

Effect of Carbon Support and Mean Pt Particle Size on Hydrogen Chemisorption by Carbon-Supported Pt Catalysts

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A series of carbon-supported platinum catalysts were prepared and characterized; the only variable during catalyst preparation was the support used. The influence of different carbon properties on the platinum dispersion is described. The results show that there is not a single carbon property that can be related to dispersion, each one playing a more or less important role. However, the surface area outside the micropores may control the Pt dispersion if the chemical nature of the support is kept constant and vice versa.

The large range of platinum particle sizes used in this work—obtained from different carbon supports and sintering treatments—has allowed us to observe that a relationship between platinum particle size and weakly chemisorbed hydrogen exists. The uptake of this kind of hydrogen increases with particle size. © 1991 Academic Press, Inc.

INTRODUCTION

There is growing evidence on the usefulness of carbon as a catalyst support. However, the results described in the literature do not show a clear relationship between the properties of the carbon used and metal dispersion or catalytic activity. Thus, Pt dispersion has been related to such carbon characteristics as surface heterogeneity (1), surface area (2), pore structure (3), and active surface area (4, 5).

In a previous study, in which all parameters were kept constant (metal precursor, solvent, impregnation method, pore structure of carbon support, etc) except the amount of oxygen surface groups of the support (6), the characteristics of the supported platinum (dispersion, sintering resistance, etc) were found to be a function of the chemical nature of the carbon support. One of the objectives of the work described here is to study catalysts prepared under the same experimental conditions but using different carbons as support and to investigate the

effect of both the pore structure and the chemical nature on the characteristics of the supported platinum.

A secondary objective was to investigate the interaction of hydrogen with the platinum surface. The adsorption of hydrogen on dispersed metals reveals the existence of at least two states of absorbed hydrogen (7-9), classified as weak and strong chemisorption, which may coexist to a certain extent at room temperature on the metal surface. The existence of the weak form of chemisorbed hydrogen, easily desorbed at room temperature, was recognized several years ago although it is not well understood and is the subject of different interpretations (7, 10-17). In this context the present paper reports experiments on Pt/carbon systems with the aim of understanding the role that particle size plays in weak hydrogen chemisorption.

EXPERIMENTAL

A. Supports

Two furnace carbon blacks (CC-40-220 and T-10157, supplied by Columbian Chemical Co., hereafter called samples C and T,

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TABLE I
Carbon Properties

Support	d_m (nm) ^a	Percentage ash	Percentage S
C	18	0.15	1.05
T	15	0.26	0.48
W	—	0.93	0.10

^a Mean diameter of the primary carbon black particles, according to the manufacturer.

respectively), a granular (1-mm) steam activated carbon from olive stones (sample W) (18), and several samples derived from them have been used as catalyst supports. The sulphur and ash contents for the three original carbons are listed in Table 1, together with the arithmetic mean particle diameter of the carbon black.

Two kinds of heat treatment have been used to remove the sulphur as well as to modify the porous texture and the chemical nature of the carbon surface: (a) helium flow at 2273K for 1 h and (b) hydrogen flow at 1223 K for 12 h (5 h for the activated carbon). The sulphur content of the carbons decreased to <0.01%. The nomenclature of the supports includes the letter corresponding to the original carbon and, in parentheses, the gas treatment used; two additional supports, obtained by oxidation of C(H₂) with H₂O₂ (8 and 12 N solutions), are included. The experimental oxidation procedure was reported elsewhere (6).

The characterization of the supports was carried out by adsorption of N₂ (77K) and CO₂ (273K) (e.g., (19, 20)).

B. Catalysts

All supports were loaded with 1-wt% platinum by impregnation with an aqueous solution of H₂PtCl₆ · 6H₂O (J. T. Baker), as described elsewhere (6). Platinum content was determined by UV spectrophotometry (wavelength, 261.8 nm).

The number of Pt surface atoms on the catalysts was determined by chemisorption

of H₂ and CO at 298K 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 in high vacuum, (ii) 12 h under a hydrogen flow (80 ml/min) at 623K (these conditions were selected after an experimental study of the more suitable reduction conditions to ensure complete reduction of the metal precursor with the minimum sintering), (iii) 1 h at 573K under high vacuum, and (iv) cooling down in vacuum to 298K, the temperature of the chemisorption. In some cases, the catalysts were heat treated for 12–36 h in hydrogen over the temperature range 623–773K in order to increase the Pt particle size by sintering.

The chemisorption of H₂ at 298K was carried out following the conventional procedure. The adsorption isotherms were linear in the range of pressures used (50–250 torr) and their extrapolations to zero pressure were used to determine the total hydrogen uptake. The catalysts were then evacuated under high vacuum for 30 min at the same temperature of chemisorption (these outgassing conditions have been carefully maintained for all catalysts) and a second adsorption isotherm was determined and extrapolated to zero pressure to determine the amount of H₂ that was desorbed at 298K.

Carbon monoxide uptakes at 298K on the same samples were determined after desorption of H₂ at 573K for 1 h under high vacuum. The dual technique of Yates and Sinfelt (21), which consists of determining the CO isotherm, in the range of 50–150 torr, evacuating at 298K, and measuring a second isotherm, has been used. Subtraction of the two isotherms at 100 torr gave the amount of CO chemisorbed on the metal.

The chemisorption of H₂ and CO on all supports was measured under the same experimental conditions and was found to be zero in all cases.

CO and total H₂ 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) (22).

The desorption of hydrogen was also studied for some catalysts using the following experimental procedure: after an H₂ isotherm the catalyst was outgassed at a determined temperature, T_1 , under high vacuum for 30 min; then, a new H₂ adsorption isotherm, at room temperature, gave the amount of H₂ eliminated at T_1 ; T_1 was gradually increased and the process repeated so that amounts of H₂ desorbed at different temperatures could be obtained.

RESULTS AND DISCUSSION

A. Supports

The platinum catalysts described here have been prepared under the same experimental conditions, the only difference between them being the carbon used as support. It is thus important to characterize the original carbons and to learn about the changes produced by the treatments used to modify both the porosity and the chemical nature of the surface.

The effect of heat treatments can be quantified by comparing the surface areas; the values calculated from the BET equation for N₂ at 77K and the Dubinin–Radushkevich (DR) equation for CO₂ at 273K are listed in Table 2. The results show that the original carbons C, T, and W have high surface areas, with a large percentage of such surface lying outside the narrow micropores (less than 0.7 nm (19)), as derived from the difference between the surface areas deduced from N₂ and CO₂ (20). The heat treatment in hydrogen and the H₂O₂ treatment do not appreciably modify the surface area. The heat treatment in helium at 2273K produces a drastic change in the porous structure of the carbons, with a large decrease in micro- and mesoporosity.

Previous works (e.g., (3)) on Pt supported on activated carbon have shown the important role played by the mesoporosity in obtaining high Pt dispersion, since the metal precursor will not be accessible to the narrow microporosity. Therefore, for a better

TABLE 2
Apparent Surface Areas of the Supports

Supports	Apparent surface areas (m ² /g)				
	α Method (after subtraction)				
	S_{N_2}	S_{CO_2}	S_{total}	S_{meso}	S_{ext}
C	956	630	459	222	122
C(He)	231	119	120	—	78
C(H ₂)	917	702	408	207	133
C(H ₂) 8 N	918	585	452	232	136
C(H ₂) 12 N	895	560	436	215	139
T	1570	872	905	355	189
T(He)	355	170	193	—	117
T(H ₂)	1406	990	845	384	187
W	1197	861	274	81	31
W(H ₂)	1282	1008	389	92	37

comparison of the supports, it is convenient to subtract the contribution of the narrow microporosity from the total surface area using an appropriate method. The CDS method (23) has been selected here. In this method, the adsorption isotherm of CO₂ at 273K is used to calculate the volume of narrow micropores and the characteristic energy of adsorption from which a theoretical isotherm for N₂ at 77K corresponding to the same microporosity can be calculated. The subtraction of this isotherm from the N₂ experimental isotherm produces a residual isotherm which may be analysed by any method, α in our case (20). The advantage of the CDS method is that the contribution of the same type of porosity is subtracted in all cases. Table 2 includes the surface area outside the narrow micropores and the contribution of mesoporosity and external surface area to the total surface area. These values are high and this is important because this porosity facilitates the access of the metal precursor.

B. Catalysts

Effect of carbon support on Pt dispersion.
The characteristics of the catalysts (the no-

TABLE 3
Some Characteristics of the Catalysts

Catalyst	Percentage Pt	Dispersion		Particle size (nm)	
		H/Pt	CO/Pt	d_{H_2}	d_{CO}
C	0.93	0.304	0.663	3.6	1.6
C(He)	0.95	0.920	0.628	1.2	1.7
C(H ₂)	0.94	0.212	0.210	5.1	5.1
C(H ₂) 8 N	0.96	0.422	0.378	2.6	2.9
C(H ₂) 12 N	1.07	0.454	0.365	2.4	3.0
T	0.95	0.205	0.359	5.3	3.0
T(He)	0.94	0.573	0.444	1.9	2.4
T(H ₂)	1.08	0.264	0.191	4.1	5.7
W	0.76	0.267	0.154	4.0	7.0
W(H ₂)	0.93	0.105	0.174	10.3	6.2

menclature is the same as that of the precursor used) obtained by chemisorption of H₂ and CO are listed in Table 3. The dispersions obtained from CO chemisorption are, in general terms, smaller than those calculated from H₂ chemisorption; similar findings observed in other Pt/C systems (3), for which H/Pt was larger than CO/Pt for dispersions larger than 0.3, were attributed to a greater contribution of bridge-bonded CO on small particles, and consequently the results obtained from hydrogen chemisorption can be taken as being more unambiguous than those from CO. To test this, the particle size of catalyst C(H₂) 8 N was measured by transmission electron microscopy (TEM) and was found to be 2.7 nm, in reasonable agreement with the value for H₂ chemisorption (6). Catalysts C and T of Table 3 are an exception to the general behaviour, probably because the sulphur contents (see Table 1) of the supports have produced an electronic deficiency on the Pt phase. This may lead to a weakening of the Pt-H bond and to a displacement of the CO molecules from bridge positions to linear coordination sites (24, 25).

The H₂ chemisorption results of Table 3 show that catalysts with a wide range of metal dispersion, from 0.10 to 0.92, were prepared. Since the preparation conditions were the same for all catalysts the results of

Table 3 are an indication of the important role played by the carbon support in the Pt dispersion.

When we attempted to correlate dispersions with support surface properties no relation with the apparent surface area of supports could be found, since the catalysts with the higher dispersions had supports with lower surface areas. It could be argued that this is because a large percentage of these areas is due to a narrow micropore contribution which is not accessible to the platinum precursor during the catalyst preparation. However, the surface area outside the narrow micropores, obtained as indicated in Table 2, could not generally be correlated with Pt dispersion. In fact, an analysis of the results in Table 3 as a whole is difficult since there are several carbon properties that change simultaneously. So it is necessary to focus attention on those supports that present common characteristics, such as similar chemical surface, i.e., C(H₂), T(H₂), and W(H₂), for which TPD experiments show no evolution of CO and only a very small amount of oxygen surface groups evolving as CO₂. The dispersion of these catalysts correlates with S_{meso} , or even better, with external surface area, as is graphically depicted in Fig. 1. This relationship can only be explained if one considers that Pt is inhomogeneously distributed, yielding a considerable enrichment of Pt in the pores located at the outside of the support's pore structure. In fact, as these sup-

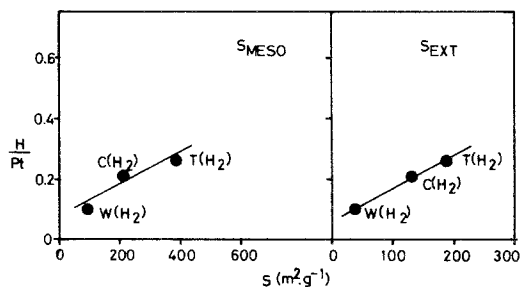


FIG. 1. Dispersion as a function of S_{meso} and external surface area of W(H₂), C(H₂), and T(H₂) supports.

ports are hydrophobic and have few oxygen groups, the aqueous solution of the metal precursor cannot penetrate the interior of the support particles and is concentrated in the external pore structure.

This relationship is only valid for samples where the chemical nature of the carbon surface is similar. If we consider the supports treated with H_2O_2 , the very small differences in S_{meso} or S_{ext} are not sufficient to explain the noticeable increase in H_2 uptake from catalyst C(H_2) to C(H_2) 8 N and C(H_2) 12 N. It has already been shown (6) that in these catalysts the dispersion increases with the number of oxygen surface groups introduced. The treatment with H_2O_2 increases the number of acidic groups of the carbon support, thus reducing its hydrophobicity and making the surface more accessible to the metal precursor during the impregnation step. On the other hand, the increase in the number of less acidic (more stable) groups enhances the interaction of the metal precursor or the metal particles with the support, thus increasing the dispersion and the sintering resistance during the reduction step.

The results of Table 3 indicate that in a series of catalysts in which the chemical nature of the support is kept constant the Pt dispersion is essentially controlled by the surface area outside the micropores. However, if the surface is kept constant the chemical nature of the carbon support will then control the dispersion. It would be difficult to decide which of the two factors is more important in a series of catalysts in which both properties of the carbon support are changed simultaneously, as in other published reports.

It is important to note that the two catalysts supported on high temperature treated carbons, T(He) and C(He), have the larger H/Pt ratios and here the dispersion is not governed by either the porosity or the oxygen surface groups (they have been eliminated by the 2000K treatment). Our findings can only be explained by the effect of an enhanced platinum-carbon electronic inter-

action. Some studies have shown that the unpaired electrons in the d band of a transition metal will interact with π electrons of the graphite in contact with the metal (26, 27). As a result, this could lead to an interaction with Pt particles that facilitates the maintenance of dispersion even at the relatively high reduction temperature. This is an aspect of our results that merits further research.

2. *Hydrogen chemisorption.* The range of carbon supports and treatments used in this work is adequate for the preparation of catalysts with a wide range of Pt dispersion; furthermore, the sintering experiments on some catalysts allow us to prepare catalysts with different Pt particle size on the same support. One of the objectives of this work was to test whether the difference in particle size, and consequently in surface structure, would be reflected in the chemisorption of hydrogen.

It is clear from the literature that there are at least two states of chemisorbed hydrogen on platinum. Two distinct types can be distinguished by chemisorption at room temperature: a weak chemisorption, which is rapidly removed under vacuum, and a rather strong chemisorption. Table 4 lists the total hydrogen chemisorbed at 298K and the hydrogen desorbed at the same temperature for all catalysts prepared. Weak chemisorption is influenced by outgassing conditions (16, 17), and those used in this work may not be ideal, but since the conditions have been the same for all catalysts studied, the hydrogen showed in the last column of Table 4 is taken to represent the hydrogen that is weakly chemisorbed (H_w) at 298K. This kind of adsorbed hydrogen, which desorbs upon evacuation at 298K, was found to be very significant in our catalysts. In some cases it is as high as 70% of the H_2 initially adsorbed at 298K.

This fraction of weakly chemisorbed hydrogen is larger than others found in the literature, where percentages between 12 and 50% are often quoted (15, 28, 29). Thus, it seems that in this Pt/carbon system hydro-

TABLE 4
Hydrogen Chemisorption

Catalyst	Reduction conditions		Total adsorption at 298K ($\mu\text{mol/g}$ catalyst)	Desorbed at 298K ($\mu\text{mol/g}$ catalyst)
	T (K)	t (h)		
C	623	12	7.3	4.7
C(He)	623	12	20.2	9.1
	673	12	19.0	8.8
	723	12	17.4	8.1
	773	12	15.0	7.3
	773	16	14.1	7.3
	773	20	13.4	6.6
	773	24	12.5	6.1
	773	36	12.1	5.5
C(H ₂)	623	12	5.5	3.3
	623	12	5.5	3.2
	623	12	5.2	3.2
	673	12	4.7	2.9
	723	12	4.1	2.6
C(H ₂) 8 N	623	12	10.4	6.3
C(H ₂) 12 N	623	12	12.5	7.0
	623	12	12.4	6.7
	673	12	11.8	6.5
	723	12	11.1	6.2
	773	24	10.3	5.5
	773	36	9.4	5.2
T	623	12	5.0	3.5
T(He)	623	12	13.8	6.6
T(H ₂)	623	12	7.3	4.3
W	623	12	5.2	3.3
W(H ₂)	623	12	2.5	1.7

gen is in general more loosely bound. To check this point a measure of H₂ desorption at increasing temperature was carried out on catalysts C(He), T(H₂), and W. The amount of H₂ desorbed, compared to the total amount chemisorbed at 298K, has been represented in Fig. 2. It can be seen that a large amount of chemisorbed hydrogen, between 85 and 95%, has already evolved at 373K, and after a vacuum treatment at 473K, there is no hydrogen chemisorbed, since the total evolved agrees with the amount initially adsorbed. This value for the temperature at which all species have been desorbed is lower than the temperature values obtained for platinum black and other supported platinum systems (9, 11, 12); for example, 600K was reported by Candy *et al.* (12) for the Pt/MgO system using a similar desorption method.

The data shown in Table 4 confirm the idea of Aben *et al.* (11) in the sense that

different hydrogen pretreatments change the proportion in which the two kinds of chemisorbed H₂ contribute to the H/Pt ratio. Since we have catalysts with a wide range of Pt particle sizes—from 1.2 to 10.3 nm—it is possible to see if the ratio of the two types of chemisorbed hydrogen—weak (H_w), desorbed at 298K and strong (H_s), remaining after desorption at 298K—is a function of the particle size. To check this, Fig. 3 shows a plot of H_s/H_w versus the mean Pt particle size calculated from the total H₂ chemisorption (as mentioned above, this particle size is in agreement with the TEM value for the catalysts tested with the latter technique).

The data in Fig. 3 fit a smooth curve rather well, keeping in mind that d is an average and a perfect correlation can be expected only if particle sizes are homogeneous. The H_s/H_w ratio decreases from 1.22 to 0.47 as the average Pt particle size increases from 1.3 to 10.3 nm. This indicates that a greater portion of hydrogen is strongly chemisorbed on smaller Pt particles than on larger ones. Catalysts C and T are not included in Fig. 3 because their sulphur contents may affect hydrogen adsorption results.

Since reversible hydrogen at room temperature has been found on Pt black as well as in supported Pt catalysts, the existence

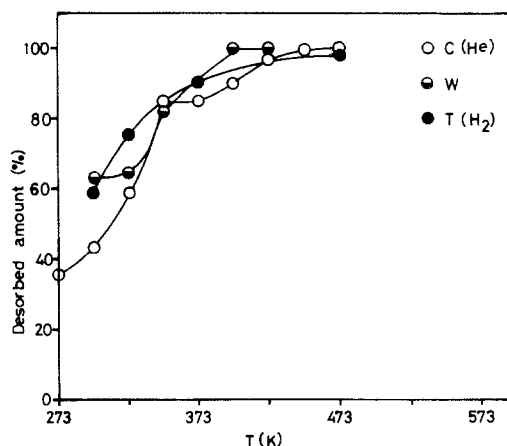


Fig. 2. Desorption under vacuum of hydrogen adsorbed at 298K.

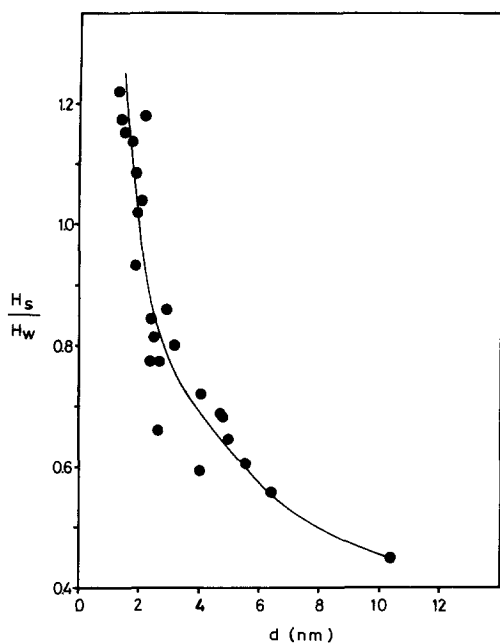


FIG. 3. Effect of Pt particle size on weak (H_w) and strong (H_s) hydrogen chemisorption on carbon-supported platinum catalysts.

of this kind of hydrogen has been recognized to be specific to the platinum metal and not caused by any metal-support interaction. In fact, if a platinum-carbon interaction were responsible for the ratio, the smaller platinum particles would have more weakly adsorbed hydrogen, but, as can be seen in Fig. 3, this is not the case. So, despite the fact that platinum-carbon interaction may affect (in a global way) the hydrogen-Pt interaction, the variation of H_s/H_w cannot be explained by a support-induced modification on the surface energetics of the platinum particles. Thus, the presence of special surface sites on platinum appears to be responsible for the existence of weak hydrogen chemisorption.

From our results it is not possible to determine the way hydrogen is bound but it seems more probable that weak hydrogen comes from chemisorption on low energy sites—Pt atoms on terraces or ensembles of Pt atoms, more numerous on terraces—rather than from multiple chemisorption on highly un-

coordinated sites, since smaller particles would be more likely to exhibit multiple chemisorption. Work on the relationship between H_2 adsorption heat and platinum particle size on some of the catalysts studied here to obtain a deeper knowledge of the H-Pt interaction is in progress.

CONCLUSIONS

The findings reported here can be summarized as follows:

(i) The results obtained show the important role of carbon properties—such as porous texture, oxygen functionalities, and surface electronic properties—on Pt dispersion. A very wide range of Pt dispersion is obtained depending on the carbon support characteristics, and there is not a single carbon property that can be related to dispersion. However, the surface area outside the micropores may control the Pt dispersion if the chemical nature of the support is kept constant and vice versa.

(ii) The amount of weak hydrogen chemisorption at room temperature increases with increasing particle size of Pt crystallites.

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