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Platinum Catalysts Supported on Activated Carbons

I. Preparation and Characterization

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Several Pt catalysts supported on activated carbons (manufactured from olive stones and almond shells) have been prepared with both $H_2PtCl_6 \cdot 6H_2O$ and $[Pt(NH_3)_4]Cl_2$ as metal precursor and using different methods. Once reduced, the supported catalysts were characterized by H_2 and CO chemisorption as well as X-ray diffraction and transmission electron microscopy. The effect of reduction conditions on metal dispersion has been studied and correlated with the surface properties of the supports. The results show that porosity with sizes ranging from 9 to 11 nm is decisive for obtaining a high Pt dispersion. To increase the dispersion of the catalysts prepared from $[Pt(NH_3)_4]Cl_2$ a treatment with He prior to reduction of the catalysts in H_2 seems to be essential in order to avoid the formation of an unstable hydride which leads to agglomeration of the Pt particles. © 1986 Academic Press, Inc.

INTRODUCTION

Although most of the supports used in heterogeneous catalysis are oxides such as SiO_2 and Al_2O_3 there is a growing interest in using carbons, especially activated carbons, as supports because they are relatively inexpensive and have a large surface area and a low intrinsic catalytic activity. However, although carbon is becoming a commercial support of growing interest, especially for Group VIII metals in hydrogenation reactions (*1*), most of the carbon-supported catalysts are prepared at the laboratory level (*2*). Much still needs to be done to explore the preparation of carbons with large textural differences in order for them to be used as supports for new catalysts. For instance, by relating the surface properties of the carbon with the supported metal dispersion it will be possible to design catalysts with different catalytic activities (*3*). In this sense, Walker and co-workers (*4–7*) have shown that, for Pt supported on a graphitized carbon black, the increase in surface area and heterogeneity of the carbon leads to a larger Pt dispersion.

On the other hand, the pore size distribution of the carbon may condition the diffusion of reactants and products, changing the activity and selectivity of the catalyst; thus, certain molecular sieve carbons have been used as catalyst supports to control the product distribution of the reaction (*8–11*).

One of the problems found when using activated carbons as catalyst supports is their large ash content which, after the activation process, is concentrated on their surface (*4*); these inorganic constitutents may interact with the metal, affecting its catalytic activity and sintering resistance (*12*) and even catalyzing secondary reaction. With this in mind, we have been developing in the last few years a series of

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activated carbons from agricultural byproducts such as olive stones and almond shells (*13–16*); these activated carbons have a very low ash content (<0.2%), no sulfur, and a large surface area (which can be conveniently modified by simple treatments).

Some of these carbons have been selected to prepare supported metal catalysts using a metal loading of 1% Pt; platinum has been chosen because, being the most widely used metal catalyst, it will allow a better comparison of the results obtained.

It is known that the properties of supported metal catalysts such as metal dispersion and catalytic activity are a function of the experimental procedure used in their preparation (*17*). Thus, only if all the effects due to the variables that can be introduced in the preparation are well known will one be able to select those most appropriate for preparing a catalyst with the best characteristics (*18*).

In the present paper we describe the effect of the surface properties of the carbons and the preparation method of the catalysts and metal compound used on the dispersion of the Pt in the supported catalysts. These catalysts will later be studied from the point of view of their behavior in the hydrogenolysis of *n*-butane and this will constitute the subject of the next paper of the series.

EXPERIMENTAL

A. Supports

The activated carbons used as supports have been prepared from almond shells and olive stones using a direct activation in a flow of CO_2 under different experimental conditions (*19*) to produce a wide range of surface properties. The nomenclature of the supports include C (from almond shells) or H (from olive stones) followed by a number (1 to 5) indicating the increasing degree of activation. The characterization of the supports has been carried out by means of adsorption of N_2 (77 K) and CO_2 (273 K) and mercury porosimetry (Carlo Erba 200), as described in previous papers for similar activated carbons (*13–16, 19*). The ash content has been determined by burning away the carbon in air at 973 K for 3 h and weighing the residue.

B. Catalysts

Two different compounds, $H_2[PtCl_6] \cdot 6H_2O$ (from J. T. Baker) and $[Pt(NH_3)_4]Cl_2$ (Alfa Ventron), have been used as metal precursors in the preparation of the catalysts. The precursor was deposited on the support following (i) an incipient wetness technique (*20*), using either a mixture of benzene and ethanol (4 : 1 in volume) or distilled water as solvents and (ii) a soaking technique in which the contact between the support and the solution is much longer. The latter method was carried out as follows (*20, 21*). A certain amount of carbon was added to a solution of the metal compound kept under continuous stirring and the solvent was evporated by passing a flow of nitrogen through the system. The solvents used in this soaking method were mixtures of benzene and ethanol (4 : 1 in volume) in the ratio of 1 g of carbon to 50 cm^3 of solution or distilled water (1 g of carbon to 10 cm^3 of solution). With the latter, the addition of NH_4OH was used in some cases to make the solution slightly basic.

The catalysts prepared by any of these procedures were dried overnight in an oven at 383 K and were later kept in a desiccator over P_2O_5 until use.

In all cases the metal compound-to-carbon ratio was selected so that the final metal loading of the catalysts was around 1% platinum. Analysis of the metal loading was carried out by atomic absorption spectrometry (Pye Unicam SP1900).

Table 1 lists the supports, impregnation method, and other variables used in the preparation of the catalysts and their Pt content.

The catalysts were reduced, before their characterization by chemisorption, using a flow of H_2 (3 liters h^{-1}) at 673 or 773 K for 1

TABLE I

Description of the Catalysts

Catalyst	Support	Impregnation method	Solvent	Metal precursor
C1–0.94% Pt	C1	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C2–0.85% Pt	C2	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C3–0.89% Pt	C3	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C4–0.96% Pt	C4	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C1A–1.05% Pt	C1	Soaking	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C1(H_2O)–1.10% Pt	C1	Incipient	Water	$H_2PtCl_6 \cdot 6H_2O$
C2–0.85% Pt	C2	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C2A–0.92% Pt	C2	Soaking	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C3–0.89% Pt	C3	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
C3(H_2O)–0.91% Pt	C3	Incipient	Water	$H_2PtCl_6 \cdot 6H_2O$
C3–1.32% Pt(N)	C3	Incipient	Water	$Pt(NH_3)_4Cl_2$
C3A–0.68% Pt(N)	C3	Soaking	Water	$Pt(NH_3)_4Cl_2$
C3Ab–1.18% Pt(N)	C3	Soaking	Water (NH_4OH)	$Pt(NH_3)_4Cl_2$
C3oxA–1.26% Pt(N)	C3ox	Soaking	Water	$Pt(NH_3)_4Cl_2$
C3ox500A–0.73% Pt(N)	C3ox500	Soaking	Water	$Pt(NH_3)_4Cl_2$
H1–0.91% Pt	H1	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
H2–0.93% Pt	H2	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
H3–0.88% Pt	H3	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
H4–0.80% Pt	H4	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$
H5–0.86% Pt	H5	Incipient	Benzene–ethanol	$H_2PtCl_6 \cdot 6H_2O$

or 12 h; the experimental cycle described in Ref. (*22*) was used to reach the reduction temperature. Once the samples were reduced they were outgassed for 1 h at 50 K below the reduction temperature to a final pressure of 10^{-6} Torr (1 Torr = 133 Pa) and later brought to 298 K, the temperature of chemisorption.

The chemisorption of H_2 and CO was determined in a grease-free volumetric system equipped with a Baratron sensor from MKS to measure the pressure (*23*). The hydrogen (99.9995%) was further purified using an oxygen trap (Regis Chemicals Co.), a drying agent (drierite), and a 0.5-nm molecular sieve. The carbon monoxide (99.97%) was purified in a similar way and the helium used for calibrations was used without further purification. The method of Benson and Boudart (*24*) and Wilson and Hall (*25*) in which the linear portion of the isotherm, determined between 50 and 250 Torr, is extrapolated to zero pressure has been used to determine the hydrogen uptake. For the chemisorption of CO the dual technique of Yates and Sinfelt (*26*) has been used: this consists of determining the CO isotherm in the range 50–250 Torr, evacuating for 2 min at 298 K, and measuring a second isotherm. Subtraction of the two isotherms at 100 Torr pressure gave the amount of CO chemisorbed on the metal.

H_2 and CO uptakes have been used to determine the metal dispersion D by assuming that one hydrogen atom or one CO molecule is chemisorbed on a surface platinum atom. The average Pt particle size $\bar{d}$ has been calculated (*24*) from $\bar{d} = 1.08/D$ nm.

The average particle size has also been determined by X-ray line broadening (XRD) and transmission electron microscopy (TEM). X-ray experiments were carried out in a Philips PW1730 diffractometer using Cu$K\alpha$ radiation; the selected peak was that corresponding to the (111) plane, and the Scherrer equation with the Warren correction was applied. Electron microscopy studies of the catalysts were con-

TABLE 2

Surface Characteristics of the Supports

Support	Burn-off (wt%)	Ash (wt%)	S (m^2 g^{-1})		S_{CO_2}/S_{N_2}	Pore volume (cm^3 g^{-1})		Hg density (g cm^{-3})
			S_{N_2}, 77 K[a]	S_{CO_2}, 273 K[b]		Micropores V_0^c	V_p, $\phi > 7.5$ nm[d]	
C1	76	0.10	659	672	1.02	0.29	0.10	1.17
C2	78	0.10	777	834	1.07	0.36	0.13	1.08
C3	81	0.12	918	944	1.03	0.41	0.20	0.96
C4	83	0.13	1118	1034	0.92	0.45	0.22	0.89
H1	73	—	352	573	1.63	0.25	0.10	—
H2	75	0.09	519	651	1.26	0.28	0.14	1.04
H3	78	0.10	690	807	1.17	0.35	0.21	0.93
H4	82	0.10	890	959	1.08	0.41	0.29	0.86
H5	85	0.13	1092	1084	0.99	0.47	0.33	0.78

[a] BET equation.
[b] Dubinin–Raduskevich (DR) equation.
[c] Adsorption of CO_2, DR equation.
[d] Mercury porosimetry.

ducted using a Philips EM300 operated at 100 kV; samples were dispersed ultrasonically in toluene and spread over self-perforated microgrids. In order to obtain meaningful data at least 2000 particles of platinum were measured for each catalyst. Direct magnification was $10^5\times$, and platinum particles were measured at a final magnification of $4 \times 10^5\times$.

RESULTS AND DISCUSSION

A. Characterization of Supports

Some of the surface characteristics of the supports are listed in Table 2. The ash content shown also in Table 2 is very low in all the supports although it slightly increases with increasing activation. The low ash content is an attractive feature of these carbons because secondary reactions will be less probable; moreover, the low ash content may mean a low resistance to metal particle sintering in the resulting catalyst (*12*).

The apparent surface areas of the carbons cover a wide range and they are very similar for carbons of the two series with similar burn-off. As shown in Table 2, the S_{CO_2}/S_{N_2} ratio is larger than unity for samples H1, H2, and H3 in which the adsorption of N_2 at 77 K is a restricted process (from a kinetic point of view) on micropores with dimensions similar to those of the adsorbate (*15*); the higher temperature of the CO_2 adsorption (273 K) makes the entrance of this molecule (with dimensions similar to those of the N_2 molecule) much easier. Upon further activation the micropores are widened and they become equally accessible to both adsorbates. As in similar carbons (13–16), for apparent surface areas larger than 1000 m^2 g^{-1} the S_{CO_2}/S_{N_2} ratio becomes lower than unity because the micropores are widened and while N_2 is still filling them as liquid, CO_2 is only covering their walls (*27, 28*). These results show that all carbons are essentially microporous and not too different in this respect from one series to another (except for samples H1, H2, and H3, with a narrower microporosity) for comparable degrees of burn-off. This is not the case for the pore volume measured by mercury porosimetry ($\phi > 7.5$ nm) since this pore volume is always larger in carbons of series H although it increases with burn-off in both series (see Table 2).

TABLE 3

Chemisorption Data and Mean Particle Size of Catalysts (Series C)

Catalyst	Reduction conditions		Uptake (μmol ads g cat^{-1})		Dispersion D		Particle size, $\bar{d}$ (nm)	
	T (K)	t (h)	H_2	CO	H/Pt	CO/Pt	H/Pt$_s$	CO/Pt$_s$ = 1/1
C1–0.94% Pt	673	1	4.6	8.5	0.19	0.18	5.7	6.0
	673	12	4.4	9.0	0.18	0.19	6.0	5.7
	773	1	3.8	8.0	0.16	0.17	6.8	6.4
	773	12	1.8	4.0	0.07	0.08	15.4	13.5
C2–0.85% Pt	673	1	10.1	15.0	0.47	0.35	2.3	3.1
	673	12	11.4	15.5	0.51	0.35	2.1[a]	3.1
	773	1	11.0	17.0	0.52	0.40	2.1	2.7
	773	12	4.9	11.5	0.23	0.27	4.7	4.0
C3–0.89% Pt	673	1	9.8	14.0	0.43	0.31	2.5	3.5
	673	12	9.6	13.0	0.42	0.28	2.6[b]	3.9
	773	1	9.0	13.0	0.39	0.28	2.8	3.9
	773	12	5.6	11.0	0.25	0.24	4.3	4.5
C4–0.96% Pt	673	1	7.0	10.0	0.28	0.20	3.8	5.3
	673	12	7.4	12.0	0.30	0.24	3.6	4.5
	773	1	9.0	14.0	0.37	0.28	3.0	3.9
	773	12	4.6	10.0	0.19	0.20	5.7	5.3

[a] The average particle size from TEM is 2.0 nm.
[b] The average particle size from TEM is 2.9 nm.

B. Characterization of Catalysts

1. Effect of the reduction conditions and surface properties of the carbons on the Pt dispersion. In this section results obtained with the catalysts prepared from hexachloroplatinic acid dissolved in a benzene–ethanol mixture following an incipient wetness technique are presented.

In order to learn about the effect of the reduction conditions on the characteristics of the supported metal, two different temperatures (673 and 773 K) and two different durations of reduction (1 and 12 h) have been used. The results obtained for the dispersion and average metal particle size of the catalysts reduced under these conditions are listed in Tables 3 and 4. The same type of experiments was conducted with some of the supports but the chemisorption of either H_2 or CO was always nil. Another factor that can influence the uptake of H_2 or CO is the duration of the outgassing of the catalysts once they have been reduced in flowing H_2. Table 5 shows the results obtained for sample C2–0.83% Pt which was outgassed (always at 50 K below the reduction temperature) for either 1 or 5 h and it is clear that there is not a significant variation in the dispersion obtained with either length of reduction, in agreement with previous reports (*20*). Consequently, all the results given in Tables 3 and 4 have been obtained after outgassing the reduced catalysts for 1 h prior to the chemisorption experiments; this seems to be sufficient to clean the platinum surface of the catalyst.

The results in Tables 3 and 4 show that the dispersion obtained is a function of the reduction treatment followed and the carbon used as support; moreover, although the H/Pt and CO/Pt ratios are quite coincident for some catalysts the difference becomes large for others, the CO/Pt ratio always being smaller in these cases. The use of CO to determine the catalyst dispersion may present problems because although it is selectively chemisorbed on the metal it

TABLE 4

Chemisorption Data and Mean Particle Size of Catalysts (Series H)

Catalyst	Reduction conditions		Uptake (μmol ads g cat^{-1})		Dispersion D		Particle size, $\bar{d}$ (nm)	
	T (K)	t (h)	H_2	CO	H/Pt	CO/Pt	H/Pt_s	CO/Pt_s = 1/1
H1–0.91% Pt	673	12	9.8	14.5	0.42	0.31	2.6	3.5
H2–0.93% Pt	673	1	9.8	14.5	0.41	0.30	2.6	3.6
	673	12	11.9	16.0	0.50	0.34	2.2	3.2
	773	1	9.6	14.0	0.40	0.29	2.7	3.7
	773	12	5.6	10.0	0.23	0.21	4.7	5.1
H3–0.88% Pt	673	1	8.4	12.0	0.37	0.27	2.9	4.0
	673	12	8.0	10.5	0.35	0.23	3.1	4.7
	773	1	7.8	13.0	0.35	0.29	3.1	3.7
	773	12	6.2	12.0	0.27	0.27	4.0	4.0
H4–0.80% Pt	673	1	5.6	8.0	0.27	0.20	4.0	5.4
	673	12	6.8	10.0	0.33	0.24	3.3	4.5
	773	1	6.6	10.0	0.32	0.24	3.4	4.5
	773	12	4.8	10.0	0.23	0.24	4.7	4.5
H5–0.86% Pt	673	1	6.8	10.0	0.31	0.23	3.5	4.7
	673	12	5.8	9.0	0.26	0.20	4.2	5.4
	773	1	5.5	9.0	0.25	0.20	4.3	5.4
	773	12	5.1	11.0	0.23	0.25	4.7	4.3

may bond in either linear or bridged form (*29*). For unsupported Pt (*30*) the CO uptake is twice that of H_2, indicating a linear bonding; however, Eischens and Pliskin (*31*) have shown that both linear and bridged forms are present in supported Pt and that their proportion is a function of the support; thus, up to 15% of bridged bonding is present in Pt/SiO_2 catalysts whereas almost 50% is found in Pt/Al_2O_3 catalysts, the difference being due to the fact that Al_2O_3 can donate electrons to the metal more readily. On the other hand, Gruber (*32*) has reported that the mechanism of CO chemisorption on supported Pt also depends on the dispersion and, thus, the fraction of the bridged form on Pt/Al_2O_3 catalysts decreases with metal dispersion. However, it seems that for other supported Pt catalysts (*33–35*) the bridged form is favored in large metal crystallites and the linear form in very dispersed catalysts.

TABLE 5

Effect of Outgassing Conditions on Uptake (Catalyst: C2–0.83% Pt)

Reduction conditions		Outgassing time (h)	Uptake (μmol ads g cat^{-1})		Dispersion, D	
T (K)	t (h)		H_2	CO	H/Pt_s	CO/Pt_s = 1/1
773	1	1	11.0	17.0	0.52	0.40
773	1	5	11.8	17.0	0.55	0.40
773	12	1	4.9	11.5	0.23	0.27
773	12	5	5.4	10.0	0.25	0.23

The chemisorption of hydrogen at room temperature on supported Pt is dissociative and it seems that one hydrogen atom is bonded to one platinum atom, independently of the metal dispersion and the support used (*2, 36, 37*). However, some supported platinum catalysts exhibit spill-over (*38–40*) and this leads to erroneous results since the hydrogen chemisorbed on the metal migrates to the support giving too large uptakes of hydrogen. This phenomenon has not been detected in the catalysts

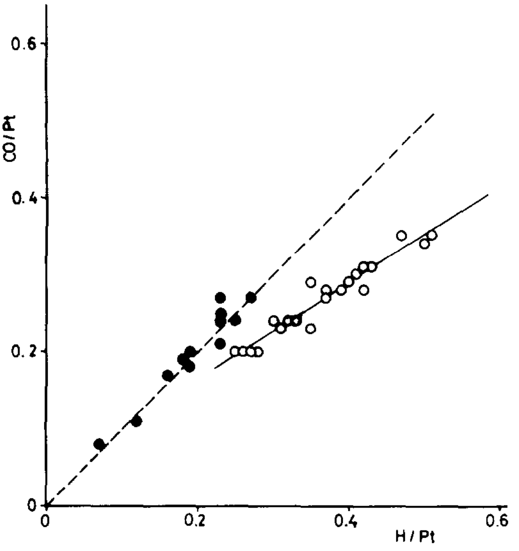

FIG. 1. Comparison of CO/Pt and H/Pt ratios: ●, experimental points giving a slope of unity; ○, experimental points giving a slope of 0.62.

described here. Furthermore, the chemisorption of H_2 by Pt catalysts may be also complicated by the fact that one surface Pt atom may be bound to more than one H atom in highly dispersed catalysts, as has been recently shown with the Euro Pt1 catalyst (*41*), but in our case the two catalysts with higher dispersion (Table 3) present an average metal particle size (by TEM) very close to that found when using H_2 chemisorption by the method of extrapolation to zero pressure and assuming that one H atom is chemisorbed on each surface Pt atom. Consequently, the results obtained with this gas can be taken as more accurate than those of CO in our case. In this sense, it is interesting to compare the dispersions obtained with both adsorbates and this has been done in Fig. 1 where the CO/Pt values have been plotted versus H/Pt for all the catalysts. There is a good correlation for H/Pt and CO/Pt ratios up to around 0.25 since the experimental points approximately fit a straight line of slope unity. However, for larger dispersions (smaller particle sizes) the CO/Pt ratios become lower than the corresponding H/Pt ratios; the best-fit line for the experimental points in the range 0.25–0.50 has a slope of 0.62 implying that on average only 0.62 CO molecule is chemisorbed per platinum surface atom; in other words, in this range of metal dispersion, either there is a growing participation of the bridged CO chemisorption or the increasing dispersion develops crystallographic planes in the platinum particles in which the packing of linearly chemisorbed CO molecules decreases.

This increase in bridge-bonding participation with increasing dispersion seems to be contradictory to the results of Dorling and Moss (*33*) mentioned above, but one should bear in mind that they used Pt/SiO_2 catalysts and that their maximum dispersion (calculated from their data) was 0.25. Our results are more similar to those described by Gruber (*32*) for Pt/Al_2O_3 catalysts. As is well known, carbon is an electronic conductor and consequently may facilitate electronic transfer toward Pt; the effect will be more pronounced with decreasing metal particle size. This would lead to an enhancement of the bridge-bonded CO since this configuration would require the electronic donation from Pt. It is also possible to assume that the proportion of atoms placed at edges and imperfection of the crystallites will be greater for smaller particle sizes, favoring the bridge form. However, the results found with our catalysts will require further investigations to clarify their behavior in CO chemisorption. In view of these uncertainties on CO chemisorption, from now on the discussion will be centered on the results obtained with H_2 chemisorption.

The effect of the reduction conditions on catalyst dispersion may be seen in the results of Tables 3 and 4. The dispersion (*D*) values obtained for a given catalyst are very similar when the reduction in hydrogen has been carried out for 1 or 12 h at 673 K or 1 h at 773 K. However, there is a considerable decrease in *D* values when the reduction takes place for 12 h at 773 K. This sintering of the platinum particles de-

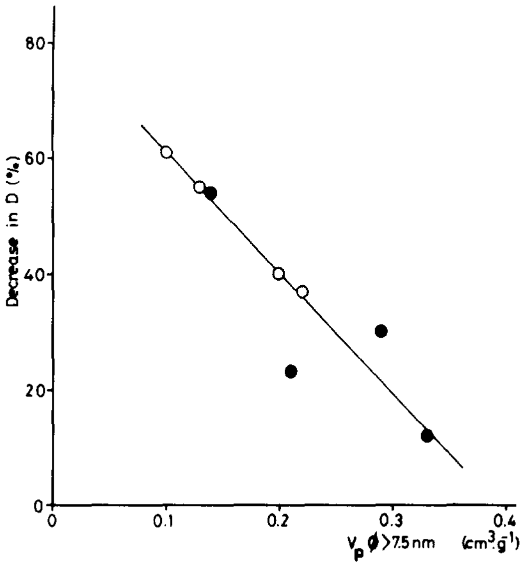

FIG. 2. Percentage of decrease in dispersion as a function of pore volume ($\phi > 7.5$ nm): ●, series H; ○, series C.

creases in both series as the pore volume of the support increases; thus, if the data for the reductions carried out for 12 h at 673 and 773 K are compared (see Tables 3 and 4) one finds that the percentage of reduction in *D* varies from 61% for C1–0.94% Pt to 37% for C4–0.96% Pt and from 54% for H2–0.93% Pt to 12% for H5–0.86% Pt. Since the microporosity of the support does not play an important role in platinum dispersion because of its inaccessibility to the platinum compound used as precursor (it should be remembered that the incipient wetness technique was used for the preparation of the catalysts), these results indicate that an increase in the meso- and macropore volume leads to a lower sintering of the metal particles. On the other hand, the previous comparison also indicates that the sintering seems to be, in general, less pronounced for catalysts prepared using supports prepared from olive stones (series H). However, when the percentage decrease in *D* is plotted versus the pore volume measured by mercury porosimetry ($\phi > 7.5$ nm) one finds (Fig. 2) that the experimental points fit a straight line, meaning that, for either of the two carbons, the reduction in sintering would be the same for a given pore volume. All these results lead us to choose the reduction at 673 K for 12 h as the best for all further studies on these catalysts since the sintering is lower and the duration of reduction is enough to ensure total reduction of the metal precursor.

In order to relate the dispersion of the catalysts to the surface characteristics of the support, the *D* values can be plotted versus the apparent surface area or the pore volume for certain pore size ranges. Because, as mentioned above, these activated carbons are very microporous and the microporosity is not accessible to the metal precursor due to the preparation method used, the plots for surface area or micropore volume are not adequate. For this reason the *D* values for all catalysts have been plotted in Fig. 3 versus the pore volume measured by mercury porosimetry ($\phi > 7.5$ nm). The experimental points for both series of catalysts seem to indicate that the maximum dispersion is obtained for a pore volume of about 0.13 cm^3 g^{-1}. Since the catalyst supported on carbon C1 (with the lowest pore volume) has the lowest dispersion, the support was further activated following a procedure (*42*) in which chemisorption of oxygen at 473 K and heating in N_2 at 1048 K are repeated several times up to an 11% burn-

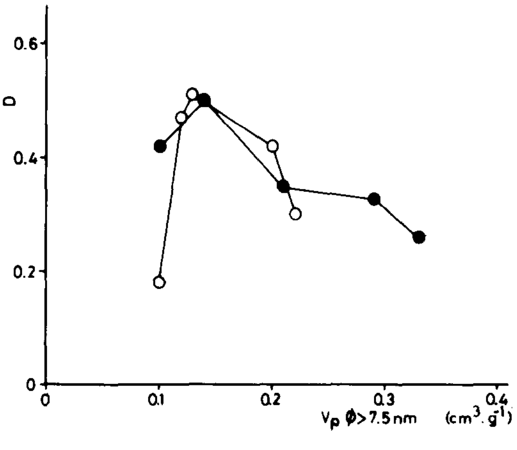

FIG. 3. Metal dispersion vs pore volume ($\phi > 7.5$ nm): ●, series H; ○, series c.

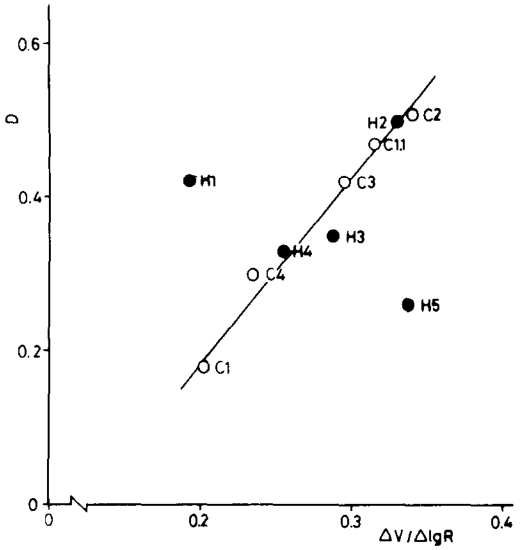

FIG. 4. Metal dispersion vs $\Delta V/\Delta \log R$: ●, series H; ○, series C.

off; the resulting sample is the support C1.1 for which the pore volume measured by mercury porosimetry is 0.12 $cm^3 g^{-1}$ (it was 0.10 $cm^3 g^{-1}$ for the original C1). When the new carbon is used as support, the resulting catalyst (C1.1–0.79% Pt) has a dispersion of 0.47 instead 0.18 for the C1–0.94% Pt, and more similar to that of catalyst C2–0.85% Pt, with comparable pore volume.

Because of the shape of the plot in Fig. 3, with a maximum of dispersion for a given pore volume ($\phi > 7.5$ nm) of the support, it was thought that there could be a critical pore size that could condition the dispersion of the metal. For this reason, the pore size distributions obtained by mercury porosimetry (plots of $\Delta V/\Delta \log R$ vs mean radius, $\overline{R}$) were analyzed to see if they had a common well-defined and distinctive maximum for all supports. The resulting maximum corresponded to a diameter of around 10 nm (these peaks of the pore size distributions were the largest and, at the same time, narrow, typically in the pore size range 9–11 nm). These peaks showed the same development with increasing activation of the carbon as the dispersion, i.e., increasing in the first stage and decreasing thereafter. Thus, if the dispersion of the catalysts is plotted versus $\Delta V/\Delta \log R$, as in Fig. 4, the resulting plot is a straight line (only two of the ten catalysts were well out of the line), meaning that the dispersion increases with the number of pores with dimensions ranging from 9 to 11 nm, as should be expected.

2. Effect of different preparation conditions of the catalysts on the Pt dispersion. Data in Table 6 show that when the catalysts were prepared by the incipient wetness technique from hexachloroplatinic acid dissolved in either a benzene–ethanol mixture or water or by the soaking technique in the former mixture there was no

TABLE 6

Influence of the Preparation Method on Metal Dispersion (Reduction at 673 K for 12 h)

Catalyst	Gas uptake (μmol ads g cat^{-1})		Dispersion, D		Particle size, $\bar{d}$ (nm)	
	H_2	CO	H/Pt	CO/Pt	H/Pt_s	CO/Pt_s = 1/1
C1–0.94% Pt	4.4	9.0	0.18	0.19	6.0	5.7
C1A–1.05% Pt	5.0	9.0	0.19	0.17	5.7	6.4
C1(H_2O)–1.10% Pt	5.8	11.0	0.21	0.20	5.7	5.4
C2–0.85% Pt	11.4	15.5	0.51	0.35	2.1	3.1
C2A–0.92% Pt	10.0	14.0	0.42	0.30	2.6	3.6
C3–0.89% Pt	9.6	13.0	0.42	0.28	2.6	3.9
C3(H_2O)–0.91% Pt	9.5	13.0	0.41	0.28	2.6	3.9

TABLE 7

Characteristics of the Catalysts from $[Pt(NH_3)_4]Cl_2$ (Reduction at 673 K for 12 h)

Catalyst	Gas uptake (μmol ads g cat^{-1})		Dispersion, D		Particle size, $\bar{d}$ (nm)		XRD
	H_2	CO	H/Pt	CO/Pt	H/Pt_s	CO/Pt_s = 1/1	
C3–0.89% Pt	9.6	13.0	0.42	0.28	2.6	3.9	[a]
C3–1.32% Pt(N)	2.6	4.0	0.08	0.06	13.5	18.0	14.1
C3A–0.68% Pt(N)	2.1	4.0	0.12	0.11	9.0	9.8	12.0
C3Ab–1.18% Pt(N)	2.4	4.0	0.08	0.07	13.5	15.4	14.1
C3oxA–1.26% Pt(N)	1.2	3.0	0.04	0.05	27.0	21.6	18.2
C3ox500A–0.73% Pt(N)	1.0	3.0	0.05	0.08	21.6	13.5	22.3
C3A–0.68% Pt(N)[b]	11.8	13.8	0.68	0.40	1.6	2.7	[a]
C3ox500A–0.73% Pt(N)[b]	3.5	6.0	0.19	0.16	5.7	6.7	—

[a] The average particle size from TEM: C3–0.89% Pt, 2.9 nm; C3A–0.68% Pt(N), 1.6 nm.

[b] Following treatment with He prior to the reduction in H_2 at 673 K for 12 h (see text).

appreciable change in the dispersion of Pt in the supported catalysts. This finding may seem surprising since in one case (benzene–ethanol) the precursor is not dissociated whereas in the other (water) it will be dissociated and one could expect that in the former the dispersion would be larger because the interaction of the $H_2[PtCl_6] \cdot 6H_2O$ with the surface should be nonspecific. The results found seem to indicate that in these carbon supports the interaction of hexachloroplatinic acid is nonspecific, probably because the number of oxygen surface complexes is low (*43*); in fact the pH values of these two carbons (C1 and C3) are 8.26 and 8.20, respectively (*44*). This is logical since the carbons were prepared by activation in CO_2 and it is known (*45*) that this activating agent leads to the development of porosity without appreciably creating oxygen surface complexes.

The data for the catalysts prepared using $[Pt(NH_3)_4]Cl_2$ as precursor are included in Table 7 (this precursor was used dissolved only in water); for the sake of comparison, the data for catalyst C3–0.89% Pt are also included (it should be remembered that this catalyst, prepared using hexachloroplatinic acid dissolved in benzene–ethanol, had the same dispersion as catalyst C3(H_2O)–0.91% Pt, prepared with the same compound dissolved in water). Comparison of catalysts C3–0.89% Pt and C3–1.32% Pt(N) shows that the metal dispersion of the latter is about a fifth of the former. Such a difference in metal dispersion cannot be explained in terms of the larger platinum content of the C3–1.32% Pt(N) and must be related to the type of compound used as precursor.

In order to see the effect of the two impregnation methods used in the preparation of the catalysts one can compare catalyst C3–1.32% Pt(N), prepared by the incipient wetness technique, with catalyst C3A–0.68% Pt(N), prepared by the soaking technique; the results in Table 7 indicate that the latter has a slightly larger metal dispersion but in this case this difference can be due just to the lower metal loading of this catalyst with respect to the former.

Benesi *et al.* (*46*) have reported, for Pt/SiO_2 catalysts, a considerabe increase in metal dispersion when NH_4OH is added to a solution of $[Pt(NH_3)_4]Cl_2$ to obtain a pH around 9 because the adsorption of $[Pt(NH_3)_4]^{2+}$ is enhanced. For this reason the catalyst C3Ab–1.18% Pt(N) was prepared as indicated in Table 1, but the results of Table 7 show that the metal dispersion is the same as in catalyst C3–1.32% Pt(N). The reason for this behavior must lie, again, in the fact that the carbon support is poor in oxygen surface complexes.

Since the compound $[Pt(NH_3)_4]Cl_2$ will be dissociated in aqueous solution the next step was to introduce oxygen surface complexes of acid character to try to increase the adsorption capacity toward the platinum compound. For this reason the catalyst C3oxA–1.26% Pt(N) was prepared by treating carbon C3 with nitric acid (10 cm^3 of concentrated acid/g of carbon) and the catalyst C3ox500A–0.73% Pt(N) was prepared using oxidized carbon C3ox heat-treated in nitrogen at 773 K for 1 h; it is known (*47*) that these treatments of carbon introduce additional oxygen surface complexes. The pH values of the two supports, C3ox and C3ox500, were 4.57 and 6.26, respectively (the pH for C3 was 8.26). The results in Table 7 for these two catalysts indicate that the metal dispersion is very low [even lower than in the catalyst C3–1.32% Pt(N)]; it seems then that the oxygen surface complexes introduced are not able to be effective in the exchange of $[Pt(NH_3)_4]^{2+}$.

Recent work (*47, 48*) indicates that square-planar complexes of Pt such as $[Pt(NH_3)_4]^{2+}$ lead to metal dispersion values lower than those of octahedral complexes such as $[PtCl_6]^{2-}$ because the latter is retained on the support with more efficiency. Although the same behavior is found in the present work, it is not possible to use the same assumption since the activated carbons do not have a large percentage of surface complexes and, furthermore, when they were introduced on carbon C3 (C3ox and C3ox500 supports) there was no increase in Pt dispersion. The low metal dispersions obtained when $[Pt(NH_3)_4]Cl_2$ was used as precursor could be explained by the mechanism proposed by Dalla Betta and Boudart (*49*) based on an infrared study of the reduction process of catalysts prepared with the same precursor and supported on zeolites: the complex, which initially is square-bipyramidal with two H_2O molecules, loses symmetry by adsorption on the zeolite upon dehydration at high temperature. When the sample is heated in H_2 there is decomposition of the complex and a consumption of H_2 given by

$$[Pt(NH_3)_4]^{2+} + 2H_2 \rightarrow Pt(NH_3)_2H_2 + 2NH_3 + 2H^+ \quad (1)$$

$$Pt(NH_3)_2H_2 \rightarrow Pt + 2NH_3 + H_2. \quad (2)$$

The unstable hydride is mobile and therefore leads to Pt agglomeration and lower metal dispersion. However, if the sample is heated in O_2 before reduction no unstable hydride is formed and a much larger metal dispersion is obtained.

To see if this mechanism is responsible for the low metal dispersion obtained in our catalysts, samples C3A–0.68% Pt(N) and C3ox500A–0.73% Pt(N) were heat-treated under a flow of helium up to 673 K, holding this temperature for 2 h; immediately afterward, the He flow was changed to H_2 at the same temperature and the reduction was held for 12 h. We used He instead of O_2 prior to the reduction because the latter would burn the carbon of the support. The results obtained in the characterization of these two catalysts are also included in Table 7 where it is shown that the dispersion has considerably increased with respect to the original catalysts; thus, the H/Pt ratio has increased from 0.12 for catalyst C3A–0.68% Pt(N) to 0.68 for the same catalyst heat-treated in helium and from 0.05 to 0.19 for catalyst C3ox500A–0.73% Pt(N). These results seem to confirm the formation of the unstable $Pt(NH_3)_2H_2$ hydride which, because of its high mobility, leads to a considerable agglomeration of Pt particles and consequently to a low metal dispersion. Thus, by avoiding the formation of such a hydride by He treatment the Pt dispersion will increase.

Once again, the $\bar{d}$ value measured by TEM for catalyst C3A–0.68% Pt(N), when treated in He prior to reduction in H_2, was coincident with that obtained by H_2 chemisorption assuming that one H atom is chemisorbed per surface Pt atom. Average particle sizes by XRD (Table 7) for catalysts with low metal dispersions are in general in better agreement with those obtained by H_2 chemisorption.

CONCLUSIONS

Hydrogen chemisorption applied using the extrapolation to zero pressure method and assuming one H atom chemisorbed per surface Pt atom gives good results of average particle size for Pt in the supported catalysts as compared with those obtained by TEM for the high dispersion catalysts and by XRD for the low dispersion catalysts.

For catalysts prepared by the incipient wetness technique, using $H_2[PtCl_6] \cdot 6H_2O$ dissolved in a benzene–ethanol mixture, the H/Pt ratio is similar to that found for the CO/Pt ratio (assuming 1 : 1 stoichiometry) when H/Pt is lower than 0.25. For H/Pt ratios in the range 0.25–0.50, only 0.62 CO molecule is chemisorbed on average per surface Pt atom. These results seem to indicate that the increase in Pt dispersion leads either to an increase in the bridged form or to a decrease in the packing of linearly chemisorbed CO molecules.

Reduction of these catalysts at 773 K for 12 h instead of at 673 K for 12 h results in a decrease in the dispersion of the metal. The sintering of the Pt particles shows a linear relationship with the meso- and macropore volumes of the supports as measured by mercury porosimetry. When the catalysts were reduced at 673 K for 12 h the dispersion found was dependent on the number of pores with diameter between 9 and 11 nm.

The dispersion of the catalysts prepared from hexachloroplatinic acid was independent of the method of preparation and solvent used. However, when using $[Pt(NH_3)_4]Cl_2$ as precursor and reducing the catalysts directly in H_2 at 673 K for 12 h, there was a marked lowering in the dispersion of the catalysts. The dispersion of these catalysts was largely increased when, prior to the reduction in H_2, the samples were treated in a He flow at the reduction temperature; this indicates that if the formation of the unstable platinum hydride pointed out by Dalla Betta and Boudart (*49*) is avoided, it is possible to reach a high Pt dispersion.

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