Properties of Carbon-Supported Platinum Catalysts: Role of Carbon Surface Sites

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The effect of oxidation treatments of the support on the properties of carbon-supported platinum catalysts has been analyzed. A set of activated carbon carriers has been prepared by oxidative treatments of a commercial carbon in liquid as well as in gas phase. The carbons obtained had largely identical pore structures but differed considerably in their surface chemistry as shown, for example, by their point of zero charge (PZC) values. The catalysts were prepared by equilibrium impregnation of the supports with an aqueous solution of hexachloroplatinic acid. N_2 adsorption, TPD, XPS, TPR, and H_2 chemisorption were used to characterize the supports and the catalysts. The Pt load of the catalysts was found to depend on the PZC of the supports. However, the Pt dispersion was found to depend on the total surface oxygen content of the supports. These results were rationalized by the assumption that the surface basic groups of the supports are anchoring sites for the strong adsorption of platinum.   © 2002 Elsevier Science (USA)

Key Words: activated carbon; oxidative treatments; platinum catalysts; strong adsorption; surface basic sites.

INTRODUCTION

Activated carbons are frequently used as catalyst supports in the fine chemical industry owing to their specific features: they are stable in both acid and basic media and carbon can be burnt off, allowing an economical and ecological effective recovery of the precious catalytic metal (1, 2). It is well known that the interaction of the active phase with the support can be modified by pretreatment of the support. There is consequently in the published literature a growing awareness of the need to consider the surface chemistry of carbon supports to achieve adequate catalyst performance (1, 2). The catalytic behavior of activated carbon-supported noble metal catalysts can be modified by oxidation treatments of the support prior to metal loading (2). Different oxidizing treatments, both in the gas and in the liquid phase, can be used to perform chemical

surface modifications of activated carbons. There is an exhaustive literature dealing with the nature of the oxygen groups thus formed on the surface of carbon and with their influence upon the properties of carbon-supported catalysts (1). It is now generally accepted that the presence of surface oxygen groups decreases the hydrophobicity of the carbon, thus making its surface more accessible to the metal precursor during the impregnation with aqueous solution (1). On the other hand, the presence of such surface oxygen groups alters the pH values of aqueous carbon slurries and can thus have a considerable influence on the impregnation step of the catalyst preparation (3, 4). Furthermore, these oxygen surface groups are frequently credited with acting as nucleation centers for the generation of highly dispersed metallic crystallites (2).

In the near future, the use of carbon materials as catalyst supports for precious metals may increase, due to the rapidly advancing development of fuel cells (5). In addition, the use of new carbon materials as industrial catalyst supports may develop rapidly with new interesting carbon materials emerging and becoming available on a commercial scale. It is thus important to achieve better basic understanding of the carbon support material and of the catalysts made there from (2).

The present work aims at contributing to the further understanding of the role of carbon oxygen surface groups on the properties of the carbons themselves and of the carbon-supported platinum catalysts prepared by impregnation.

EXPERIMENTAL

Pretreatment of carbon.   A commercial activated carbon (NORIT ROW 0.8s) was used as the starting material. To eliminate some mineral impurities commonly found in activated carbons, such as Mg, Al, K, Ca, and Fe, the commercial sample was extracted for 14 h with 2 mol/L hydrochloric acid at boiling temperature. Subsequently, the sample was washed with distilled water until it reached constant pH and was dried in an oven at 383 K overnight. This sample is denoted as C1.

Oxidative treatments of carbon. The modification of the surface chemistry of the carbon was carried out through different treatments, both in liquid and in gas phase. Supports C2 and C3 were obtained by oxidizing C1 with 5 mol/L nitric acid in a Soxhlet extractor for 3 and 6 h, respectively, at refluxing temperature. Support C4 was prepared by adding C1 to a 5 mol/L nitric acid solution and keeping the mixture at boiling temperature for 6 h. In all oxidative procedures in liquid phase the proportion 1 g (carbon)/10 mL (solution) was used. After the oxidative treatment the supports were extensively washed with distilled water until neutral pH of the rinsing waters was obtained. Subsequently, samples C2–C4 were dried overnight at 383 K. Another sample, C5, was prepared from C1 by oxidative treatment in the gas phase with 5% O_2/N_2 at 723 K for 10 h, with a burn-off of 13%.

Porosity and surface area. The texture of all supports was characterized through nitrogen adsorption. The adsorption isotherms were determined at 77 K with a Coulter Omnisorp 100 CX apparatus. Micropore volumes, W_0, mesopore surface areas, S_{me}, and the mean micropore width, L, were calculated as described previously (6).

Temperature-programmed desorption. Surface functional groups were studied by temperature-programmed desorption (TPD). The analyses were carried out in an apparatus already described elsewhere (6). The samples were submitted to a 5 K/min linear temperature rise up to 1373 K under a helium flow of 25 mL/min. A SPECTRAMASS Dataquad quadrupole mass spectrometer was used to monitor the desorption of CO and CO_2.

Point of zero charge. The point of zero charge (PZC) of the supports was determined by mass titration following the procedure proposed by Noh and Schwarz (7). Three different solutions, with initial pH values of 3, 5, and 11, were prepared from 0.1 mol/L $NaNO_3$, using 0.1 mol/L HNO_3 and 0.1 mol/L NaOH to adjust the pH. For each initial pH, seven containers were filled with 100 mL of the respective solutions, and different amounts of a support sample (0.1, 0.5, 1, 2.5, 5, 10, and 15% mass fraction of support) were added. The equilibrium pH was measured after vigorous stirring for 96 h at 298 K. For each initial pH, when the equilibrium pH values are plotted as a function of the mass fraction of the corresponding container, a plateau is found. The PZC value of each sample was taken as the average of the pH values of the three corresponding plateaus.

Impregnation and drying. The catalysts were prepared at 293 K by impregnating 1 g of carbon with 15 mL of an aqueous solution of hydrated hexachloroplatinic acid with the appropriate concentration to obtain a nominal Pt load of about 5.5 wt%. The initial pH of the impregnation solution was 1.6. After 12 h of stirring, the excess solution was removed by filtration. The catalysts were dried at 383 K and kept in a desicator until use. The catalysts were denoted Pt/C1–Pt/C5, according to their corresponding support.

Platinum content, oxidation state (TPR and XPS), and dispersion. Platinum content was determined by UV spectrophotometry at $\lambda = 261.8$ nm (8) after the carbon was burned off in air at 1273 K and the residue was dissolved in aqua regia. XPS analysis was carried out in a VG Scientific ESCALAB 200 A spectrometer using nonmonochromatized Mg$K\alpha$ radiation (1253.6 eV). Basically, the Pt4f high-resolution spectrum was analyzed for the Pt oxidation states by deconvoluting the peaks with mixed Lorentzian–Gaussian functions. Fresh catalysts reducibility was evaluated by temperature-programmed reduction (TPR). The TPR analyses were carried out in the same apparatus used for the TPD analysis, with a reductive gas flow (1% H_2/He); CO, CO_2, H_2, CH_4, and HCl were monitored. Catalyst dispersion was determined by hydrogen chemisorption at 308 K in Micromeritics ASAP 2000 equipment. Previously, the samples were submitted to an *in situ* reduction under hydrogen at 673 K for 5 h. Hydrogen isotherms were considered until 35 kPa, as hydrogen chemisorption on the supports was found to be negligible. The values for the platinum dispersion were calculated by assuming a stoichiometry (H : Pt) of 1 : 1.

RESULTS AND DISCUSSION

Characterization of the Supports

Textural properties. All supports presented quite similar nitrogen adsorption isotherms with a hysteresis loop in the desorption branch indicative of a significant mesoporosity. However, support C5 presented a higher adsorption capacity and a steeper isotherm at moderate relative pressures, showing that this samples has a more developed micro- and mesoporous structure (Table 1).

The results for samples C1–C4 show that the liquid-phase oxidation does not significantly modify the textural properties of carbon, except for the more severe HNO_3 treatment (C4), which leads to a slight decrease of the micropore volume and to an increase of the mean micropore width. These observations are in close agreement with other results reported for different carbons mildly oxidized in aqueous solutions of HNO_3, H_2O_2, NaOCl, or $(NH_4)_2S_2O_8$ (4, 6–10).

TABLE 1

Textural Properties of the Supports

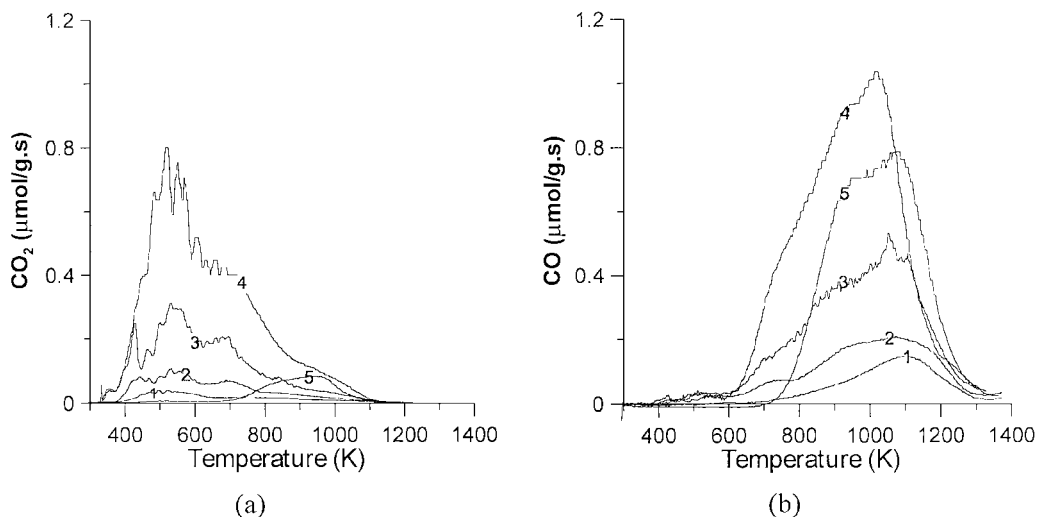| Support	S_{BET} (m^2/g)	S_{me} (m^2/g)	W_0 (cm^3/g)	L (nm)
C1	1141	122	0.440	1.05
C2	1163	128	0.443	1.05
C3	1128	125	0.452	1.00
C4	1099	116	0.400	1.25
C5	1437	143	0.578	1.25

FIG. 1. TPD spectra of the supports C1 to C5 (labeled 1 to 5 respectively): (a) CO_2 evolution; (b) CO evolution.

On the other hand, the results for supports C1 and C5 show that the gas-phase oxidation with O_2, which was accompanied by some degree of gasification, leads to an increase of the micropore volume as well as of the mesopore surface area and of the mean micropore width (6).

Functional groups of supports. Figure 1 shows the results obtained by TPD for the different supports. The support C1 presents a residual number of CO_2-evolving surface oxygen groups, while the CO_2 spectra of the HNO_3-treated supports (C2–C4) are characterized by different peaks and/or shoulders at relatively low temperatures (between 400 and 800 K), with a tail up to 1100 K. The number of CO_2-evolving surface oxygen groups, **CO_2**, measured by the areas under the spectra (Table 2), grow with the severity of the treatment, so that the most oxidized C4 support presents an appreciable number of CO_2-generating groups up to ~1100 K. On the other hand, the CO_2 spectrum of air-oxidized support C5 exhibits only a low-intensity broad peak between 700 and 1100 K, with a maximum at ~950 K.

The CO spectra of the different supports (Fig. 1b) show that CO-evolving surface oxygen groups decompose at temperatures higher than those that generate CO_2. For the supports C1–C4 the CO spectra fall in the interval 600–1300 K, with maxima between ~1000 and 1100 K; the number of CO-evolving surface groups, **CO**, increases with the severity of the treatment (Table 2). The CO spectrum of support C5 is shifted to higher temperatures with a broad maximum at ~950–1100 K. These results—namely, the ratio **CO_2/[CO_2 + CO]**, the temperature of the CO_2 peaks of the spectra for the air-char and the HNO_3-chars, and the ratio **CO/CO_2**, which is greater for the air-char than for the HNO_3-chars—are in close agreement with those presented in the literature (11). The total amount of oxygen,

O_t (wt%) (Table 2), can be taken as a measure of the degree of oxidation of the supports, allowing us to set the sequence C4 > C3 > C5 > C2 > C1.

Acidic and basic sites: PZC values. In describing the surface chemistry of carbon, two main types of oxygen surface groups are considered, acidic and basic groups (3). The analysis by TPD allows the detection of two other categories of surface oxygen groups, those that generate CO_2 and those that generate CO. The CO_2-evolving surface groups are identified with the more acidic surface oxygen complexes: carboxyl ($pK_a \sim$ 4–5), which generate CO_2 at lower temperatures (<800 K), and carboxylic anhydrides and lactones, which generate CO_2 at higher temperatures (800–1000 K). The CO-evolving surface groups, on the other hand, are identified with the less acidic surface oxygen complexes, such as phenols ($pK_a \sim$8–11), quinones, and neutral groups such as carbonyls. It should, however, be kept in mind that the carboxylic anhydrides decompose at ~800 K by releasing both CO_2 and CO (1:1) (6). The total acidity of carbon, measured by titration with NaOH or KOH, is related to the total number of surface oxygen groups, measured by TPD, in such a way that the acidity of carbon increases when the

TABLE 2

Total Amounts of CO and CO_2 Released by TPD and Values of PZC for the Supports

Support	CO_2 (mmol g^{-1})	CO (mmol g^{-1})	O_t (wt%)	CO/CO_2	PZC
C1	0.126	0.570	0.65	4.52	9.09
C2	0.380	1.082	1.47	2.85	3.95
C3	1.099	2.253	3.57	2.05	2.76
C4	2.576	4.292	7.55	1.67	1.88
C5	0.248	3.036	2.83	12.24	6.94

$$C_\pi \quad + \quad H_3O^+ \quad \rightleftarrows \quad \left[C_\pi - H_3O\right]^+$$

$$C_\pi \quad + \quad 2H_2O \quad \rightleftarrows \quad \left[C_\pi - H_3O\right]^+ + OH^-$$
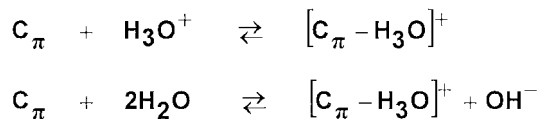
FIG. 2. Protonation of oxygen-free basic carbon sites (19).

number of its surface oxygen complexes increases and vice versa (12–16).

Oxidized carbons always contain basic surface sites in addition to the acidic functions. However, their number is usually smaller than that of the original carbon (3). The nature of the carbon surface basic sites is still a subject of discussion (17). The carbon surface basic sites are frequently associated with pyrone-like structures. Such structures, which have a $pK_b > 11$ and which decompose thermally at ~1050–1200 K, generating CO (3, 18), would present a strong electronic interaction with the surface carboxyl groups, which leads to their destruction by surface oxidation (18). Other authors are, however, of the opinion that the surface basic sites are essentially of Lewis type and are associated with π-electron-rich regions within the basal planes (13, 15, 19). According to Leon y Leon *et al.* (19), the protonation of such oxygen-free basic carbon sites would lead to an electron-donor–acceptor complex (Fig. 2), where C_π is probably a graphitized carbon surface platelet in which single π electron pairs may become partially localized as a result of the H_3O^+ addition.

In any case, the number of basic sites on carbon, as measured by titration with HCl, decreases as the total number of oxygen surface groups measured by TPD increases. This means that the surface oxidation of carbon destroys basic surface sites. Thus, according to Barton *et al.* (15), for a homologous series of oxidized carbons the increase in the number of basic sites 15 accompanied by a much larger de-

crease in acidic site concentration, with roughly six acidic sites disappearing for one basic site created.

As shown in Table 2, there is a sharp decrease of the PZC from C1 to C4 because the PZC of carbon decreases as the surface concentration of acid groups increases (16, 20). Moreover, support C5 has a PZC higher than those of supports C2–C4 but lower than that of C1. Because the PZC value was found to decrease when the carbon surface became more oxidized, it has been suggested that the PZC would be a function of the total oxygen content of the carbon O_t (13, 15). However, according to its definition, the PZC of a carbon should depend not only on its total surface oxygen but also on the nature and distribution of the surface oxygen sites. For the present work a correlation between PZC and CO_2 is found to work better than one between PZC and O_t (Fig. 3). Thus, the PZC of a carbon seems to be determined mainly by its CO_2, that is, by the concentration of the stronger surface acid sites, which is normally greater than that of the surface basic sites (21).

Characterization of the Catalysts

TPD of the fresh dried catalysts. In comparison with the TPD spectra of the supports, the desorption peaks of the CO and CO_2 spectra of the dried fresh catalysts (Fig. 4) shift to lower temperatures, with the elimination of the CO_2 groups evolving below ~400 K. Besides, the CO spectra of the fresh catalysts, mainly those prepared from the less oxidized supports, present new peaks at low temperatures (600–700 K). Another main characteristic of the TPD profiles of the catalysts is a reduction of the amount of the surface oxygen groups for the liquid-phase oxidized supports, as expressed by ΔCO and ΔCO_2, the differences between the CO and CO_2 values of the supports and those of the corresponding catalysts (Table 3).
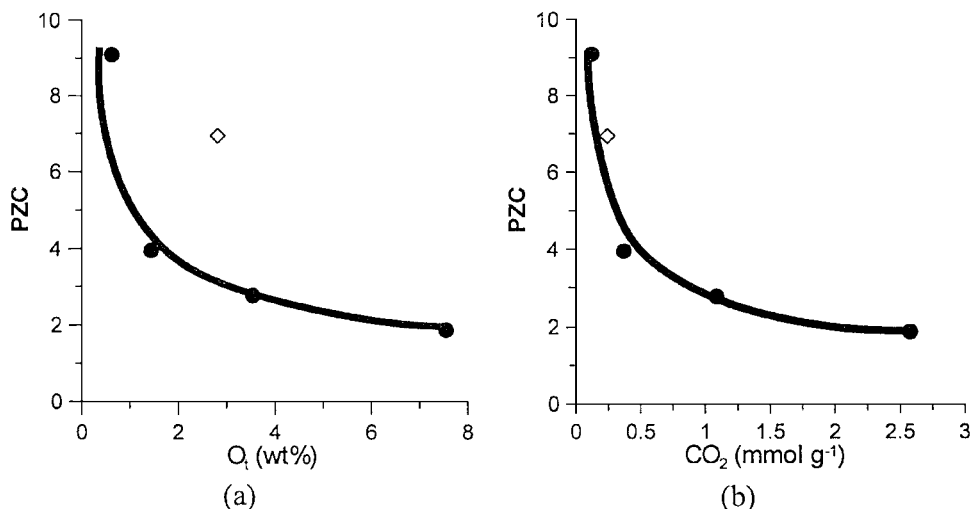

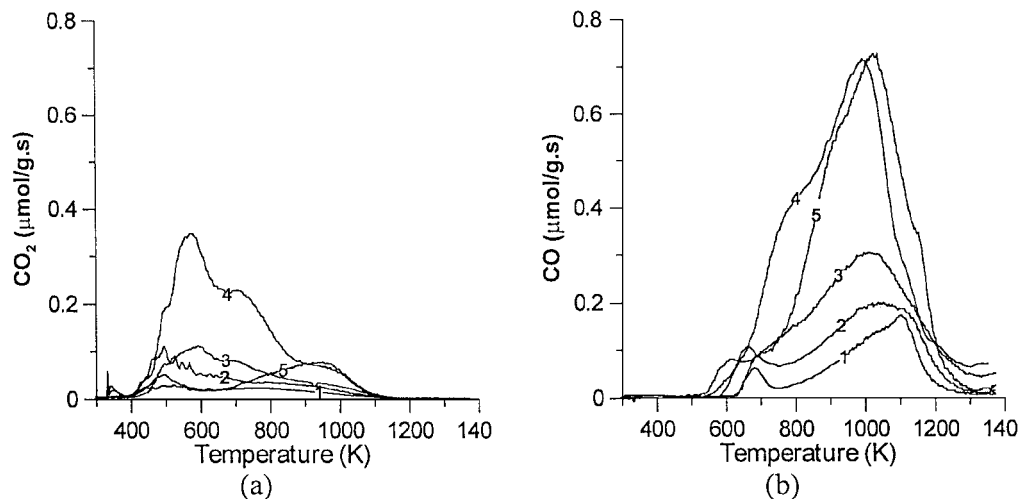**FIG. 3.** PZC values vs O_t (a) and vs CO_2 (b) [(●) C1–C4; (◇) C5].

FIG. 4. TPD spectra of the dried fresh catalysts: (a) CO_2 evolution; (b) CO evolution.

The decrease of the concentration of surface oxygen groups during impregnation can be attributed to the desorption of the less stable carboxylic groups, either originally present on the carbon surface or formed by hydrolysis of groups such as carboxylic anhydrides. Such a decrease is in apparent disagreement with literature results, which sometimes even show significant increases of **CO** and **CO2** in the TPD spectra of the fresh Pt catalysts. It should, however, be taken into consideration that the TPD spectra of the fresh catalysts obtained here cannot be directly compared with the vast majority of such spectra presented in the literature. In fact, most of the carbon-supported Pt catalysts whose characteristics have been discussed up to now in the literature were prepared using methods such as incipient wetness and impregnation with solvent evaporation or even ion exchange, which are different from the equilibrium impregnation method used in this work. On the other hand, those catalysts have been frequently prepared so that the amount of noble metal loaded on the support did not exceed ∼1 wt% (8, 22–24).

The peaks observed at low temperature (∼650 K) in the CO spectra of the fresh catalysts (Fig. 4b) are generally attributed to new types of oxygen surface groups created by the redox interaction between the carbon surface and the **PtCl$_6^{2-}$** anion during the impregnation (23).

Reduction of platinum during impregnation. Several authors have observed the presence of divalent platinum in the catalysts after impregnation of the carbon supports with aqueous solutions of H_2PtCl_6 (4, 23). The presence of Pt^{II} in the catalysts Pt/C1 to Pt/C5 after impregnation is confirmed by the results of Table 4, which were obtained by XPS analysis of the dried fresh catalysts. This partial reduction is frequently analyzed with the help of TPR studies of the fresh catalysts. The TPR profiles of the fresh catalysts (Fig. 5) show basically the presence of two H_2-consumption zones. A first hydrogen consumption peak at low temperatures (∼500 K) is attributed to the reduction of platinum species to the metallic state with the concomitant desorption of HCl. A second broader consumption peak is observed at higher temperatures, with a maximum at ∼900 K. It is generally accepted that during and after the reduction of Pt hydrogen is chemisorbed on the metal and is then spilt over the surface of the support, occupying unsaturated reactive sites originated by the decomposition of surface oxygen groups. This interpretation is confirmed by the evolution of

TABLE 3

TPD Spectra of the Fresh Catalysts

Catalyst	CO_2 (mmol g^{-1})	CO (mmol g^{-1})	ΔCO_2 (mmol g^{-1})	ΔCO (mmol g^{-1})	CO/CO$_2$
Pt/C1	0.145	0.534	−0.019	0.036	3.68
Pt/C2	0.319	1.042	0.061	0.040	3.27
Pt/C3	0.449	1.367	0.650	0.886	3.04
Pt/C4	1.228	2.679	1.348	1.613	2.18
Pt/C5	0.303	2.574	−0.055	0.462	8.50

TABLE 4

The Surface State of Platinum in the Fresh Catalysts

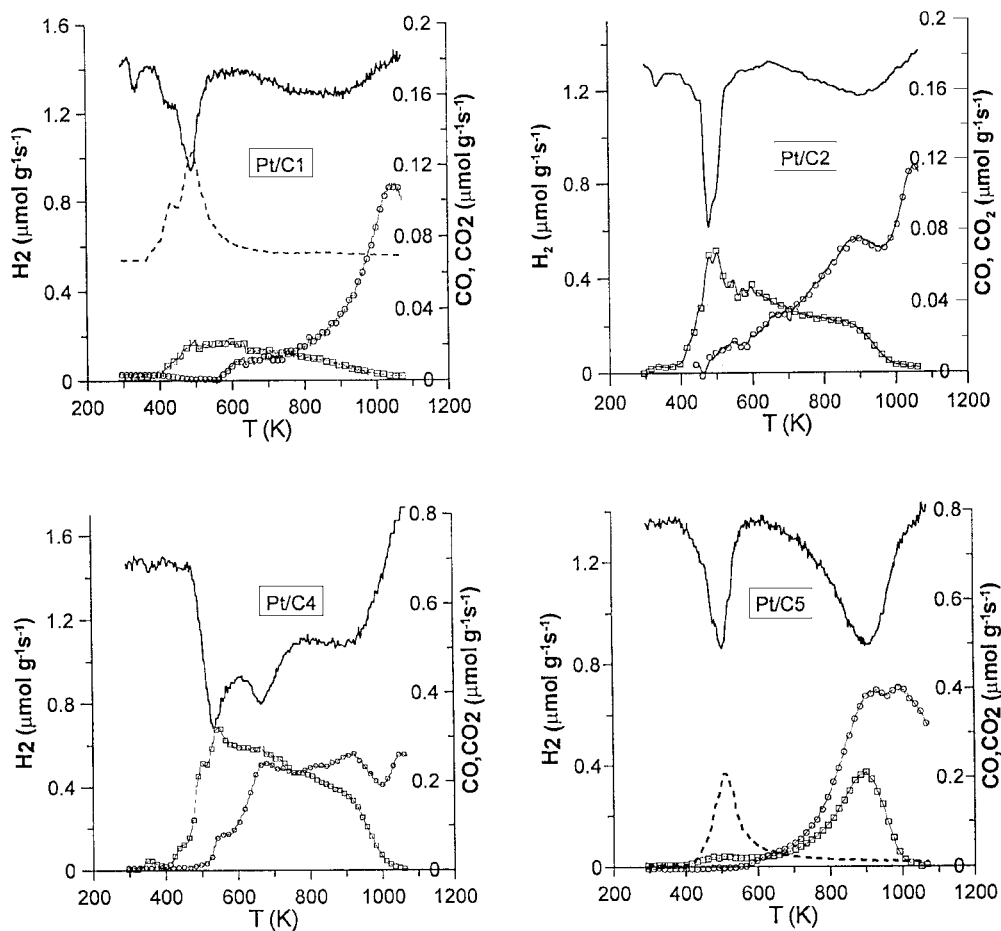| Catalyst	Pt (mmol g^{-1})	Pt^{4+} (%)[a]	Pt^{2+} (%)[a]
Pt/C1	0.294	34.78	65.22
Pt/C2	0.280	46.25	53.75
Pt/C3	0.238	52.37	47.63
Pt/C4	0.132	56.09	43.91
Pt/C5	0.300	45.41	54.59

[a] From XPS.

FIG. 5. TPR profiles of catalysts [(——) H_2; (- - -) HCl; (□) CO_2; (○) CO].

CO that occurs during the second H_2-consumption peak. The evolution of CO_2 apparently does not generate sites capable of H_2 adsorption, which agrees with the relative instability of such groups.

Table 5 shows values of the amounts of hydrogen necessary for the reduction of platinum, calculated through different methods. The relatively good agreement between the values of $H_{2, TPR}$, calculated by integration of the low-temperature peak of the TPR profiles, and of $H_{2,XPS}$, cal-

TABLE 5

Hydrogen Consumption Calculated from the Pt Content, the TPR Profiles, and the XPS Analysis of the Fresh Catalysts

Catalyst	$H_{2, \%Pt}$ (mmol g^{-1})	$H_{2, TPR}$ (mmol g^{-1})	$H_{2,XPS}$ (mmol g^{-1})
Pt/C1	0.588	0.470	0.461
Pt/C2	0.560	0.486	0.459
Pt/C3	0.476	0.468	0.400
Pt/C4	0.263	0.229	0.225
Pt/C5	0.599	0.494	0.490

culated by assuming that Pt is present as Pt^{IV} and Pt^{II} as measured by XPS, confirms again the partial reduction of Pt during the impregnation ($H_{2, \%Pt}$ is the value calculated assuming that all the Pt is present as Pt^{IV}).

Platinum content of the catalysts. Table 6 shows values of the Pt content of the catalysts after impregnation as well as the values of the dispersion. An attempt to correlate the Pt content of catalyst values with O_t failed to give a satisfactory result, mainly due to Pt/C5 (Fig. 6a). However, as shown in Fig. 6b, these values could be satisfactorily correlated with the PZC values of the corresponding supports. An alternative correlation between the Pt content of the catalysts and the acidity of the corresponding supports, as defined by their CO_2 value (Fig. 7), was derived from Figs. 3b and 6b. The Pt content of the catalysts is thus related to the oxidative treatment of the supports. Such a relationship is supported by the analysis of the adsorption isotherms of hexachloroplatinic acid on activated carbons (4, 26). These isotherms cannot be described as a Langmuir-type process, and this would indicate that Pt adsorption on the carbon surface is not a simple process (26). In fact,
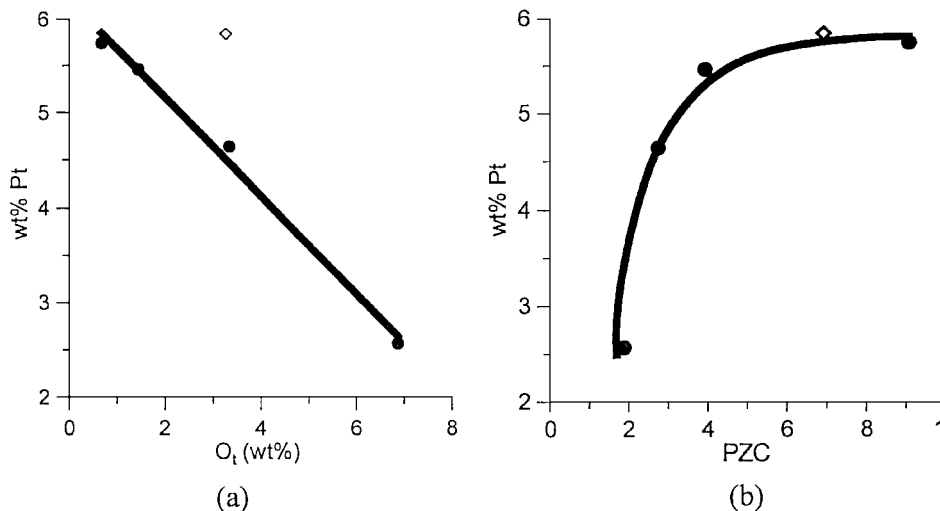
FIG. 6. Weight percentage of Pt vs (a) O_t and (b) **PZC** [(●) Pt/C1–Pt/C4; (◇) Pt/C5].

all isotherms display a first portion where H_2PtCl_6 is very strongly adsorbed and a second portion where weak adsorption appears to be occurring and is virtually independent of the surface chemistry of the carrier. Moreover, these isotherms show that the oxidative pretreatment of the carrier decreases the strong adsorption of Pt (4).

Notwithstanding the numerous studies on the role of surface functional groups in carbon-supported catalysts it must be recognized that a surface ionization model, which will quantitatively describe the surface characteristics of a carbon, still remains to be developed (15, 21, 24). Thus, the surface ionization of oxidized carbons is frequently modeled by assuming that there are surface amphoteric oxygen groups, which ionize according to equilibria as shown in Fig. 8. Here **C** denotes the carbon solid matrix and the hydroxyl groups are considered to be part of the surface
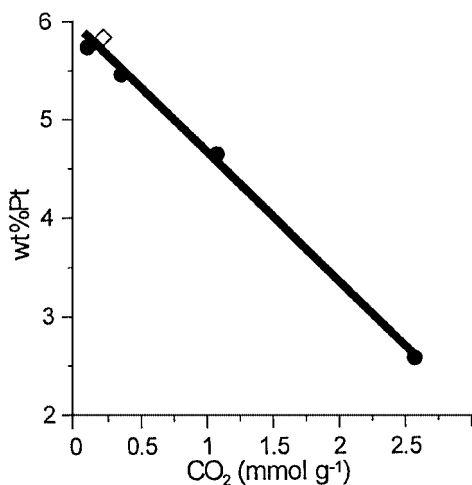
layer (23, 25). This is the same type of model used to describe the surface charging of metal oxide supports such as alumina and silica, for which some detailed models of platinum impregnation are available (27–29). The protonation of undissociated conventional acidic oxygen groups present on carbon surfaces is, however, quite unlikely to take place in aqueous solutions, due to the low pK_a values of these groups (19, 30) such as, for example,

$$RCOOH + H^+ \rightarrow RCOOH_2^+ \quad (pK_a = -6.0),$$
$$ArOH + H^+ \rightarrow ArOH_2^+ \quad (pK_a = -6.4).$$

A more realistic model for an oxidized carbon surface would thus be one based on independent acid and basic groups, which ionize according to equilibria of the type shown in Fig. 9, where **A** and **B** denote sites of the carbon solid matrix or surface oxygen groups (21).

On the other hand, according to van Dam and van Bekkum (4), a simple electrostatic mechanism cannot explain all the features of the adsorption of hexachloroplatinic acid on carbon supports with different degrees of oxidation, particularly the observed partial reduction of Pt and the influence of oxidative pretreatments of the carrier on the strong adsorption. Therefore, the authors proposed a model to describe the chemistry of the impregnation of hexachloroplatinic acid on carbon: In a first step, carbon reduces the Pt^{IV} complex to a Pt^{II} complex, **Pt(II)Cl$_4^{2-}$**, which is then coordinatively bound to the carrier (Fig. 10). The ligand site **S** is assumed to be either a π-complex structure or an oxygen surface group. Although the authors do not
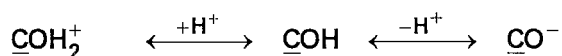

FIG. 7. Weight percentage of Pt vs **CO$_2$** of the support [(●) Pt/C1–Pt/C4; (◇) Pt/C5].

$$\underline{C}OH_2^+ \quad \xleftarrow{+H^+} \quad \underline{C}OH \quad \xleftarrow{-H^+} \quad \underline{C}O^-$$

FIG. 8. Amphoteric surface oxygen groups.

TABLE 6

Pt Content of the Catalysts and Catalyst Dispersion

Catalyst	Pt_{ads} (mmol g^{-1})	Pt (wt%)	Dispersion (%)
Pt/C1	0.294	5.74	42
Pt/C2	0.280	5.46	23
Pt/C3	0.238	4.64	11
Pt/C4	0.132	2.57	3
Pt/C5	0.300	5.84	10

$$H\underline{A} \leftrightarrow \underline{A}^- + H^+$$

$$\underline{B} + H^+ \leftrightarrow \underline{B}H^+$$
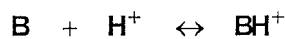
FIG. 9. Model with independent acid and basic groups.

$$H_2Pt(IV)Cl_6 + \equiv C-H + OH_2 \rightarrow Pt(II)Cl_4^{2-} + 2Cl^- + \equiv CO^- + 5H^+$$

$$Pt(II)Cl_4^{2-} + \underline{S} \rightarrow Pt(II)Cl_3\underline{S}^- + Cl^-$$
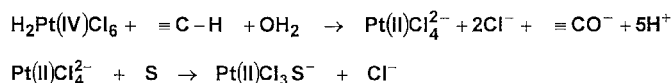
FIG. 10. The model of van Dam and van Bekkum for the adsorption of hexachloroplatinic acid on carbon (4).

a. $Pt(IV)Cl_6^{2-} + [C_\pi - OH_3]^+ \rightarrow [C-OH_2-Pt(IV)Cl_5]^- + HCl$

b. $Pt(IV)Cl_6^{2-} + [C_\pi - OH_3]^+ \rightarrow [C-O-Pt(II)Cl_3]^- + 3HCl$
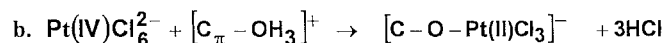
FIG. 11. Alternative models for the strong adsorption of hexachloroplatinic ion by carbon.
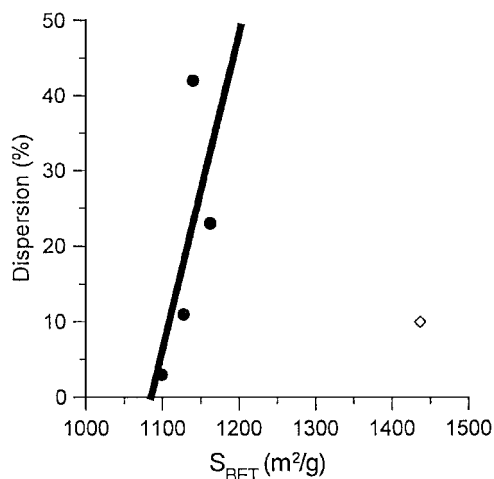

FIG. 12. Dispersion vs BET surface area of the supports [(●) Pt/C1–Pt/C4; (◇) Pt/C5].

make explicit the exact nature of such ligand sites, it is reasonable to assume that they sites are identical to the basic sites in Fig. 2. Thus, the combination of the model of van Dam and van Bekkum with the model for the ionization behavior of the carbon surface based on independent acid and basic groups (Fig. 9) leads to the conclusion that the acid oxygen surface groups should not be considered as strong anchoring sites, at least for a significant part of the platinum complexes. On the other hand, in the model of van Dam and van Bekkum the two steps of the strong adsorption of Pt, the reduction and the coordination of the platinum complex, are not directly connected, while the adsorption experiments show that the reduction of hexachloroplatinic acid takes place simultaneously with its strong adsorption (4, 26). Alternative formulations of the model of van Dam and van Bekkum for the strong adsorption of $PtCl_6^{2-}$ can be developed using the mechanism of inner-sphere adsorption (28). Figure 11a shows such an alternative model for the adsorption of $PtCl_6^{2-}$ without reduction, while Fig. 11b presents a possible adsorption model with simultaneous reduction of Pt. According to these models, surface groups would replace some of the original ligands (Cl^-) of the transition metal in solution. In the case of Fig. 11a an insertion of a water ligand (an "aquation" reaction) takes place, while for the adsorption with reduction a $C–O–Pt$ linkage would be formed (28). Because the $C_\pi–OH_3^+$ group is assumed to be one of the basic surface groups of carbon, as defined in Fig. 2, the equations of Fig. 11 should not be taken as stoichiometric ones. Besides, it has been shown by FT-EXAFS that for some Pt/carbon catalysts prepared by impregnation with hexachloroplatinic acid the strong interaction between the Pt precursor and the support is associated with a change in the Pt coordination from Cl to O atoms (31, 32). Moreover, according to the mechanisms of Fig. 11 the reduction of the number of the basic surface sites due to the oxidative pretreatments of the supports would naturally explain the observed decrease of the strong adsorption caused by those pretreatments.

Catalyst dispersion. The values obtained for the platinum dispersion are presented in Table 6. It is well known that the size and distribution of the metal crystallites ultimately produced by impregnation are affected by the physical structure (porosity and surface area) of the support. However, Fig. 12 shows that, although the BET surface area of the supports has indeed some influence on it, the dispersion of the catalysts for the present case is more strongly determined by some other factors.

The effect of the carbon surface oxidation on the dispersion of Pt/carbon and on other carbon-supported group VIII metal catalysts is certainly one of the most controversial points about the influence of carbon surface chemistry on the properties of the catalysts. The chemical nature of the carbon surface is known to influence the dispersion characteristics of carbon-supported metal catalysts. This explains
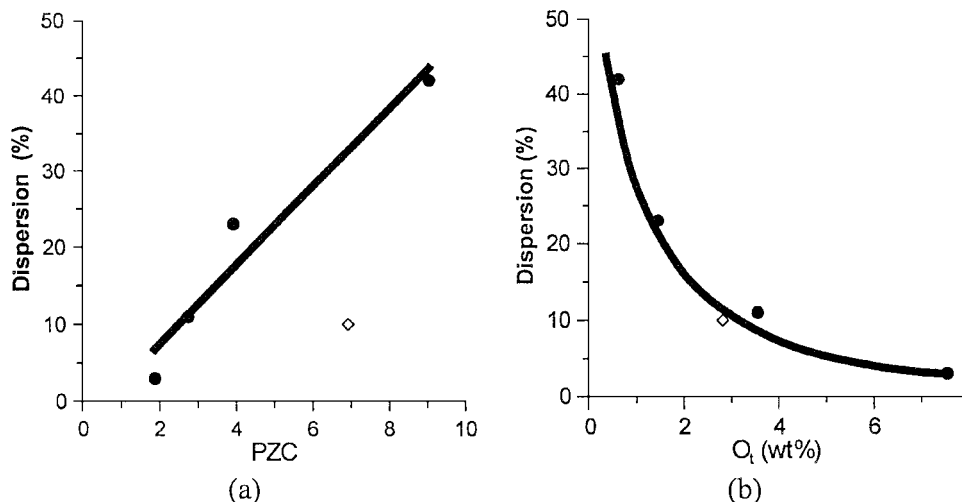
FIG. 13. Dispersion vs (a) PZC and (b) O_t [($\bullet$) Pt/C1–Pt/C4; ($\diamond$) Pt/C5].

the avalanche of studies devoted to understanding the role of the support oxygen surface groups in the preparation, dispersion, and activity of carbon-supported noble catalysts (1). However, the literature data on the role of surface functional coverage in carbon-supported catalysts are controversial and can rather unambiguous statements on the effect of the surface oxygen coverage rarely be made. Thus, for example, it was observed recently that the origin of the carbon support and the temperature of the catalyst reduction had a profound influence on the properties of Pt/carbon and Pd/carbon catalysts, while, in contrast, no unambiguous correlation between catalyst properties and the pretreatments of the respective carbon supports has been found (24, 33). Conflicting results concerning the influence of oxidative pretreatments of the carbon on the metal dispersion have regularly been reported in the literature. So, according to some references, for carbon-supported platinum catalysts prepared by impregnation both dispersion and resistance to sintering increase with the increasing number of oxygen surface groups in the support (8, 26, 32, 34). For similar catalytic systems the opposite conclusion is also reported, namely, that the presence of oxygen surface groups on carbon leads to lower metal dispersions and lower resistance to sintering (23, 31, 35, 36). Frequently, the reasons given for such behavior also differ from work to work. In this way, while most authors agree that carbon properties such as porous structure and oxygen functionalities have an important role on Pt dispersion, there is not a single carbon property that could be related to dispersion.

The results presented in Table 6 show that the dispersion decreases monotonically for the series Pt/C1 to Pt/C4. Figure 13a shows that there is indeed a correlation between the values of the dispersion of the catalysts and the PZC of the respective supports for Pt/C1 to Pt/C4, but such a correlation is not valid for catalyst Pt/C5. On the other hand, in

the present case an acceptable correlation is found between the values of the dispersion and O_t, the total surface oxygen content of the supports, as shown in Fig. 13b. The decrease of the dispersion with increasing O_t can be due either to the increase in the surface negative charge (decrease of PZC) or to the decrease in the number of initial nuclei (4).

As there is no general correlation between the dispersion of the catalysts and the PZC of the supports (Fig. 13a), the observed decrease in the dispersion should be associated with a decrease in the number of initial nuclei. That is, the number of initial nuclei decreases when the total surface oxygen of the supports increases. Furthermore, as discussed previously, when the number of surface oxygen groups increases, the number of the surface basic sites decreases. On the other hand, the assumption that the surface basic sites are anchoring sites for the strong adsorption of hexachloroplatinic acid is a natural extension of the van Dam and van Bekkum model. The correlation shown in Fig. 13b is then a natural consequence of these assumptions or, otherwise, it can be taken as a further confirmation of these assumptions.

These results can thus be rationalized by assuming that for the Pt/carbon catalysts prepared in this work by equilibrium impregnation with an aqueous solution of hexachloroplatinic acid the decrease in the dispersion with the increase in the total surface oxygen is due to the reduction of the number of surface basic sites, which are centers for the strong adsorption of $PtCl_6^{2-}$.

CONCLUSIONS

Oxidative treatments of carbon lead to the creation of surface acidic sites and to the simultaneous destruction of surface basic sites. Under normal conditions these acidic and basic sites do not have an amphoteric behavior, so that

a surface ionization model based on independent acidic and basic surface groups should be used to describe the acid–base properties of a carbon dipped in aqueous solutions.

Oxidative treatments of carbon increase its hydrophilicity, thus making its surface more accessible to the metal precursor during impregnation with aqueous solutions of the precursor. Under favorable wetting conditions electrostatic effects mainly determine the amount of Pt adsorbed by carbon in the equilibrium impregnation with an aqueous solution of hexachloroplatinic acid.

Carbon surface basic sites behave as anchoring sites for the hexachloroplatinic anion and are mainly responsible for the strong adsorption of platinum on carbon. This strong adsorption as well as the accompanying partial reduction of Pt can be described by assuming the formation of transition metal complexes involving the surface basic sites of carbon and the Pt anions.

The dispersion of Pt/C catalysts prepared by equilibrium impregnation with aqueous hexachloroplatinic acid of mildly oxidized supports derived from the same carbon (and thus having similar structures) decreases as the total surface oxygen of the support increases, due to the reduction of the number of initial nuclei.

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