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Heat-Treated Carbon Blacks as Supports for Platinum Catalysts

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The effect of the degree of graphitization of the support on the dispersion, sintering resistance, and catalytic activity of a series of platinum catalysts supported on heat-treated carbon blacks has been determined. The supports were prepared by heat treatment of a furnace carbon black in an inert atmosphere at temperatures up to 2473 K. The resulting samples were characterized by physical adsorption (nitrogen at 77 K and carbon dioxide at 273 K), X-ray diffraction, and surface acidity measurements. Platinum catalysts were prepared by impregnating the supports with aqueous hexachloroplatinic acid; metal dispersions were measured by hydrogen and carbon monoxide chemisorption at room temperature and by transmission electron microscopy. Benzene hydrogenation was used as a test reaction to assess the possible effect of the support on the catalytic behavior of platinum. Platinum dispersions as high as 0.99 were achieved, and they can be well correlated with the surface acidity characteristics of the supports. The only sample not following the observed trend is the catalyst prepared with the less pregraphitized support. On the other hand, the highest resistance to sintering was found for the catalyst supported on the carbon black with the highest degree of graphitization, and this is attributed to an interaction between the metal particles and the π sites on the support. However, this interaction is not strong enough to affect the catalytic behavior for benzene hydrogenation. Thus, the metallic dispersion seems to be the result of, at least, two factors: (a) an adequate metal precursor support interaction during the impregnation step and (b) a high sintering resistance under the reduction conditions which hinders the metal particle growth during this stage of the catalyst preparation. © 1995 Academic Press, Inc.

1. INTRODUCTION

Platinum-based catalysts supported on carbonaceous materials are widely used in a large variety of reactions including hydrogenation (1–3), hydrogenolysis, and isomerization (4), and also in fuel-cell systems (5). In these applications, highly dispersed platinum is required in order to achieve a better utilization of the noble metal. Several studies have been carried out which relate platinum dispersion to support characteristics such as surface heterogeneity (6), porous structure (7), and content of oxygen surface groups on the support (8, 9). Solar *et al.* (10) have recently reported that interaction of the carbon surface with both the metal precursor and the solvent during the impregnation step in the process of catalyst preparation greatly influences the metal uptake and dispersion. These interactions can be estimated from a deep knowledge of the surface properties (isoelectric point, nature and amount of surface complexes, etc) and of the characteristics of both the metal precursor (anionic or cationic) and the pH of the solution. However, it is necessary to bear in mind that in some cases the carbon surface may be modified during the impregnation step. In this way, previous work from this laboratory has evidenced the interaction between the carbon surface and hexachloroplatinic acid in aqueous solution during the impregnation step in the preparation of pregraphitized carbon-black-supported platinum catalysts, which causes the reduction of Pt^{IV} to PT^{II} species and the subsequent formation of oxygen surface groups on the carbon surface (9).

An important aspect in the field of carbon-supported catalysts is the role of surface oxygen groups on the support. These complexes, besides determining the surface characteristics of the support, can act as anchoring centers for the metal precursors, favoring the dispersion of the final metal phase. However, some of the surface oxygen groups may not be stable under the reduction conditions to which the catalysts are subjected to obtain the active phase and may decompose at this stage, which favors the sintering of the metal species. Also, oxygen surface complexes may influence other kinds of centers on the carbon surface. In this way, the strength of the so-called π sites, which are defined as sites on the carbon surface with maximum density of delocalized π electrons (11) that can also act as anchoring centers for platinum, is diminished by the presence of oxygen complexes, due to the electron-withdrawing effect exerted by the oxygen atom.

In this context, the aim of this work is to study the effect of surface characteristics of pregraphitized carbon blacks with a very small number of oxygen surface groups on the dispersion, resistance to sintering, and catalytic

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activity of platinum when they are used as catalyst supports.

2. EXPERIMENTAL

2.1. *Supports*

The starting material for support preparation was a furnace carbon black (CC-40-220) supplied by Columbian Chemical Co., with a mean particle diameter of 18 nm and an ash content of 0.15% (Carbon S). This carbon was heat-treated at several temperatures (1273, 1873, 2073, 2273, and 2473 K) for 1 h under a helium flow to obtain supports S10, S16, S18, S20, and S22, respectively.

The characterization of the porous texture of the carbons was carried out by physical adsorption of N_2 at 77 K and CO_2 at 273 K in a conventional gravimetric system using silica spring balances. The sulfur content of the supports was determined with a Carlo Erba EA1108 analyzer and is reported in Table 1. Information about the degree of carbon black pregraphitization attained with the heat treatment in an inert atmosphere was obtained with X-ray diffraction by using CuKα radiation to measure the size of the graphite microcrystallites. The half-width of the (002) and (10) diffraction peaks were used to determine the crystallite thickness, L_c, and the crystallite diameter, L_a, respectively; also, the interlayer spacing, d_{002}, was determined from the position of the (002) diffraction peak near $2\theta = 26.5°$ (12).

The acidity of aqueous carbon slurries (pH_{slurry}) was measured with a PHM82 Standard pH meter. Slurries were prepared by placing 1 g of carbon support and 25 cm^3 of preboiled distilled water in a beaker and thoroughly mixing them with a magnetic stirrer while they were heated and allowed to boil for 3 min. Then the solid was separated by filtering the hot slurry, and the clear liquid was allowed to cool to room temperature in a stoppered flask to avoid dissolution of atmospheric CO_2. Finally, the pH values of the solutions so obtained were measured after calibration of the pH meter with standard buffers. The error in the measurements was ±0.01 pH units; they were repeated three times for each sample, the results being identical. So the experimental error is that of the apparatus.

TABLE 1

Effect of Heat Treatment on Some Characteristics of the Carbon Black Supports

	N_2, 77K		CO_2, 273K		
Support	S_{BET} ($m^2 \cdot g^{-1}$)	V_0 (D–R) ($cm^3 \cdot g^{-1}$)	V_0 (D–R) ($cm^3 \cdot g^{-1}$)	Sulfur (%)	pH_{slurry}
S	956	0.38	0.19	1.09	6.76
S10	1024	0.42	0.18	0.93	9.21
S16	431	0.17	0.08	0.13	7.45
S18	300	0.12	0.04	n.d.[a]	7.49
S20	212	0.09	0.03	n.d.[a]	7.43
S22	175	0.07	0.02	n.d.[a]	7.06

[a] n.d. means not detected.

2.2. *Catalysts*

Catalysts were prepared by impregnation of the supports with an aqueous solution (10 $cm^3 \cdot g^{-1}$ of support) of $H_2PtCl_6 \cdot 6H_2O$ (reagent for synthesis, from Merck), with the appropriate concentration to obtain a Pt loading of about 1 wt% Pt. The excess of solvent was removed by flowing nitrogen through the slurry, and the remaining solid was dried overnight at 393 K and then kept in a desiccator until used. The whole procedure was carried out in the dark to avoid the decomposition of the platinum precursor. The platinum content was measured by burning away the carbon in air at 973 K and analyzing by UV spectrophotometry (wavelength 261.8 nm) the residue dissolved in aqua regia.

The number of Pt surface atoms on the catalysts was determined by chemisorption of H_2 and CO at 298 K in a volumetric system. A previous common treatment of the catalysts (in the same experimental system) was as follows: (i) 20 min at room temperature under high vacuum; (ii) 12 h under a hydrogen flow (50 $cm^3 \cdot min^{-1}$) at 623 K; (iii) 1 h at 573 K under high vacuum, and (iv) cooling to 298 K under vacuum. In some cases, the catalysts were heat treated for 12–36 h in hydrogen over the temperature range 623–773 K in order to increase the Pt particle size by sintering. Chemisorption on supports was found to be zero in all cases, as measured under the same experimental conditions. CO and H_2 uptakes were used to determine the metal dispersion, D, by assuming that either one hydrogen atom or one CO molecule is chemisorbed on a surface platinum atom. The average Pt particle size, d, was calculated from $d = 1.08/D$ (nm) (13), using the dispersion value obtained from hydrogen chemisorption.

Transmission electron microscopy (TEM) was used to check chemisorption results. Experiments were carried out using a Zeiss EM10 electron microscope. Samples were dispersed ultrasonically in toluene and spread over self-perforated microgrids.

Catalytic activities for benzene hydrogenation were measured at 323 K under differential conditions. Catalysts were previously reduced *in situ* in flowing hydrogen at 623 K for 12 h and then cooled under hydrogen to the reaction temperature. The reduced catalysts were contacted with a reaction mixture (50 $cm^3 \cdot min^{-1}$) containing purified hydrogen and benzene (Merck, reagent grade) in a H_2/C_6H_6 ratio of 11.0. About 50 mg of sample was used without further dilution and benzene conversion was kept lower than 5% in all cases. Reactants and products were analyzed by gas chromatography every 5 min; cyclohexane and unreacted benzene were the only compounds detected.

3. RESULTS AND DISCUSSION

3.1. *Supports*

The nitrogen (77 K) adsorption isotherms (*n*, amount adsorbed in mmol/g vs relative pressure) for the supports are shown in Fig. 1. The adsorption isotherm corresponding to the starting carbon black (carbon S) indicates that this support has a well-developed porosity over the whole range of pore sizes. The amount adsorbed at low relative pressures is high enough and indicates an important contribution from narrow micropores. Furthermore, at higher relative pressures, the isotherm shows an open knee, which indicates the presence of wider micropores, and a linear part with a considerable slope, which is due to the contribution of mesopores (2 nm $< d <$ 50 nm) to the total porosity. After the heat treatment at 1273 K (support S10) it seems that the wider microporosity has been slightly developed, as the isotherm's knee is somewhat more open; in any case, the largest modifications are achieved after heat treatment at 1873 K and above. Thus, a great decrease in microporosity is observed, as indicated by the decrease in the amount adsorbed at low relative pressures; also, the isotherm's knees become progressively less open and the slopes of the isotherms at relative pressures between 0.2 and 0.6 also decreased.

This evolution of the support's porosity with the heat treatment temperature (HTT) can be better followed by plotting the nitrogen adsorption data in Dubinin–Radushkevich (D–R) coordinates (log *n* vs. $\log^2 (P_0/P)$) (14) (Fig. 2). It can be seen that the shape of the plots is similar for all the samples: a linear portion at low relative pressures (up to $P/P_0 = 0.2$), due to the filling of micropores, and an upward deviation at higher relative pressures, ascribed to the coverage of the surface of wider pores. Furthermore, the amount adsorbed even at the lowest relative pressures decreases when the HTT increases. The extrapolation of the linear portions at low relative pressures to $P/P_0 = 1$ allows the determination of the micropore volumes (V_0, $\mathrm{cm}^3_{\mathrm{liq}} \cdot \mathrm{g}^{-1}$), which are reported in Table 1, together with the BET surface areas, also calculated from nitrogen adsorption at 77 K, and the micropore volumes obtained from CO_2 adsorption at 273 K. As shown previously (15, 16), the comparison between the micropore volumes deduced from adsorption of N_2 (77 K) and CO_2 (273 K) can provide good information on the microporosity of porous carbons since CO_2 (273 K) gives the volume of only narrow micropores (up to about 0.7 nm) whereas N_2 (77 K)—if no restricted diffusion is present at the low temperatures of adsorption—would provide the volume of narrow and wider micropores (up to 1.8 nm). If one compares the micropore volumes calculated from the two different adsorptives, N_2 and CO_2, it can be observed that V_0(D-R-N_2) is much higher than V_0(D-R-CO_2) (2 times higher for the starting carbon and up to 3.5 times higher for that heat-treated at 2473 K), which indicates an increasing contribution of wider micropores (>0.7 nm) to the total porosity as the HTT increases. The treatment of the starting carbon black at 1273 K (S10) slightly modifies the textural characteristics of the carbon, as can be deduced from the N_2 adsorption isotherms (Figs. 1 and 2) and the porosity data obtained from N_2 (77 K) and CO_2 (273 K) adsorption (Table 1). However, the treatments at higher temperatures cause a strong decrease in both the BET surface areas and the micropore volumes of the resulting carbons. Also, the sulfur content is sharply decreased by increasing the HTT, so that no sulfur is detected in samples treated at $T \geq 2073$ K.

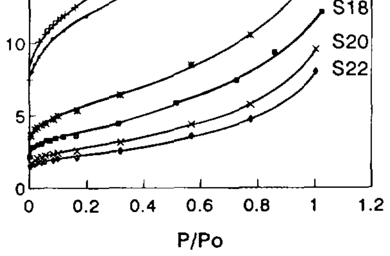

FIG. 1. N_2 adsorption isotherms (77 K) on heat-treated carbon blacks.

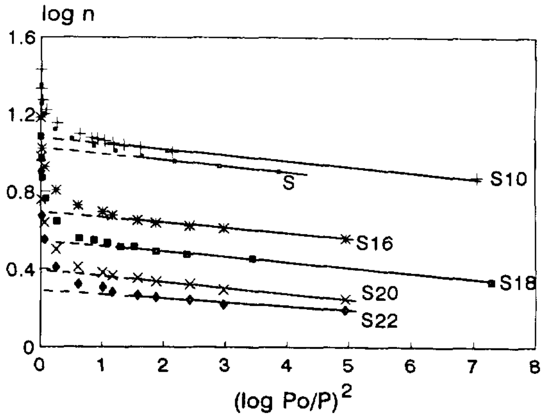

FIG. 2. Dubinin–Radushkevich (D–R) plots for N_2 adsorption at 77 K on heat-treated carbon blacks.

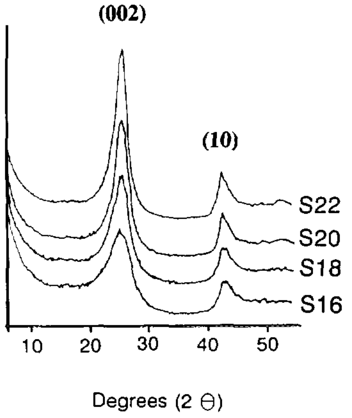

FIG. 3. X-ray diffraction patterns of supports.

The main effect of the heat treatment on the porosity of the supports is the loss of microporosity, involving a reduction in the contribution of both narrower micropores measured by CO_2 adsorption and wider micropores which can be calculated from nitrogen adsorption at 77 K. This loss of porosity is a consequence of the pregraphitization of the carbons induced by heat treatment in an inert atmosphere. This kind of treatment also causes an ordering and limited growth of crystallites (12) which can be followed by means of X-ray diffraction. The XRD patterns of carbons S16, S18, S20, and S22 are plotted in Fig. 3. The patterns of carbons S and S10 have not been included because as is characteristic of amorphous material, they do not show well-defined peaks. The structural parameters (crystallite thickness (L_c) and diameter (L_a) and interlayer spacing (d) corresponding to supports S16, S18, S20, and S22 are reported in Table 2. As could be expected, the graphite crystallites in the carbon black supports grow in size as the treatment temperature increases, whereas the interlayer spacing slightly decreases, except in the case of carbon S18, which has a d value somewhat higher than that corresponding to support S16 (0.358 vs 0.353 nm). These high values of the interlayer spacing indicate the nongraphitizable character of the starting carbon black, although some degree of ordering can indeed be achieved upon thermal treatment, as can be deduced from the values given in Table 2.

Measurements of pH_{slurry} are commonly used to assess the surface charge of solids in suspension, since this value can be taken as equivalent to the point of zero charge of the solid (17) and the technique has some advantages in respect to electrophoretic determinations (18). This surface charge arises from the interaction between the carbon surface and the aqueous solution, and will determine the strength of the interaction with the metal precursor in the catalyst preparation step (10). The pH_{slurry} of the carbons studied here are reported in Table 1. The starting carbon black (S) is slightly acidic; the heat treatment at 1273 K yields a basic carbon (S10) with a pH_{slurry} of 9.21. The further increase in the temperature of the heat treatment lowers the pH_{slurry} values in such a way that they become nearly similar for carbons S16, S28, and S20, and somewhat smaller for S22.

When carbons are heat treated at high temperatures in an inert atmosphere, a shift of its isoelectric point (IEP) towards higher values is usually observed (10, 19). This effect is attributed, at least in part, to the pyrolysis of acidic oxygen surface groups and the subsequent formation of pyrone-type groups upon exposure to air at lower temperatures, these groups acting as basic sites (20). Carbon S has a certain amount of acidic surface oxygen complexes, as evidenced by temperature programmed desorption measurements (8), but their decomposition upon the treatment at 1273 K gives rise to a carbon (S10) with a relatively high basicity. The loss of sulphur during this treatment is likely to be too small to have any influence on the increase of basicity. Furthermore, the more important removal of sulphur takes place upon the treatment at 1873 K, leading to a decrease in the basicity of the resulting carbon black (S16). It can be assumed that sulphur evolution leaves sites on the carbon surface which can chemisorb oxygen upon exposure to atmospheric air at room temperature, originating oxygen surface complexes which are more acidic that the pyrone-type ones. On the other hand, a model has been proposed (11) to explain the basic behavior of high-temperature graphitized carbons, based on the interaction of water with the electronic structure of the basal planes of the graphite crystallites,

$$C_\pi + 2\,H_2O \rightarrow C_\pi H_3^+O + OH^-, \qquad [1]$$

C_π being an idealized surface platelet with maximum electron conjugation. However, our results do not show any correlation between basicity and degree of graphitization, and the more ordered carbon black, S22, is even slightly more acidic than its counterparts (S16, S18, and S20) which show similar behavior. These results can be better explained by the model proposed by Arico' *et al.* (21), in which a different acid–base behavior of hydroxyl groups is expected, depending on the environment of such

TABLE 2

Structural Parameters of the Supports

Support	L_a (nm)	L_c (nm)	d (nm)
S16	7.63	2.23	0.353
S18	7.84	2.71	0.358
S20	8.62	3.21	0.349
S22	8.90	3.61	0.347

groups. Considering the carbon black to be composed of a macromolecular aromatic structure with an amorphous part containing tetrahedrically bonded carbon atoms, these authors proposed that hydroxyl groups bonded to aliphatic carbon atoms would behave as a base because of the electron-donor inductive effect of the adjacent groups, whereas OH groups bonded to the edges of carbon layers would be much less basic because of the electron withdrawing resonance effect exerted by the aromatic ring. Thus, an increase in the ordering of the carbon black structure, such as that obtained by heat treatment, would increase the possibility of formation of phenolic-type hydroxyls, less basic, upon exposure of the carbon black to air at room temperature. It should be remarked that the amount of oxygen surface groups on the heat-treated carbons is very small, in such a way that their temperature programmed CO and CO_2 desorption profiles are nearly flat.

3.2. *Catalysts*

Carbons S16, S18, S20, and S22 have been used as platinum supports. This will enable us to study the effect of the degree of graphitization of the support on the properties (metal dispersion, sintering resistance, and catalytic performance) of the resulting catalysts. Carbons S and S10 are not included in this series because their high sulphur content would represent a new variable to be considered, besides being a poison for platinum. The nomenclature used for the catalysts is the same as that for the parent supports except that C is substituted for S to distinguish between support and catalyst.

The platinum content and the characteristics of the catalysts obtained by chemisorption of H_2 and CO are listed in Table 3. The Pt dispersion, as measured by the H/Pt ratio, is very high in all the catalysts, the maximum value (0.99) being that for the catalyst supported on the carbon treated at 2073 K. The mean particle size of the platinum crystallites in catalysts C18 and C20 has been checked by transmission electron microscopy; by this technique, Pt particles very homogeneously dispersed, with an average particle size of 1.2 nm (C18) and 1.5 nm (C20), have been observed. The good agreement of these results with the chemisorption values (1.1 and 1.2 nm for C18 and C20, respectively) negates the possibility of an overestimation of the Pt dispersion due to hydrogen spillover from the metal crystallites to the carbon support; this conclusion is also supported by the fast kinetics of the hydrogen adsorption during the chemisorption measurements. The dispersions obtained from CO chemisorption are smaller than those calculated from H_2 chemisorption; similar results have been observed previously in other Pt/C systems (7, 22) for which H/Pt was larger than CO/Pt for dispersions higher than 0.3, and they have been attributed to a greater contribution of bridge-bonded CO on small particles. Furthermore, as stated above, the high H/Pt values have been confirmed by TEM observations.

TABLE 3

Hydrogen and Carbon Monoxide Chemisorption

Catalyst	Pt (%)	H/Pt	CO/Pt	*d* (nm)[a]
C16	0.97	0.67	0.58	1.6
C18	1.01	0.99	0.77	1.1
C20	0.99	0.92	0.62	1.2
C22	1.04	0.83	0.57	1.3

[a] Calculated from hydrogen chemisorption.

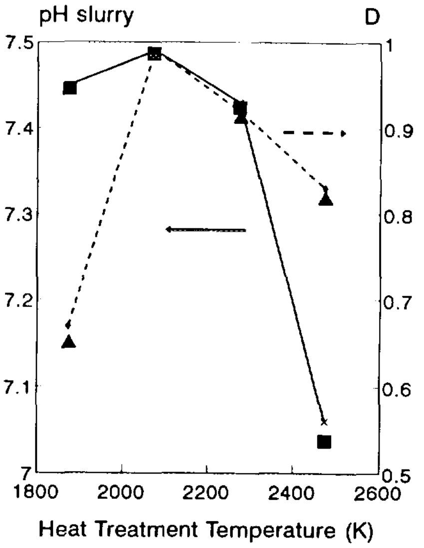

FIG. 4. Evolution of $\mathrm{pH}_{\mathrm{slurry}}$ of supports (■) and metal dispersion of catalysts (▲) with support heat treatment temperature.

The platinum dispersion can be correlated with the $\mathrm{pH}_{\mathrm{slurry}}$ values measured for the supports. Figure 4 compares the evolutuion of these two parameters with the temperature at which the carbon blacks have been pregraphitized, and it can be observed that the metal dispersion decreases when the $\mathrm{pH}_{\mathrm{slurry}}$ value for the support becomes more acidic, both plots showing a maximum at 2073 K. Only catalyst C16, the one with the less pregraphitized support, behaves anomalously, showing a lower dispersion than that expected from its relatively high $\mathrm{pH}_{\mathrm{slurry}}$ value. The general trend can be explained by assuming that the greater the difference between the pH of the impregnating solution (2.06 in our case) and the isoelectric point (I.E.P.) of the carbon, the better the interaction between the surface and an anionic precursor ($PtCl_6^{2-}$ or $PtCl_4^{2-}$) will be. The case of catalyst C16 is somewhat different; the $\mathrm{pH}_{\mathrm{slurry}}$ of the support is higher than, for example, that of S20 or S22, but the catalyst has a lower platinum dispersion. We have previously shown that some amount of oxygen surface groups can be formed on the carbon surface upon impregnation with an aqueous solution of hexachloroplatinic acid (9). Carbon S16 shows the highest reactivity among the four supports used in this study; this is evidenced by its active surface area, 4.01 $m^2 \cdot g^{-1}$, measured by using oxygen adsorption from air (473 K, 8 h) following a heat treatment in N_2 (1223 K, 1 h), which was much higher than those of its counterparts (3.36, 3.19, and 3.24 $m^2 \cdot g^{-1}$ for S18, S20, and S22, respectively). Bearing this in mind, it is likely that the formation of oxygen surface groups on the support S16 exerts a harmful effect on the metal dispersion. Furthermore, the next step in the catalyst preparation procedure includes a thermal treatment under hydrogen to decompose the impregnated metal precursor in order to obtain metallic platinum and so the final metallic dispersion will also depend on the ability of the support to avoid the sintering of the supported phase during the reduction treatment.

Sintering tests carried out in H_2 using different temperatures and lengths of treatment have been accomplished with catalysts C16, C18, C20, and C22. Samples were subjected to a given sintering treatment after determining the metal dispersion resulting from the previous one. Table 4 reports the dispersion ratio D/D_0 (D_0 is the dispersion of the catalysts after the first treatment at 623 K for 12 h) obtained after each treatment. The results show an increase in the resistance to sintering of the platinum crystallites with the degree of graphitization of the supports, in such a way that catalysts C20 and C22 lost only 20% of their initial dispersion after 84 h of treatment (48 of them at 773 K). Catalyst C16 is the least resistant to sintering in spite of the fact that it has the largest metal particles before the sintering treatments and a higher support surface area. Since the increase in the pregraphitization temperature lowers the surface area of the supports, as described above, this would reduce the mean distance between metal particles and the sintering would be facilitated. However, this is not the observed behavior. It can be concluded that the interaction between the metal particles and the support increases with the degree of graphitization, this leading to an improved resistance to sintering. The increease in metal–support interaction as the degree of graphitization increases may be related to the increasing strength of the π sites on the support (11), which can act as anchoring centers for platinum.

TABLE 4

Effect of Sintering Treatments on Platinum Dispersion

Sintering treatment		$[D/D_0]^a$			
T (K)	t (h)	C16	C18	C20	C22
623	12	1.00	1.00	1.00	1.00
673	12	0.92	0.95	0.96	—
723	12	0.81	0.88	0.90	0.91
773	12	0.59	0.78	0.89	0.86
773	36	0.33	0.66	0.79	0.79

[a] Determined by H_2 chemisorption at 298 K. D_0 is the platinum dispersion after the first H_2 treatment at 623 K for 12 h.

TABLE 5

Benzene Hydrogenation Activities at 323 K for the Different Catalysts

Catalyst	$\text{Rate}_{(t=0)}$ (μmol $\cdot$ $min^{-1} \cdot$ g Pt^{-1})	$\text{T.O.F.}_{(t=0)}$ (h^{-1})
C16	3376	59
C18	7250	86
C20	6881	88
C22	6509	92

Benzene hydrogenation has been carried out on these catalysts in order to gain insight on the possible influence of the above-mentioned metal–support interaction on their catalytic behavior. This reaction is considered structure-insensitive (23) and so the results are not expected to be affected by the different particle sizes of platinum in the catalysts. Table 5 reports the initial activities (μmols of cyclohexane produced per minute and per gram of platinum) after 1 min of reaction at 323 K as well as the turnover frequencies based on the hydrogen chemisorption data. In selected cases, the catalytic activity was also measured at 313 K. The turnover frequencies obtained at that temperature for catalysts C18 and C20 were 43 h^{-1} and 50 h^{-1}, respectively. These values, along with those obtained 323 K (Table 5), allow the calculation of a two-point activation energy for the reaction on these catalysts: 58 KJ $\cdot$ mol^{-1} on C18 and 51 KJ $\cdot$ Mol^{-1} on C20. These values (bearing in mind the low precision attained with only two points) and the turnover frequencies obtained are close to the values reported in the literature for supported platinum catalysts under similar reaction conditions (23).

Catalyst C16 is the least active in the series. But its low activity is not due to the poorer dispersion of the metal phase because its turnover frequency, i.e., the activity per platinum surface site, is also lower than that of its counterparts. This can be explained by the relatively small amount of sulphur remaining in the support after heat treatment under He at 1873 K, which may act as a poison for the hydrogenating activity of platinum. None of the other supports (S18, S20, or S22) have any detectable amount of sulphur, so their activities are higher. When one compares these sulphur-free catalysts, it is clear from the data in Table 5 that the initial activity (Rate$_{(t=0)}$) is not affected by the support, the turnover frequencies being similar for all of them. The small apparent increase in the turnover frequencies when going from catalyst C18 (86 h^{-1}) to C22 (92 h^{-1}) in not significant. Indeed, a higher degree of graphitization and, consequently, an increase in the strength of the π sites on the support would increase the charge density of the platinum particles, thus decreasing the probability of C=C bond activation and lowering the catalytic activity. Therefore, it can be concluded that the metal–support interaction leading to a higher resistance to sintering of the metal particles is not enough to modify the catalytic behavior of platinum in the reaction of benzene hydrogenation.

4. CONCLUSIONS

The heat treatment of a carbon black in an inert atmosphere at high temperature (up to 2473 K) modifies its textural and surface characteristics, the latter being determinant when the resulting pregraphitized carbon blacks are used as supports for platinum catalysts. Thus, dispersions as high as 0.99 have been achieved together with a high resistance to sintering in hydrogen at 773 K. The surface charge of the supports in solution, the small contents of oxygen surface groups, and the extent of graphitization, which determines the strength of the π sites on the support, are the main factors influencing the behavior of these heat-treated carbon blacks as supports. Furthermore, the activity of the resulting catalysts for benzene hydrogenation is not affected by the support, thus indicating that the metal–support interaction which provides a high resistance to metal particle sintering does not influence the catalytic behavior of the platinum catalysts.

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