible for the Pt/C-P catalyst. At higher reduction temperatures (373 K), it would take place an increase in the concentration of the metallic particles (giving higher activity). In the range of 373–623 K, it can be observed that the catalytic activity in NBZ hydrogenation is constant for the Pt/C-P catalyst. This result would indicate that the sintering, the complete Pt reduction and the metallic location effects [20] would lead to a neutral result in the activity of this catalyst.

4. Conclusions

From the results presented above, it can be concluded that the Pt/ACF-P catalyst reduced at room temperature (298 K) showed a very high activity in NBZ hydrogenation in contrast with the C–P based one, which was inactive in this condition. Besides, the Pt/ACF-P catalyst reduced at 298 K showed a delay at the beginning of the reaction. For low reduction temperature (298 K), the centers that are active for H_2 chemisorption (pairs of contiguous atoms) are inactive to hydrogenate the NBZ molecule. Thus, during the equilibrium and lag steps, the centers would be turned into small active ensembles able to hydrogenate the NBZ molecule probably due to an additional Pt reduction in the vicinity of the pairs of Pt atoms. The H_2 spillover can play an important role in this process. When the reduction temperature increases from 298 to 373 K in the ACF-based catalyst, the catalytic activity decreases in an important way, but the H_2 chemisorption decreases in a lower extension. This behavior could be attributed to different reasons: a sintering of the metallic phase and the location of a fraction of active centers into the inner porous structure of the support, which are less accessible to large molecules (NBZ) than to small molecules (H_2). For higher reduction temperatures between 373 and 623 K, the NBZ activity does not change very much for both catalysts, Pt/C-P and Pt/ACF-P. In this zone of reduction temperature, it appears that different processes would take place for both catalysts: the complete Pt reduction, an important metal sintering and metallic location effects.

Acknowledgements

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