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METAL-SUPPORT INTERACTION IN Pt/C CATALYSTS. INFLUENCE OF THE SUPPORT SURFACE CHEMISTRY AND THE METAL PRECURSOR

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Abstract—The influence of support surface chemistry and metal precursor species on the properties of Pt/C catalysts has been analyzed. The char of a phenolformaldehyde polymer is the carbon source for obtaining four different supports: three with different degree of surface oxidation and another one modified by ion-exchanged calcium. These supports have been impregnated with aqueous solutions of two platinum precursors with different ionic character: chloroplatinic acid and tetraaminplatinum chloride. The study of the system consists of a preliminary characterization of the supports (surface chemistry and textural properties), an EXAFS analysis of the fresh impregnated catalysts and the determination of platinum dispersion. The platinum precursor-support interaction, established after the impregnation step, and the platinum precursor distribution have been related to the surface chemistry of the supports and the platinum precursor used. The effect of these parameters in the final metal dispersion has also been investigated. The results obtained show that the degree of support surface oxidation has a strong influence on the distribution of the metal precursor on the support and, consequently, on the final platinum dispersion. The surface oxidation of the supports seems to have a negative effect on the platinum dispersion, independently of the platinum precursor used. Thus, the lower the number of surface oxygen complexes, the higher the metal dispersion. The reduction of precursor H_2PtCl_6 by interaction with the carbon has also been found to depend on the surface chemistry of the supports.

Key Words—Metal-support interaction, EXAFS, Pt/C catalysts, support surface chemistry.

1. INTRODUCTION

The design of supported catalysts is grounded mainly on the knowledge of the interaction and location of the active phase within the support[1-3]. It is well known that the interaction degree depends not only on the nature of the system, but also on the preparation method, and that it can be modified in different ways, such as pretreatment of the support or the addition of promoters[4]. Surface oxygen complexes of the support exhibit an outstanding role in this field due to their double function: a) they are anchorage sites for the metal precursor during catalyst preparation and, b) they can act as active centers in multifunctional catalysts due to their acid-base or red-ox properties[2].

When the support is a hydrophobous material, like carbon, surface complexes also contribute to improve its wettability and so make the impregnation with polar solvents easier[5]. This aspect and others relating the surface chemistry of carbons to possible interactions with impregnants, or its adsorption capacity, have been the subject of several studies[5-18].

It seems that the functionalization of supports is an interesting method to get better catalysts. However, substituent groups or impurities on the carbon surface may limit its adsorption capacity, by repelling or failing to attract the molecules of the adsorbate[7]; they may also limit the diffusion through the grain if they

strongly attract these molecules. In this sense, it is very important to consider the influence of the surface complexes in the acidic properties of carbons, mainly because if catalysts are prepared by impregnation (which is most frequent), attracting or repelling forces can emerge between the precursor molecules and the support[11-13]. This fact has a significant effect in the resulting metal dispersion of catalysts.

Some authors[14,15] have found that the interaction of metal precursor molecules with carbonaceous supports (carbon black and active carbon), by means of surface oxygen complexes, leads to a high dispersion. However, in other studies[16,17] it is shown that the oxidation of an active carbon used as support has a negative influence on getting a catalyst with a high dispersion. The same has been found using a carbon black[18].

With respect to those apparent discrepancies, it must be kept in mind that the properties of the resulting catalysts are greatly influenced by several factors (i.e., the preparation method, the textural and chemical properties of supports, the nature of the metal precursor used, etc).

The present study deals with the system Pt/C in an attempt to look into the influence of the support surface chemistry on the properties of the catalysts prepared by impregnation. Supports with different amounts and types of surface oxygen groups have

been used to prepare platinum catalysts. Furthermore, in a sample with a large amount of carboxylic groups, the H^+ ions from these groups were exchanged by Ca^{2+} ions[19] to modify the support surface chemistry. On the other hand, two platinum compounds of different ionic character have been used as platinum precursors (i.e., chloroplatinic acid, anionic, and tetraamminplatinum chloride, cationic). A substantially different platinum precursor-support interaction is expected with these two compounds.

The characterization of the catalysts has consisted of:

1) a preliminary study of supports (textural properties and surface chemistry),
2) an EXAFS analysis of the fresh samples, after the impregnation step, to deepen the nature of the interaction between the precursor and the support, and
3) measurement of metal dispersion, by H_2-chemisorption and XRD, after the reduction stage.

2. EXPERIMENTAL

2.1 *Supports*
2.1.1 *Preparation.* The four different supports used in this study were prepared according to the following procedure: support A was prepared by carbonization of a phenolformaldehyde polymer resin in N_2 flow (80 ml/min, STP). The temperature was raised at a rate of 5 K/min up to 1273 K, and maintained at this temperature for two hours. The obtained carbon has a high purity, a high apparent surface area, and a well-developed porosity.

By oxidation of carbon A, support A2 was obtained. The oxidation process was carried out by treatment of the carbon with HNO_3 15M (in a ratio of 10 ml solution per gram of carbon), keeping the mixture of 353 K until dryness. The carbon was then exhaustively washed to the complete removal of nitrates.

The modification of the surface chemistry of support A2 in two different ways results in the following supports:

Support A4: prepared by selective removal of some oxygen complexes. Support A2 was treated in N_2 atmosphere at 800 K during 1 hour in order to decompose the more unstable complexes, mainly carboxylic groups.

Support Ca-A2: prepared by addition of calcium. Support A2 added to a saturated solution of calcium acetate was maintained at 333 K in a thermostatic-stirred bath for 24 hours. In these conditions, an ion-exchange of Ca^{2+} with H^+ from the carboxylic complexes occurs[19]. After that, the

sample was filtered and washed. The calcium content of this sample is 2.6 wt%.

2.1.2 *Textural properties.* Apparent surface area and porosity of the supports were studied by physical adsorption of N_2 at 77 K and CO_2 at 273 K. The porosity was also studied by mercury porosimetry. Physical adsorption experiments were carried out in a conventional gravimetric apparatus. For N_2-adsorption data and, using the B.E.T. equation, the apparent surface area was determined. Micropore volume was calculated from the CO_2 adsorption isotherm, using the Dubinin-Radushkevich equation. The volume of supermicropore was calculated, subtracting the pore volume measured with CO_2 from that measured with N_2. To determine mesopore volume, two contributions were added[20]: one calculated from the N_2-adsorption isotherm, by subtracting the adsorbed volumes at 0.7 and 0.2 relative pressure (which accounts for pores of diameter between 2 and 7.5 nm) and the other one from mercury-porosimetry measurements by selecting the volume of pores with diameter between 7.5 and 50 nm.

2.1.3 *Surface chemistry.* The surface chemistry of the supports has been analyzed by TPD experiments and pH measurements. The apparatus used to carry out the temperature-programmed experiments consists basically of a differential flow reactor coupled to a mass spectrometer. The equipment includes a system of valves that allows rapid changes of gases (within a few seconds) without any effect on the total flow. At the outlet of the reactor, a portion of the gas is sent to the mass spectrometer through a classical introduction system, consisting of a capillary tube, a mechanical vacuum pump, and a porous leak. In these experiments, about 200 mg of sample was heated at 50 K/min up to 1250 K, while He was flowed through with a flow rate of 60 ml/min (298 K, 0.1 MPa).

The pH of the aqueous slurry of the supports was measured as follows: the slurries were prepared in a ratio of 10 ml of water per 1 gram of carbon; this mixture was stirred and the pH was measured several times until a constant value was reached. The apparatus used was a STANDARD pH-meter PHM82 Radiometer Copenhagen.

2.2 *Catalysts*
2.2.1 *Preparation.* Pt/C catalysts were prepared with two different precursors: (1) hexachloroplatinic acid, H_2PtCl_6 (referred to as precursor a) and (2) tetraamminplatinum chloride, $[Pt(NH_3)_4]Cl_2$ (referred to as precursor c). The supports were impregnated with aqueous solutions of the precursors in the appropriate concentration to obtain platinum loadings of about 1wt%. The impregnation was carried out in excess solution (10 ml of solution per 1 g of carbon), and nitrogen was kept flowing through the suspension until total elimination of the liquid. All catalysts were dried at 383 K overnight and kept in a desiccator until use. To determine the platinum content, the carbon was

burnt off in air at 973 K and then the dissolved residue was analyzed by UV spectrophotometry (261.8 nm).

2.2.2 *EXAFS analysis*. The X-ray absorption experiments were performed at BL-7C of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) Tsukuba, Japan. A Si(111) double crystal was used to monochromatize the X-ray from the 2.5-GeV electron storage ring. The Pt L_{III}-edge absorption spectra were recorded in the transmission mode at room temperature, in a range of photon energy extending from 11300 to 12700 eV. Fourier transformation was performed on k^3-weighted EXAFS oscillations, $k^3\chi(k)$, in the range of 3–12 Å^{-1} (FT-EXAFS). The physical basis and numerous applications of XAFS spectroscopy have been discussed elsewhere[21–25].

Wafers for EXAFS experiments were prepared by pressing a homogeneous mixture of the carbon supported catalyst and polyethylene. The samples were then sealed with a polyethylene film to prevent air contact during handling.

2.2.3 *H_2-chemisorption measurements*. Pt dispersion was measured by H_2 chemisorption, according to the following general procedure: 1) heat treatment in H_2 at 623 K, 12 hours, 60 ml/min, 2) outgassing for 1 hour at 573 K in vacuum and cooling to 298 K, 3) hydrogen dosage. The adsorption isotherms were lineal in the range of pressures used (50–250 Torr) and the monolayer of H_2 chemisorbed was calculated by extrapolation of the isotherm to zero pressure.

It must be pointed out that, in the case of catalysts prepared with $[Pt(NH_3)_4]Cl_2$ (precursor c), a precaution must be considered in the reduction step[26]. The heat treatment (at 623 K) of the fresh impregnated catalysts in H_2-atmosphere, produces the formation of an intermediate hydride, which is mobile and leads to a fast agglomeration of platinum particles[26]. To avoid this problem the decomposition of the cationic complex was done under He-atmosphere and then the gas was switched to H_2 to complete the reduction.

2.2.4 *XRD measurements*. XRD measurements were carried out in the samples reduced (but not *in situ*) in the same way as explained before. The experiments were performed at the Institut für Anorganische Chemie in the University of Frankfurt. The apparatus was a STOE Powder Diffraction System and Co $K_\alpha(KL_{III})$ the radiation used. Particle sizes were determined from the Debye-Scherrer equation.

3. RESULTS AND DISCUSSION

3.1 *Study of supports*

3.1.1 *Porosity*. Table 1 shows the data corresponding to surface area and meso- and micropore volumes for the different supports prepared. It can be observed that the original char, support A, has a high surface area and a well-developed porosity. The other supports show a very similar micropore volume, but some differences are found in the range of supermicro and mesopore volumes and, obviously, in the surface area. The oxidizing treatment (that results in support A2) produces some increase of the wider micropore volume (supermicropores). The removal by heat treatment of surface groups (that conduces to support A4) leads to additional development of both supermicro and mesopore volumes.

3.1.2 *Surface oxidation*. It is well known that the oxidation treatment of carbonaceous materials is the origin of a great variety of surface oxygen complexes. By Temperature Programmed Desorption (TPD) it can be seen that these surface complexes decompose to form CO_2 and CO. There are a large number of publications dealing with the characterization of surface oxygen complexes in carbons[6,27–30]. They are classified as acidic, basic, or neutral groups, depending on the pH of the carbon aqueous slurry. Carboxylic, anhydride, and lactone are acidic groups, while phenolic, carbonyl, quinone, and ether groups are neutral or weakly acidic. Basic complexes are mainly the pyrone and chromene groups. During the thermal decomposition of the surface complexes, CO_2 evolves from carboxylic groups and their derivatives, such as lactones and anhydrides, while CO is mainly a decomposition product of quinones, hydroquinones, and phenols[27].

TPD experiments give interesting information about the amount, thermal stability, and nature of the surface oxygen groups. The application of this technique to the study of the supports (A, A2, A4, and

Table 1. Textural properties of the supports

Support	$S_{B.E.T.}$ (m^2/g)[a]	V_{micro} (cm^3/g)[b]	$V_{supermicro}$ (cm^3/g)[c]	V_{meso} (cm^3/g)[d]
A	580	0.266	0.25	0.39
A2	730	0.272	0.31	0.36
A4	830	0.285	0.38	0.51
Ca/A2	530	0.260	0.23	0.31

[a]From the N$_2$ adsorption isotherm (77 K).

[b]From the CO$_2$ adsorption isotherm (273 K).

[c]Calculated as follows: the pore volume from N$_2$ isotherm minus the pore volume from CO$_2$ isotherm.

[d]Calculated by addition of two contributions: 1) from the N$_2$ isotherm in the pressure range between 0.2 and 0.7 relative pressure and 2) from mercury porosimetry.
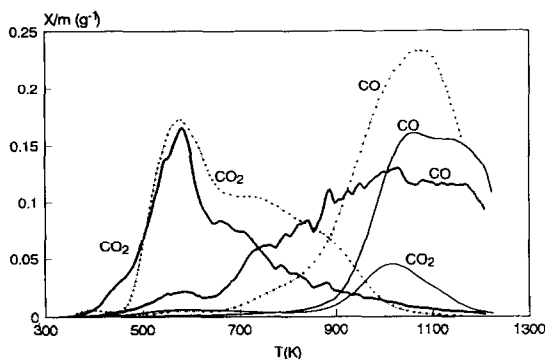
Fig. 1. TPD spectra of supports A2 (————), A4 (————), and Ca-A2 (- - - - - -).

Ca-A2) shows the great differences in surface chemistry among them.

Figure 1 presents the TPD spectra obtained for supports A2, A4, and Ca-A2. The spectrum corresponding to support A has been not included, because the low amount of surface oxygen complexes of this sample is not appreciated in the scale used. Table 2 collects the quantification of the TPD spectra as CO and CO_2 evolved. The pH of the aqueous slurry of these carbons, which gives a good orientation about the electronic surface properties[31], has also been included.

It can be observed in Fig. 1 that treatment with HNO_3 generates an intense oxidation that results in a large evolution of CO_2 and CO during the TPD experiment. As explained above, complexes evolving as CO_2 have acidic properties, and this is the reason of the low pH measured for support A2 (see Table 2). Support A also contains some oxygen complexes. The small amount of oxygen present in the char could be due to room-temperature oxidation during its storage[28,29]. The TPD profile of support A4 shows the effect of the selective removal of surface oxygen complexes. To obtain support A4 (from support A2), most of the acidic groups (CO_2-type complexes) have been eliminated from the carbon surface. The CO-type groups that decompose at T < 800 K have been also taken away. The removal of acidic groups produces, as expected, an important increase in the measured pH compared to that of sample A2 (see Table 2). The high-temperature CO_2 evolution observed in the TPD profile of support A4 (Fig. 1) suggests that, in addition to the elimination of the surface oxygen complexes, there is also a partial transformation of these oxygen

groups. It is supposed that during heat treatment up to 800 K, some carboxylic groups can be transformed into more stable anhydride groups (dehydration reaction)[32]. Support Ca-A2 is very similar to support A2 in the degree and sort of oxidation, but its TPD spectrum shows a higher CO_2 evolution and slight differences in the CO_2 desorption profile over 700 K (see Fig. 1). In this sample, Ca^{2+} ions are ion-exchanged with H^+ of carboxylic groups[19]. The removal of these protons makes the pH of support Ca-A2 higher (see Table 2). The excess of desorbing CO_2 in respect to support A2 was suggested to be related to the coordination of calcium ions with CO_2 molecules[19].

The results obtained in the study of the supports reflect the very different surface chemistry of the carbons used in this work. In relation to their porous texture, it can be considered that, despite the above-mentioned differences among them, the samples show quite similar textural properties.

3.2 *Study of catalysts*

TPD experiments of the impregnated samples show that the amount of decomposing surface oxygen groups and the TPD curves were almost identical to those of carbon itself. This observation implies that the catalyst preparation step and the presence of platinum do not appreciably change the surface functionality of the supports. However, it is expected that, due to the different surface chemistry of supports, catalysts with different properties emerge.

Metal dispersion of a supported catalyst strongly depends on the distribution of the active phase within the support, and on the type and degree of interaction reached. During the impregnation process, the acidic or basic character of supports and of the metal precursor solution have an important influence on the way in which the precursor molecules diffuse into the support and interact with it. If the pH of the impregnating solution is higher than the pH of the aqueous slurry of the support, then the adsorption of cations is favored[11]. Anions adsorb easier when the impregnating solution is more acidic than the aqueous slurry of the support[11]. Together with these electrostatic considerations, the nature and amount of surface oxygen complexes must be taken into account and, what is important, their location in respect to the porous network of the support. Interaction with the carbon basal planes is also an important parameter in defining the metal dispersion and the catalytic properties[33,34].

This section is divided into two parts, each of them aimed at catalysts prepared with one of the platinum precursors used, with the following content: 1) possible interactions that could be established between the platinum precursor molecules and the supports, in relation to the pH values of the aqueous slurry of the supports and the platinum precursor solutions, 2) results of the EXAFS analysis of the fresh samples, and 3) results of the metal dispersion of catalysts after the reduction stage. A global discussion has been included in each part to relate results and in order to explain the characteristics of the resulting catalysts.

Table 2. CO_2 and CO evolution in the TPD experiments of supports and pH of the supports aqueous slurries

Support	CO_2 (μmol/g)	CO (μmol/g)	pH
A	160	280	7.2
A2	1800	2800	3.3
A4	600	1600	7.2
Ca/A2	2600	2900	5.4

3.2.1 Catalysts prepared with [Pt(NH₃)₄]Cl₂.

3.2.1.1 *Impregnation:* The pH of the aqueous solution of [Pt(NH₃)₄]Cl₂ (precursor c), in the same concentration used for catalyst impregnation, is 6.4. Considering the pH values presented in Table 2, the strongest interaction is expected to occur with support A2. The ion exchange of the cation [Pt(NH₃)₄]$^{2+}$ with H^{+} of carboxylic complexes is favored in these conditions. It can be thought that this situation conduces an atomic distribution of the platinum precursor in the support and, thus, a high dispersion should be expected.

In the case of supports A and A4, whose aqueous slurry has a pH higher than that of the solution of precursor c (see Table 2), electrostatic adsorption should not be favored. Nevertheless, it must be taken into account that carbon A4 contains a noticeable number of CO-type complexes that can cause a negative character of the carbon surface, which, in turn, could cause a weak interaction between the cation [Pt(NH₃)₄]$^{2+}$ and the surface of this support. A similar situation can be found during the impregnation of support Ca-A2. Although support Ca-A2 is highly oxidized, the exchanged Ca^{2+} ions neutralize the acidic complexes. The possible centers for the [Pt(NH₃)₄]$^{2+}$ cations to be anchored (carboxylic-type complexes) are occupied by calcium. However, the CO-type complexes can act in the same way as in the case of support A4, perhaps with a higher contribution to the negative character of the carbon surface because of the lower pH of its aqueous slurry. Moreover, in this case, the ion exchange between Ca^{2+} ions and the cationic species of Pt(II) cannot be, in principle, discarded.

3.2.1.2 *EXAFS analysis:* The results of the EXAFS analysis are useful in understanding the interaction between the platinum precursor and the surface of the supports. Figure 2 shows the Fourier Transformation of the EXAFS oscillations (FT-EXAFS) obtained for the precursor compound [Pt(NH₃)₄]Cl₂ and the four c-catalysts (fresh samples). The spectra are presented without the shift phase correction that, in this case, is around 0.38 Å (this value must be added to that measured in the FT-EXAFS to have the correct distance).

The FT-EXAFS spectrum of [Pt(NH₃)₄]Cl₂ (Fig. 2a) consists of a main peak at 1.7 Å, that corresponds to the first coordination sphere of platinum formed by N atoms. In the same range of distances, the spectra of the catalysts show a composite peak that changes depending on the support. Both contributions to the composite peak have a quite similar intensity in catalyst c/A (Fig. 2b). In catalyst c/A2, the peak at higher distance (Fig. 2c) clearly predominates; in catalysts c/A4 and c/Ca-A2 (Figs. 2d and 2e), the peak at lower distance is more intense. By comparison to the reference compound (Fig. 2a), the contribution to the composite peak at lower distance (around 1.7 Å) can be assigned to Pt—N bonds. Considering the surface chemistry of the supports and the ion-exchange mechanism, the other contribution to the composite peak can be related to a Pt—O interaction. This assignment is reasonable be-
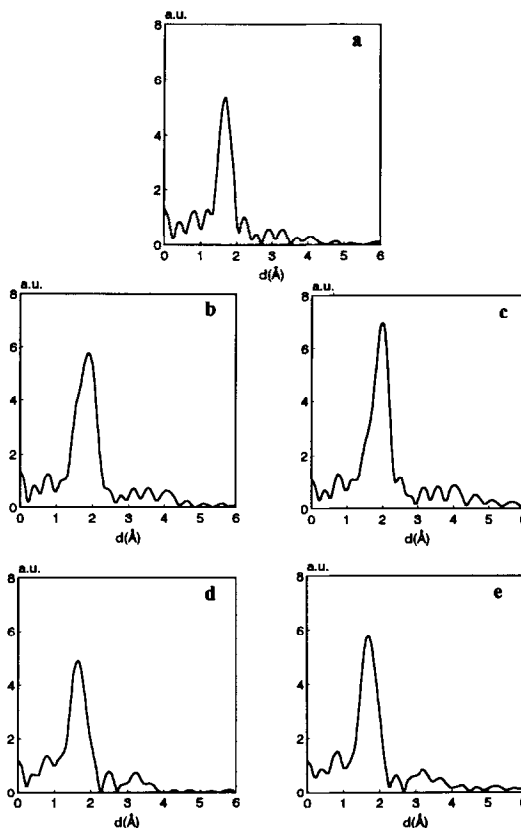

Fig. 2. FT-EXAFS spectra of samples a) [Pt(NH₃)₄]Cl₂, b) c/A, c) c/A2, d) c/A4, and e) c/Ca-A2.

cause the observed distance is akin to that in the tetrameric [Pt(CH₃COO)₂]₄ compound (where there are two Pt—O bonds 2Å long and the other two 2.16Å long)[35]. Since no more peaks are observed at higher distances, it can be concluded that after the impregnation the Pt species present an atomic distribution on the carbon surface. The different intensity of both contributions to the composite peak, depending on the support, show the different degree of interaction between the platinum precursor and the carbon surface. This is evidence of the change in the platinum coordination as a consequence of the ion-exchange process. Comparing the four spectra, it is evident that the Pt—O interaction occurs to the largest extent with support A2 (catalyst c/A2) and it results in an important decrease of the N-coordination sphere of platinum. In the case of catalyst c/A, there is also some interaction with the oxygen complexes, although to a lower extent than in c/A2. For catalysts c/A4 and c/Ca-A2, the very low intensity of the peak assigned to Pt—O indicates that the interaction between the platinum precursor compound and the surface oxygen complexes is weak and that the N-coordination sphere is kept.

The EXAFS results show that, as expected, the main interaction between the cationic precursor and the carbon surface occurs with the acidic groups, and that the larger the acidic character of these groups the

stronger the established interaction. Therefore, the interpretation of the EXAFS results provides information about the metal precursor-support interaction and to relate it to the impregnation conditions. However, at this point we cannot relate this interaction to the final distribution of platinum within the catalyst and, hence, with the Pt dispersion after the reduction step.

3.2.1.3 *Dispersion measurements:* 1) H_2-chemisorption — the platinum dispersion values determined by H_2-chemisorption are collected in Table 3. It must be remembered that, in the case of samples prepared with $[Pt(NH_3)_4]Cl_2$, the decomposition of this platinum precursor must be done under He atmosphere (see experimental section part 2.2.3). Table 3 contains the results obtained with and without the treatment in He previous to the reduction in H_2 (columns D and D*, respectively). As can be observed, the direct reduction with H_2 renders a very low catalyst dispersion. There is only one exception: the result obtained for catalyst c/Ca-A2 that will be discussed later.

Data in Table 3 (column D) show that the dispersion of these catalysts varies in a wide range. Excluding sample c/Ca-A2, it has been found an inverse and almost linear relationship between the metal dispersion and the amount of surface oxygen complexes (see also Table 2). The less disperse catalyst is c/A2; in contrast, in sample c/A a very high dispersion is obtained, being the dispersion of catalyst c/A4 between the two other cases.

These results indicate that the surface chemistry of the supports has a great influence on the metal dispersion.

2) XRD — Catalysts prepared with $[Pt(NH_3)_4]Cl_2$ do not present peaks corresponding to reflection on platinum planes. This result indicates that the diameter of the platinum particles is not larger than the detection limit (about 5 nm). Considering spherical particles and a density of 65.94 Ptatoms/nm^2, the relation $d = 1.08/D$ (d = diameter (nm); D = dispersion) results[36]. According to this, the dispersion calculated from XRD data for catalysts of series c is larger than or close to 0.2, in agreement with H_2-chemisorption measurements.

It should be noted that the XRD pattern of catalyst c/Ca-A2 shows diffraction peaks not related to platinum, but to calcium (Fig. 3). Compared to reference compounds, these peaks have been attributed
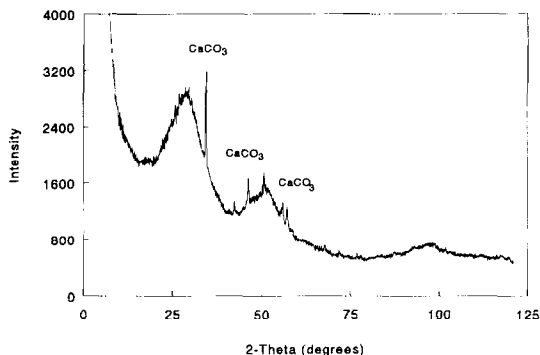

Fig. 3. X-ray difractogramm of catalyst c/Ca-A2.

to $CaCO_3$. On the other hand, XRD measurements in support Ca-A2 (after the same reduction treatment) do not reveal the presence of such a compound. The difference in the state of calcium in these two samples suggests that the presence of Pt leads to a change in the calcium dispersion, presumably due to the existence of interactions between Pt and Ca. This result also supports the behavior of sample c/Ca-A2 in relation to the H_2-chemisorption measurements: as above exposed, catalyst c/Ca-A2 constitutes an exception in series c because it shows the same platinum dispersion, with and without a treatment in He prior to the reduction with H_2.

3.2.1.4 *Global discussion:* To explain the results obtained with the catalysts of the c series, it must be considered that the interaction with the oxygen complexes of the support surface could hinder a good diffusion of the precursor molecules into the support grain (i.e., if there are a large number of oxygen complexes on the external surface (case of support A2 and also A4), they can act as anchoring centers, retaining the metal precursor molecules and thus leading to a non-uniform distribution of platinum). Nevertheless, a poor distribution is not the only reason for obtaining a low metal dispersion. It must also be considered that, during the reduction stage, the heat treatment (up to 623 K in this case) produces the decomposition of the less stable oxygen complexes. Thus, the mobility of platinum on the support surface may be favored and in consequence the agglomeration of platinum particles enhanced. This effect has been observed before in similar systems (i.e., Pt/C[37] and Mo/C catalysts[12].

Support A contains a low number of surface oxygen complexes. So, in relation to the above comments, the impregnation of this support proceeds with adequate diffusion conditions and, thus, the precursor could be better distributed, reaching the inner porous network of the carbon support. The EXAFS analysis (part 3.2.1.2) reveals the existence in this sample of some Pt—O interaction; that is, part of the Pt-precursor is ion-exchanged with protons of carboxylic groups. However, the small number of of these groups at the external surface only retains part of the platinum precursor and hence, it can reach the inner sur-

Table 3. Platinum content and platinum dispersion of catalysts

Precursor $[Pt(NH_3)_4]Cl_2$(c)				Precursor H_2PtCl_6(a)		
Sample	% Pt	D	D*	Sample	% Pt	D
c/A	0.62	0.70	0.05	a/A	0.98	0.80
c/A2	0.96	0.28	0.07	a/A2	0.96	0.15
c/A4	1.05	0.40	0.03	a/A4	0.92	0.20
c/Ca-A2	0.91	0.20	0.20	a/Ca-A2	0.78	0.70

*Dispersion measured without the previous treatment in He (see the text).

face of the support. According to the EXAFS results, a larger part of the catalyst precursor interacts with carboxylate groups because, though the total amount is low, they constitute the strongest anchorage points for the $[Pt(NH_3)_4]^{2+}$ ions. The heat treatment to reduce the metal does not greatly affect the dispersion of platinum. This result agrees with the proposed location of platinum precursor molecules inside the porous network, because of the lower sintering rate expected in porous systems[38].

The impregnation conditions (part 3.2.1.1) allows us to expect a strong adsorption of $[Pt(NH_3)_4]^{2+}$ on support A2 by means of an ion-exchange process involving carboxylic type complexes. This possibility is confirmed by the strong Pt—O interaction found in the FT-EXAFS analysis (Fig. 2c). Thus, it can be thought that, though precursor c is atomically distributed (see EXAFS results), it has a poor distribution because on the external surface of the support there are enough carboxylic groups to anchore all the $[Pt(NH_3)_4]^{2+}$ cations. Due to this bad distribution, the reducing treatment leads to a low platinum dispersion.

If the adsorption of the metal precursor on the support is not so strong, then the diffusion of the impregnated species into the support is expected to proceed more easily and, regardless any other factors, a better distribution could be attained. This is what seems to happen with support A4. As commented in part 3.2.1.1, during the preparation of catalyst c/A4 the adsorption of the platinum precursor on the support is not favored. The EXAFS results confirm that there is not a strong interaction between the platinum precursor and the oxygen groups of the support surface (Fig. 2d). However, a weak interaction cannot be discarded because the support surface contains a large amount of CO-type groups. The finding of a metal dispersion lower than in catalyst c/A (see Table 3) indicates that, probably, the so-called weak interaction still has an important influence in leading a nonuniform distribution of platinum in the support. Nevertheless, the effect of the heat treatment in the reduction stage has also to be considered because, in spite of the thermal stability at 673 K of most of the oxygen complexes contained in support A4, it must be taken in mind that this is a dynamic system and some transformation or rearrangement of oxygen groups can happen and favor platinum mobility.

The lowest dispersion is found for the c/Ca-A2 catalyst and, only in this case, the measured dispersion with and without the previous He-treatment (Table 3 columns D and D*) shows the same value. Because this is the only c-catalyst with a relatively high dispersion after the direct reduction in H_2, it is inferred that an influence of calcium in the stabilization of the platinum precursor avoids its mobility and, as a consequence, the sintering. The EXAFS results show that there is not an important Pt—O interaction. This result, together with the finding of a similar amount of calcium in Ca-A2 and c/Ca-A2 samples (2.6% and 2.4% respectively) allows us to discard an ion ex-

change between Ca^{2+} and $[Pt(NH_3)_4]^{2+}$ ions. In this sense, because the ion-exchanged calcium gives a positive charge to the support surface, the interaction with the Pt(II) cation is not favored and, here, a bad platinum distribution is achieved. This bad distribution is responsible of the low platinum dispersion measured. The fact that the EXAFS spectrum of c/Ca-A2 catalyst is very similar to that of the reference compound, means that the interaction of the platinum precursor with the calcium cations is not important. In this way, the same platinum dispersion observed with and without the He pretreatment suggests that calcium acts as a barrier that hinders the mobility of the Pt precursor.

As a summary, from the above results it can be concluded that, in the case of $[Pt(NH_3)_4]Cl_2$ the platinum precursor, the distribution of platinum in the support depends on the acidic character and number of surface oxygen complexes on the support. However, the reduction stage plays an important role in the final platinum dispersion because of the decomposition and transformation of surface oxygen complexes during the heat treatment. In general, it can be said that, although the presence of surface acidic oxygen complexes could lead to an atomic distribution and a strong platinum precursor-support interaction, due to the reduction heat treatment, the net result is a negative influence in the final platinum dispersion. Calcium is supposed to have an stabilizing effect during the reduction treatment.

3.2.2 Catalysts prepared with H_2PtCl_6.

3.2.2.1 *Impregnation:* The aqueous solution of H_2PtCl_6 (precursor a) used to impregnate the supports has a low pH, ~2.2; this value is lower than the pH of the slurries of all the supports (see Table 2). In these conditions, the adsorption of the $PtCl_6^{2-}$ anions should be favored in all the cases (it can be pointed out that the case of support A2 is less favorable because its aqueous slurry has a pH close to that of the precursor solution). Differences between the catalysts can arise from the different amount and nature of surface oxygen complexes of the supports. Thus, although supports A and A4 give the same pH in aqueous slurry, they have a very different surface chemistry and, for this reason, the established interactions during the impregnation stage must differ.

Nevertheless, using H_2PtCl_6 as platinum precursor, the carbonaceous support can act itself as an anchorage site. In means, as previously demonstrated[16,17], that during the impregnation stage the precursor H_2PtCl_6 is reduced in some extent to Pt^{2+} and also to Pt^0 by the support. The number of crystallites formed in this process will have a clear influence on the resulting metal dispersion. The results found in the literature about the effect of surface oxygen complexes in the extent and efficiency of the reduction are contradictory. Van Dam *et al.*[16] explain that the reduction capacity decreases in the oxidized supports; however, Czárán *et al.*[17] put forward a mechanism by which the presence of surface oxygen complexes favors the reduction process.

3.2.2.2 *EXAFS analysis:*

The FT-EXAFS spectra of H_2PtCl_6 and the a-catalysts are presented in Fig. 4. The main feature in the FT-EXAFS spectrum of H_2PtCl_6 (Fig. 4a) is a peak, centered at ~2Å (without phase correction) attributed to a Pt—Cl bond. This peak shows an intensity higher than that observed for the Pt—N bond in the FT-EXAFS spectrum of $[Pt(NH_3)_4]Cl_2$ (compare Fig. 4a to Fig. 2a), mainly due to the larger atomic scattering factor of Cl atoms. Figure 4a also shows a small peak centered at ~4Å that would correspond to the second coordination sphere of this platinum compound.

The catalysts of series a exhibit two types of FT-EXAFS spectra that can be related to two different types of platinum precursor-support interaction. In this sense, catalysts a/A and a/A2 exhibit some similarities. In both cases, the following features are observed: 1) the main peak centered at ~2Å has the largest intensity, more similar to that found for the reference compound than in the other catalysts; this means that the chlorine coordination sphere still exist (i.e., $PtCl_6^{2-}$ and/or $PtCl_4^{2-}$ structures remain on the support surface[16]); 2) the peak at ~4Å, characteristic of the reference compound, is clearly observed, and 3) a small peak (not observed for the reference compound) appears at about 2.5Å. This peak can be assigned to Pt metal (the distance measured after correction of the phase shift gives a value close to the

Pt—Pt distance[39].) From these results, it is inferred that in samples a/A and a/A2 there is a weak interaction between the platinum precursor and the surface oxygen complexes (the local structure of the precursor is maintained), and that reduction of the platinum precursor occurs to some extent, being more significant in the case of a/A2. Due to this reduction of the precursor, the chloride coordination number decreases.

The other two catalysts a/A4 and a/Ca-A2 show important differences. In these cases, the peak at about 2Å has an intensity lower than in samples a/A and a/A2. This indicates an important change in the coordination sphere of platinum, probably in a way in which part of the Cl atoms are replaced by O atoms from the surface oxygen complexes. It must be taken in mind that a Pt—O bond produces also a peak at about 2Å (without phase correction) in the FT-EXAFS, but with an intensity lower than in the case of a Pt—Cl bond because of the smaller atomic weight of oxygen. The observed change in the Pt coordination, from Cl to O atoms, can be related to a stronger interaction between the platinum precursor and the support. However, due to the different surface chemistry of supports A4 and Ca-A2, the nature of their interaction with the platinum compound must be different.

3.2.2.3 *Dispersion measurements:*

1) H_2-chemisorption—The dispersion data determined by H_2-chemisorption are presented in Table 3. As happens with c-catalysts, a large number of surface oxygen complexes is a negative factor for obtaining a high metal dispersion. Catalysts a/A2 and a/A4, prepared with oxidized supports, are the less disperse, both having a similar Pt dispersion. This is in contrast with the high dispersion measured for the catalyst prepared with the original char, a/A. It is noticeable that the result obtained for the catalyst a/Ca-A2, in spite of having been prepared with an oxidized support, shows an outstanding high dispersion.

2) XRD—For catalysts prepared with H_2PtCl_6, the XRD patterns obtained show clear diffraction peaks from platinum crystal planes. As an example, Fig. 5 shows the diffractogram obtained for sample a/Ca-A2. This kind of diffractogram has been found
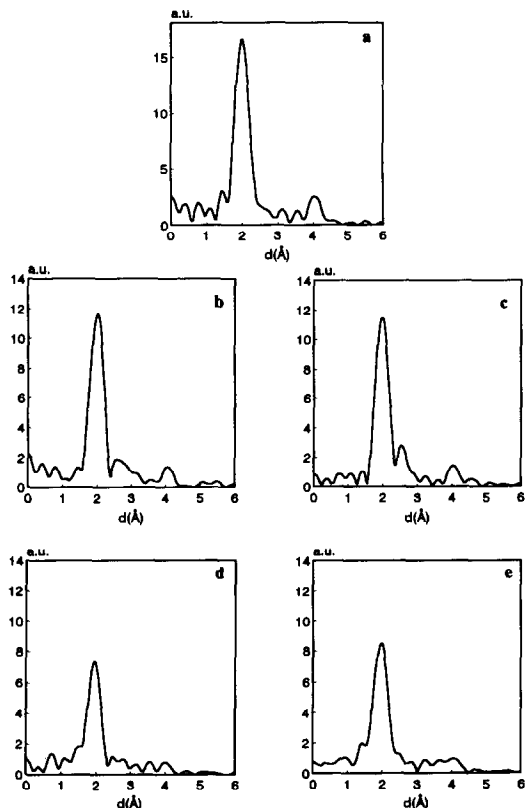

Fig. 4. FT-EXAFS spectra of samples a) H_2PtCl_6, b) a/A, c) a/A2, d) a/A4, and e) a/Ca-A2.
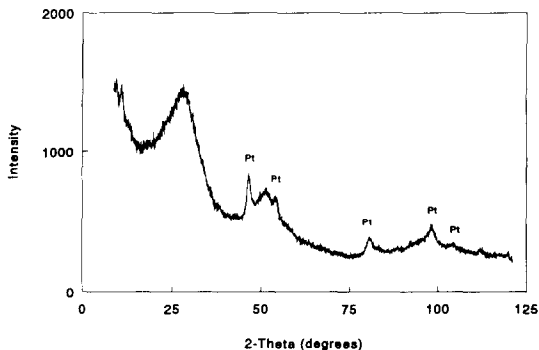

Fig. 5. X-ray difractogramm of catalyst a/Ca-A2.

for all the a-catalysts, that is, for the little and highly dispersed catalysts. Considering the results in Table 3, this indicates that the impregnation with precursor a results in a wide particle size distribution, probably related to the ability of this molecule to be reduced by the carbonaceous support; a process that produces some platinum nuclei that could grow rapidly. In this way, the wide particle size distribution could be an evidence of different growth rates[16].

To check the particle size distribution, some samples have been studied by TEM. The results are in agreement with the XRD observations. A wide particle size distribution has been found (in contrast with the homogeneity observed in the case of c-catalysts).

It must be also mentioned that, for catalyst a/Ca-A2, no diffraction peaks from calcium species have been observed (compare Fig. 5 to Fig. 3). This finding shows that the final state of calcium in catalyst a/Ca-A2 is very different from that in c/Ca-A2. In accordance with the EXAFS results, it constitutes evidence of the different interaction established, after the preparation step, between the platinum species and the carbonaceous support in both catalysts. These differences are also reflected in the very distinct dispersion (measured by H_2-chemisorption) of these two catalysts.

3.2.2.4 *Global discussion:* In agreement with the arguments exposed for catalysts prepared with precursor c, the small amount of oxygen complexes contained on the surface of support A allows a good diffusion of the platinum precursor through the support grain; thus, the $PtCl_6^{2-}$ ions can penetrate the porous network and interact mainly with the carbon basal planes (metal-ligand interaction). Precursor a reaches, thus, a good distribution and a location that hinders its mobility during the heat treatment done in the reduction stage. In these conditions, a catalyst with the highest dispersion emerges.

For catalyst a/A2, due to the similarity of the support aqueous slurry pH and the impregnating solution pH (3.3 and 2.2 respectively), a negative surface charge that repels the precursor anions probably exists on the support. This situation will produce a bad distribution and, as shown in the FT-EXAFS spectrum (Fig. 4c) a lack of interaction with the surface oxygen complexes. Moreover, the existence of a repulsive effect between negative charges (carboxylate groups and $PtCl_6^{2-}$ ions) hinders the penetration of the platinum precursor into the pores. The poor distribution, in conjunction with the decomposition of surface oxygen complexes and subsequent surface mobility during the reduction stage, results in a very low dispersion.

In spite of the differences in platinum dispersion, the observation in the EXAFS spectra of Pt reduced states in samples a/A and a/A2 indicates that, in both cases, a reduction of Pt(IV) during the impregnation step occurs. However, due to the very different surface chemistry of supports A and A2, it is supposed that the reduction proceeds in a different way. As commented before, explanations can be found in the literature for this process to occur, preferably when the support contains an important amount of surface

oxygen complexes[17], or when it does not[16]. In any case, the reduction takes place by interaction with the carbon basal planes. In this process, some nuclei are formed; when they reach a critical size, fast growth occurs[16]. In respect to the influence of the surface oxygen complexes in this reduction process, our findings (i.e., reduction in both sample a/A and a/A2) allow us to discard any significative chemical influence of these complexes in the reaction. During the impregnation of support A, the platinum precursor molecules can easily contact the carbon basal planes and be, at least, partially reduced. However, in the case of support A2, the large number of surface oxygen complexes constitutes an impediment for the platinum precursor molecules to reach the carbon basal planes, and probably fewer nuclei can be formed. Nevertheless, because of the repulsive effect between the platinum precursor molecules and the carbon surface (by means of the surface oxygen complexes), the nuclei formed would be preferred sites of anchorage; it is possible that larger particles can be formed in an autocatalytic reduction process. This possibility supports the low dispersion found for catalyst a/A2.

In the case of catalyst a/A4, the pH of the H_2PtCl_6 aqueous solution is much lower than that of the aqueous slurry of support A4 (see Table 2). This situation favors a electrostatic interaction with the support (it also happens with support A). Support A4 contains a large number of surface oxygen groups; most of them are CO-type groups but, also, an important number of oxygen complexes that decompose as CO_2 at high temperatures exist (see Table 2). By comparison with support A, which contains some amount of CO-type and low-temperature CO_2-type complexes, but shows the best precursor distribution and the smallest change in the coordination sphere of Pt after the impregnation (see Fig. 4b), it can be supposed that these groups do not act as anchoring centers. From that we suggest that the high-temperature CO_2 complexes found in support A4[32] could be responsible for the strong interaction between the precursor and the support shown in the EXAFS experiments. This strong interaction with the surface oxygen complexes means that the platinum precursor molecules are retained on the external surface of the support, giving rise to a bad Pt distribution and a low platinum dispersion after the reduction step.

The dispersion of catalyst a/Ca-A2 constitutes an exception to the above explanations. Support Ca-A2 is highly oxidized and the pH of its aqueous slurry, in respect to that of H_2PtCl_6 solution, favors the adsorption of anions. In this case, a poor Pt distribution and a low Pt dispersion should be expected after the reduction treatment, but a large Pt dispersion is obtained. It seems that, in this case, the presence of calcium is responsible for this behavior. The FT-EXAFS pattern found for catalyst a/Ca-A2 shows a low intensity in the peak at about 2Å. This indicates that a strong metal precursor-support interaction occurs in this case, that produces an important decrease in the Cl-coordination sphere of Pt. Maybe the interaction

between the Cl atoms of the $PtCl_6^{2-}$ ion and the Ca^{2+} ions can favor an ion-exchange of the Pt(IV) ions with calcium ions linked to carboxylate groups. In this sense, note the similarity of FT-EXAFS of the sample a/Ca-A2 (Fig. 4d) and sample c/A2 (Fig. 2c), where Pt—O bonds exist due to an ion-exchange process with H^+ ions of the carboxylic groups. Thereby, the final state of the a/Ca-A2 sample after the impregnation would consist of platinum ions interacting with carboxylate groups and surrounded by a large number of Ca^{2+} ions, also linked to carboxylate groups. Note that the amounts of Pt and Ca loaded on the sample are ~50 μmol/g and ~650 μmol/g, respectively. If we consider the proposed anchorage of Pt(IV) ions in the carboxylate complexes due to an ion exchange with Ca^{2+}, the resulting location of platinum among calcium-based structures could hinder a sintering process during the reduction stage. This is the same idea proposed before for sample c/Ca-A2. The possibility of this exchange of calcium is supported by the observed loss of calcium in catalyst a/Ca-A2 in respect to Ca/A2 and c/Ca-A2 samples. The calcium content of samples Ca/A2 and c/Ca-A2 is very close, 2.6% and 2.4%, respectively, while that of sample a/Ca-A2 is lower, 2.0%. Because no Pt ion exchange is observed in sample c/Ca-A2 (see Fig. 2e), it is supposed that the presence of Cl determines this possibility.

Finally, the very different effect of the presence of calcium in the support depending on the nature of the platinum precursor used must be pointed out. As exposed earlier, for catalyst a/Ca-A2 no diffraction peaks from calcium species have been observed, which means that the final state of calcium in catalyst a/Ca-A2 is very different from that in c/Ca-A2. On the other hand, the EXAFS results show that a very different interaction is established between the platinum species and the carbonaceous support in these two catalysts, after the preparation step. Furthermore, in relation to these differences, catalysts c/Ca-A2 and a/Ca-A2 have a very distinct platinum dispersion (measured by H_2-chemisorption).

4. CONCLUSIONS

The distribution of the platinum precursor on the carbonaceous supports under study, and the established metal precursor-support interaction, are strongly dependent on the support surface chemistry, that is, on the amount and the nature of the surface oxygen complexes and on the presence of ion-exchanged calcium.

In general, a large number of surface oxygen complexes conduces to a poor distribution of the platinum precursor. This is the result of either a preferred anchorage of the platinum precursor in these complexes or of a repelling electrostatic interaction. Both cases hinder the platinum precursor from penetrating the porous network of the supports. Nevertheless, this situation is not against a high dispersion because, considering the low amount loaded, platinum can be atomically distributed. The heat treatment in H_2 to reduce the catalysts has a decisive influence in the re-

sulting platinum dispersion, because this treatment leads to the decomposition and some redistribution of surface oxygen complexes, producing the mobility and, consequently, the agglomeration of platinum particles. When the platinum precursor can reach into the porous network, the heat treatment does not produce particle agglomeration. The ion-exchanged calcium also plays a role in this way, that is, it has been shown to have a stabilizing effect on the platinum precursor. It has been suggested that calcium, or the species formed after the corresponding treatments, act as a barrier that impedes the particle mobility during the reduction heat treatment.

In any case, the platinum precursor used has a decisive influence on the properties of the resulting catalysts because of the different interaction with the supports. The cationic precursor, $[Pt(NH_3)_4]Cl_2$, is anchored by the supports mainly by an ion-exchange mechanism in which the acidic groups perform an important role. The interaction of the anionic precursor, H_2PtCl_6, with the supports is more complex, being strongly influenced by the amount and the nature of surface oxygen complexes and by the presence of calcium. All these factors also determine the extent of the reduction of H_2PtCl_6 by the carbonaceous supports.

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