

## The Effect of Oxygen Surface Groups of the Support on Platinum Dispersion in Pt/Carbon Catalysts

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A series of Pt catalysts supported on carbon black has been prepared; the original support was treated in such a way as to ensure carbons with the same porous texture but with an increasing amount of oxygen surface groups. Pt catalysts (about 1% loading) were prepared with these carbons using the same experimental procedure and the metal dispersion was calculated from hydrogen chemisorption measurements. Both dispersion and resistance to sintering were found to be a function of the number of oxygen surface groups of the support. © 1989 Academic Press, Inc.

### INTRODUCTION

The general effect that the different variables used in the preparation of heterogeneous catalysts—nature of support, metal precursor, impregnation method, metal loading, etc.—have on the properties of the final catalyst (metal dispersion, sintering resistance, metal–support interactions) has been extensively studied. These variables are well established for most conventional supports.

The use of carbon as catalyst support is continuously growing and it is not surprising to find in the recent literature many reports on the effect of some of the variables mentioned above (1–9) in an attempt to relate metal dispersions with the properties of the support. Earlier studies in a Pt–carbon system in which the support was a graphitized carbon black (V3G) subjected to varying levels of carbon burn-off in air had shown differences in the Pt dispersion as a function of carbon burn-off (5, 6). The increase in the Pt dispersion with the extent of gasification of the carbon support was related to (i) an increase in surface heterogeneity—which in turn increases the potential energy barrier for the diffusion of plati-

num species across the carbon surface during sample preparation (5)—and (ii) an increase in surface area of the support—the number of surface platinum atoms per unit area of support was almost constant and independent of the extent of carbon burn-off (6). On the other hand, Ehrburger (8, 9), analyzing the dispersion of small particles on carbon surfaces with other metal/V3G systems, has pointed out the importance that active surface area may have in the dispersion of metal in a carbon. This apparent discrepancy about the factor conditioning the Pt dispersion may be due to a lack of knowledge of the surface chemistry of the carbon support. In fact, during the gasification of V3G and subsequent cooling to room temperature in air, the chemical nature of the carbon support changes progressively with burn-off.

Therefore, a systematic study of the effect of the chemical nature of the carbon support—especially that of oxygen surface groups—on the characteristics of the final catalysts seems very appropriate at this stage. It is expected that such surface groups will have a decisive effect on the formation of the dispersed metal phase of the supported catalysts. This paper presents the results obtained in a systematic study of the role of oxygen surface groups

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of carbon supports on the Pt dispersion of the catalyst, maintaining constant all other variables concerned with the support and catalyst preparation.

## EXPERIMENTAL

### A. Supports

The following supports have been used for the preparation of Pt catalysts: (i) carbon C, a furnace carbon black kindly supplied by Columbian Chemical Co. (USA); (ii) carbon C(H<sub>2</sub>), resulting from a heat treatment in pure hydrogen (1223 K, 12 h at a flow of 80 ml/min) of carbon C; and (iii) carbons C(H<sub>2</sub>)8N and C(H<sub>2</sub>)12N, obtained from C(H<sub>2</sub>) by treatment, for 48 h, with 8N and 12N solutions of H<sub>2</sub>O<sub>2</sub> following the procedure described in Ref. (10).

The characterization of the porous texture of the four carbons was carried out by physical adsorption of N<sub>2</sub> at 77 K in a conventional gravimetric system using silica spring balances (11).

The determination of the amount of oxygen surface groups of the carbons was carried out by temperature-programmed desorption (TPD) under helium; the decomposition products (CO and CO<sub>2</sub>) of the surface groups were measured by mass spectrometry.

Information about the nature of the oxygen surface groups has been obtained from FTIR. Samples were prepared as KBr pellets (120 mg, 0.1 wt%) pressed at 20 MPa and dried under vacuum with P<sub>2</sub>O<sub>5</sub> for 48 h to minimize the moisture (12). Spectra were recorded on a Nicolet 10MX infrared spectrometer by co-adding 128 scans (interferograms) at a resolution of 2 cm<sup>-1</sup>.

### B. Catalysts

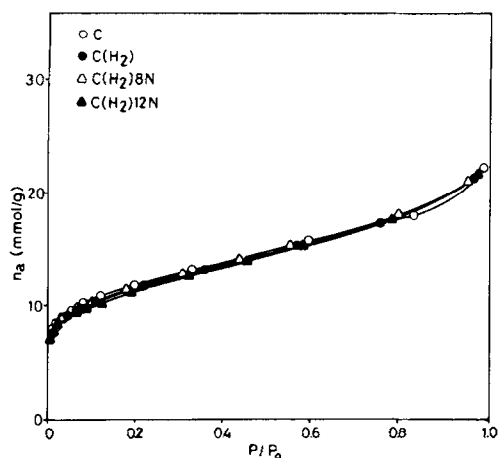
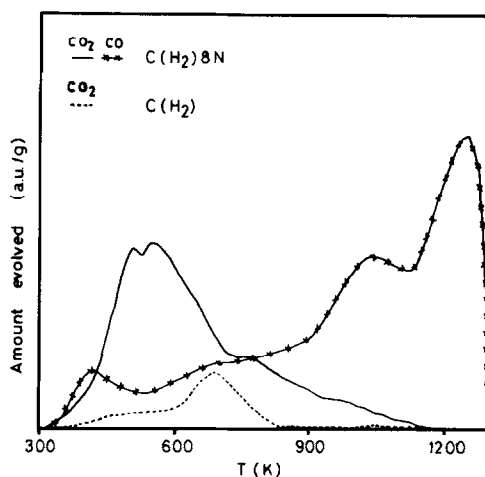
Catalysts were prepared using an impregnation method. One gram of carbon was impregnated with 10 ml of aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O (J. T. Baker) with the appropriate concentration to obtain a Pt load of about 1 wt%. N<sub>2</sub> was flowed through the

suspension up to total elimination of liquid and the remaining solid was dried overnight in an oven at 393 K and kept in a desiccator until use. Pt loading was measured by burning away the carbon in air at 973 K and analyzing by UV spectrophotometry (261.8 nm) the residue dissolved in aqua regia.

The number of Pt surface atoms of the catalysts was determined by chemisorption of H<sub>2</sub> at 298 K in a volumetric system. The hydrogen (99.998%) was further purified by passing it through an oxytrap (Alltech Assoc.) and a molecular sieve (Supelco Inc.). A common previous 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 flow (80 ml/min) of hydrogen at 623 K; (iii) 1 h at 573 K under high vacuum; and (iv) cooling down under vacuum to 298 K, the temperature of chemisorption. In some cases, the catalysts so prepared were heat treated for 12–36 h in hydrogen in the temperature range 623–773 K in order to increase the Pt particle size by sintering.

The chemisorption of H<sub>2</sub> was carried out following the conventional procedure. The adsorption isotherms were lineal in the range of pressures used (50–250 Torr) and the amount chemisorbed was taken as the extrapolation of the isotherm to zero pressure. The chemisorption of hydrogen on the supports was measured under the same experimental conditions and was found to be nil in all cases. The amount of hydrogen chemisorbed was used to calculate the metal dispersion, *D*, assuming that each Pt surface atom chemisorbs one atom of hydrogen. The average Pt particle size was calculated from  $d = 1.08/D$  (nm) (13).

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. In order to obtain representative data at least 2000 particles of platinum were measured.

FIG. 1. N<sub>2</sub> adsorption isotherms (77 K).FIG. 2. Temperature-programmed desorption profiles for C(H<sub>2</sub>) and C(H<sub>2</sub>)8N supports.

## RESULTS AND DISCUSSION

## A. Supports

The N<sub>2</sub> (77 K) adsorption isotherms for the supports shown in Fig. 1 are almost coincident in the whole range of relative pressures; this means that either the heat treatment in H<sub>2</sub> or the treatment in H<sub>2</sub> followed by oxidizing treatment in H<sub>2</sub>O<sub>2</sub> does not change appreciably the porous texture of the carbon. This is confirmed by the BET surface areas (cross-molecular section for N<sub>2</sub>, 0.162 nm<sup>2</sup>) listed in Table 1. The small changes introduced in the large surface area of the carbons—during H<sub>2</sub> treatment (≈5%) and H<sub>2</sub>O<sub>2</sub> treatment (≈1%)—will allow the analysis of only the effect of oxygen surface

groups on the Pt dispersion and on its sintering behavior.

It is well known that the oxygen surface groups of a carbon decompose to CO and CO<sub>2</sub> upon heating in an inert atmosphere. The TPD curves obtained are of the type shown in Fig. 2 for carbons C(H<sub>2</sub>) and C(H<sub>2</sub>)8N, taken as typical examples; as expected, CO<sub>2</sub> is desorbed at lower temperatures than CO. By integration of the curves for both CO<sub>2</sub> and CO, the amounts of both gases evolved have been obtained; such amounts are listed in Table 1. The data indicate that the heat treatment in H<sub>2</sub> eliminates the surface groups desorbed as CO (hereaf-

TABLE I

Some Characteristics of Supports and Catalysts

Sample	S <sub>N<sub>2</sub></sub> BET (m <sup>2</sup> /g)	TPD			% Pt	H/Pt	d (nm)
		CO <sub>2</sub>	CO (μmol/g)	Total			
C	956	68	145	213	0.93	0.304	3.55
C(H <sub>2</sub> )	917	72	n.d. <sup>a</sup>	72	0.94	0.212	5.10
C(H <sub>2</sub> )8N	918	326	377	703	0.96	0.422	2.56
C(H <sub>2</sub> )12N	895	338	453	791	1.07	0.454	2.38

<sup>a</sup> n.d., not detected.

ter, CO complex), those desorbed as CO<sub>2</sub> (hereafter, CO<sub>2</sub> complex) remaining unchanged.

The amount of CO<sub>2</sub> measured in carbon C(H<sub>2</sub>) could correspond to a regeneration of CO<sub>2</sub> complex by room temperature oxidation during its storage. In fact, the CO<sub>2</sub> peak of the TPD curve is displaced toward higher temperatures in carbon C(H<sub>2</sub>) with respect to all other carbons. Similar displacements have been found in this laboratory for carbons oxidized in air in relation to carbons oxidized in H<sub>2</sub>O<sub>2</sub>. The inability of CO complex to regenerate after the hydrogen treatment may be related to the chemisorption of hydrogen on highly reactive carbon atoms made available by the decomposition of CO complex at temperatures above 900 K during the H<sub>2</sub> treatment (14). As shown in Table 1, the H<sub>2</sub>O<sub>2</sub> treatment of the C(H<sub>2</sub>) carbon black produces new oxygen surface groups and the amount increases with the concentration of the H<sub>2</sub>O<sub>2</sub> solution used in the oxidation process.

The chemical nature of the oxygen surface groups of carbon has been the subject of many investigations. In general terms, a carbon treated with oxidizing aqueous solutions at room temperature will mainly have acidic groups (15). Boehm carried out a detailed analysis of the acidic groups (16) and arrived at the conclusion that the more important functional groups are (in order of decreasing acidity) as follows: carboxylic acid and anhydride groups, phenolic hydroxyl groups, and quinonic carbonyl groups. The more acidic species decompose upon heating to give CO<sub>2</sub> and the weaker species, phenolic acid and quinonic groups, decompose to give CO.

FTIR is a very useful and direct technique for the study of the nature of oxygen surface groups. However, there are well-known experimental difficulties involved in obtaining carbon spectra. There is also a common consensus on the fact that the interpretation of the surface groups in carbons is a difficult task since it is unrealistic to consider these groups as isolated func-

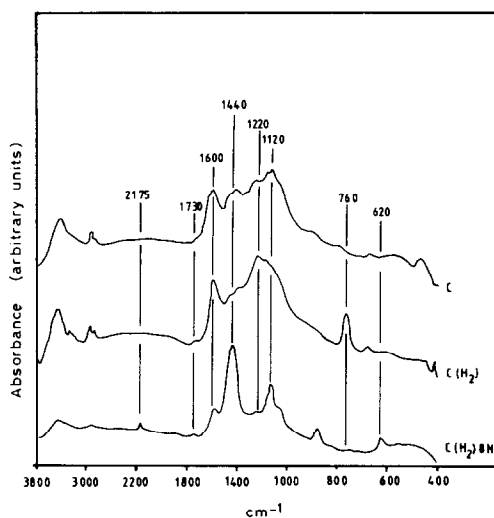


Fig. 3. FTIR spectra for supports C, C(H<sub>2</sub>), and C(H<sub>2</sub>)8N.

tions like in classic organic chemistry (17). Figure 3 includes the FTIR spectra for the supports C, C(H<sub>2</sub>), and C(H<sub>2</sub>)8N that must be considered only qualitatively. The spectra have been corrected with respect to the slope and the baseline, expanded in absorbance, and resolved again at a low resolution (8 or 16 cm<sup>-1</sup>) in order to eliminate the noise level. The high absorbance of these samples required the use of very low concentrations ( $\approx 0.1\%$ ); therefore, the initial region (3800–3000 cm<sup>-1</sup>) will not be considered since it may be affected by contamination (especially water). Absorption bands are observed in the regions 1730, 1670–1570, 1500–1340, 1300–1230, and 1180–1000 cm<sup>-1</sup>, which are associated with acidic surface groups (18). The spectrum of carbon C exhibits an absorption band at 1600 cm<sup>-1</sup> which can be assigned to an aromatic ring stretching mode (19), to quinonic structures (20, 21), or to carboxylate groups (18, 22, 23). The spectrum also shows some indications of oxygen bonds in the form of (i) –O–H, the region 1480–1340 cm<sup>-1</sup> is characteristic of –O–H bending vibrations; this peak may be associated with phenolic and carboxylic OH (12, 18, 24); (ii) C–O, the region of 1230–1250 cm<sup>-1</sup> is characteristic

of C–O stretching vibrations and could indicate the existence of aromatic ethers (21, 25), such as lactonic structures –C–O–C– (26) and carboxylic groups (20, 22, 24); and (iii) C–O, a band at 1180–1000  $\text{cm}^{-1}$  is characteristic of phenolic C–O stretching vibrations (18).

The spectrum of carbon C(H<sub>2</sub>) has, with respect to that of carbon C, a narrower band at 1590  $\text{cm}^{-1}$  and this could be an indication of a more homogeneous aromatic structure; there could also be a contribution of carboxylates and quinonic structures to this band. However, according to the TPD results it seems that the presence of quinonic structures (evolving as CO) is less probable. A small band is seen at 1730  $\text{cm}^{-1}$  which would correspond to C=O stretching vibrations in carboxylic or lactonic groups (18, 20–25). The spectrum also exhibits a new band at 760  $\text{cm}^{-1}$ —which can be assigned to aromatic structures with a low degree of substitution (24, 27)—and a larger peak at 1220  $\text{cm}^{-1}$  (aromatic ethers, carboxylic groups).

The spectrum of carbon C(H<sub>2</sub>)8N shows—with respect to that of carbon C(H<sub>2</sub>)—new bands at 1440 and 1130  $\text{cm}^{-1}$  which can be assigned to carboxylic and phenolic OH groups. The peak at 880  $\text{cm}^{-1}$  could be due to aromatic C–H bonds; the displacement from the 760  $\text{cm}^{-1}$  observed for C(H<sub>2</sub>) seems to indicate a larger degree of aromatic substitution produced by introduction of phenolic hydroxyls in the aromatic rings.

All these data indicate that in general terms the heat treatment in H<sub>2</sub> has produced a larger homogeneity of the aromatic structures. This is to be expected since the high-temperature treatment could induce the elimination of heteroatoms (such as S and O) from the aromatics rings. The breaking down of fragments would cause saturations or free radicals which could saturate with H<sub>2</sub> giving C–H bonds (band at 760  $\text{cm}^{-1}$ ). This is in agreement with the above comments about the TPD curve obtained for sample C(H<sub>2</sub>) in which CO complex is

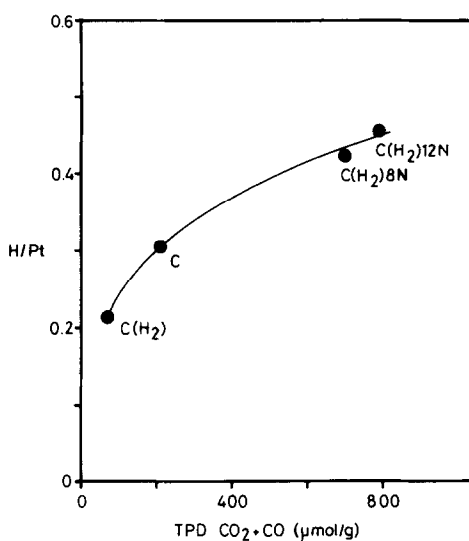


FIG. 4. Relationship between Pt dispersion of catalysts and amount of oxygen surface complexes (measured as  $\mu\text{mol/g}$  of CO<sub>2</sub> and CO evolved) of the supports.

not evolved after H<sub>2</sub> treatment. The oxidizing treatment with H<sub>2</sub>O<sub>2</sub> introduces carboxylic and phenolic groups and this is in agreement with the TPD results since the former would be desorbed as CO and the later as CO<sub>2</sub>, the amount of both increasing with the oxidation treatment.

### B. Catalysts

As stated above, the main objective of this work was to relate the dispersion of the platinum with the amount of oxygen surface groups. The Pt dispersion, measured by hydrogen chemisorption, has been checked out by TEM in catalyst C(H<sub>2</sub>)8N; the former gave a value of 2.6 nm and the latter 2.7 nm, in very good agreement. Figure 4 clearly shows that the H/Pt ratio increases with the increasing amount of surface groups. It should be noted that the support C (which has not been treated in hydrogen) also fits the plot for the other three samples. Consequently the oxygen surface groups of the carbon support play a major role in the final Pt dispersion.

Since the carbon supports have very similar porous textures and the catalysts have

been prepared following the same experimental procedure, it is clear that the increase in metal dispersion is mainly due to the oxygen surface groups. In fact, the dispersion of catalyst C(H<sub>2</sub>)8N is more than twice the dispersion of catalyst C(H<sub>2</sub>) because of the larger amount of surface groups of the former.

The final state of dispersion of the catalyst will depend (keeping constant all other factors) on the interactions of the precursor with the carbon support at the different stages of preparation. The clear dependence described here between the Pt dispersion and the amount of surface groups could be explained by any (or both) of the following phenomena.

(a) The metal precursor distribution throughout the carbon support is an important aspect in the impregnation technique; both the solvent-carbon interactions and the charge of the impregnating metal complex may play an important role. Our results indicate that solvent-carbon interaction will be more important because the acidic nature of the carbons is not favorable to the anionic character of the metal precursor. In fact, since the metal precursor—H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O—is in aqueous solution, the changes in hydrophobicity of the carbon upon treatment with H<sub>2</sub>O<sub>2</sub> are important because acid groups are introduced in the carbon. These surface groups will then increase the wettability of the carbon facilitating the access of the aqueous solution to the internal pore structure. This in turn leads to a more homogeneous distribution of the precursor than in a nonoxidized carbon. Of course, carboxylic groups (CO<sub>2</sub> complex) are expected to be a major influence in that step of catalyst preparation.

This finding is somewhat related to the results described by Machek *et al.* (1-4) when studying the effect of solvent polarity in the adsorption of hexachloroplatinic acid on activated carbon and Al<sub>2</sub>O<sub>3</sub>. They found that the use of a nonpolar solvent led to a higher dispersion than when polar solvents

for activated carbon were used. For Al<sub>2</sub>O<sub>3</sub> (since its surface is hydrophilic) the distribution of the precursor was more homogeneous and the dispersion of Pt was larger when aqueous solution was used (4).

(b) Once the metal precursor is distributed on the carbon support, the maintenance of this distribution during the reduction stage is important. Metal and/or its precursor might interact with the support through its surface groups hindering a redistribution and agglomeration of the metal and affecting its final state of dispersion. This interaction could be important during the reduction of the precursor if the metal-support interaction is weak. In fact, Flynn and Wanke (28) have pointed out that the sintering of a Pt catalyst may start at temperatures as low as 573 K. On the other hand, Ehrburger *et al.* (8), when studying the dispersion and sintering of iron-phthalocyanine, concluded that the oxygen surface groups of the support acted as anchorage centers, maintaining the metal dispersion. According to this idea, for H<sub>2</sub>PtCl<sub>6</sub> the oxygen surface groups may act as chemical anchorage centers, probably through the formation of some type of Pt-O complex on the surface.

Furthermore, this work allows one to relate the dispersion with a given type of oxygen surface group since it would be expected that not all of them would have the same effect. The more stable is the surface group the more effective the anchorage of the platinum and the larger the metal dispersion. Figure 5 includes the plots for the metal dispersion (expressed as the number of surface atoms) as a function of the amount (expressed as number of molecules) of surface complexes desorbed as CO<sub>2</sub> and CO. It is clearly shown that there is a much better linear correlation when considering the CO complex. This means that the less acidic groups (especially phenolic according to the FTIR results) are more responsible for the anchorage. They hinder the sintering of the metal particles

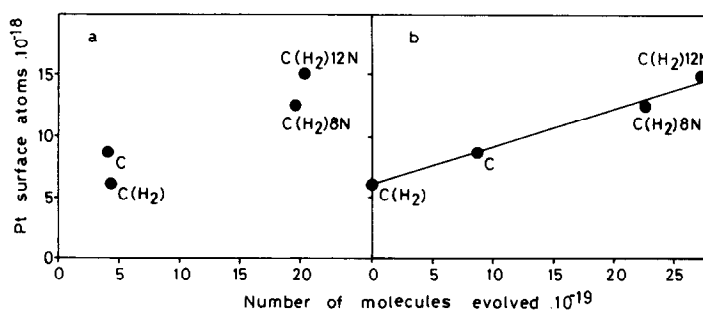


FIG. 5. Relationship between the Pt surface atoms and the number of molecules evolved: (a)  $\text{CO}_2$ , (b) CO.

during decomposition and reduction of the metal precursor. These results could be expected if we consider that only the CO complexes are stable at the reduction temperature whereas an important amount of the  $\text{CO}_2$  complexes has already been evolved at this temperature, as deduced from Fig. 2.

Consequently with these results and the comments stated above about points (a) and (b) it is concluded that the increase in oxygen surface groups of the carbon supports can affect the Pt dispersion in both the impregnation and the decomposition–reduction steps. A decrease in hydrophobicity—caused mainly by the carboxylic groups—would enhance the diffusion of the metal precursor toward the internal porosity of the carbons during the impregnation in aqueous solution, therefore giving a better distribution. An increase in the Pt–carbon interactions—caused mainly through the CO complexes which act as anchorage centers—would also increase the Pt dispersion during the decomposition–reduction step.

A further test of the interaction between the metal and the support could be to follow the sintering behavior of the catalysts prepared. The sintering experiments have been carried out in  $\text{H}_2$  using different temperatures and lengths of treatment. Two catalysts were selected,  $\text{C}(\text{H}_2)$ —with a small content of surface groups—and  $\text{C}(\text{H}_2)12\text{N}$ —with a large content of surface groups, but having almost identical porous textures. The data for these catalysts have

been listed in Table 2 which also includes the increase (expressed as percentage) in particle size.

The results of Table 2 indicate that both catalysts show different behavior toward sintering. The behavior is opposite that expected on the basis of only particle size. The sintering should be easier for the smaller particles, that is for the  $\text{C}(\text{H}_2)12\text{N}$  catalyst. However, the increase in particle size with temperature and length of treatment is much larger for catalyst  $\text{C}(\text{H}_2)$  (136.2%) than for catalyst  $\text{C}(\text{H}_2)12\text{N}$  (33.3%). This effect is more clearly seen in Fig. 6 where the dispersion ratio  $D/D_0$  ( $D_0$  is the dispersion of the original catalysts) is plotted versus time of treatment for the dif-

TABLE 2  
Dispersion and Mean Particle Size  
of Sintered Catalysts

Sintering conditions		$\text{C}(\text{H}_2)$			$\text{C}(\text{H}_2)12\text{N}$		
$T$ (K)	$t$ (h)	H/Pt	$d$ (nm)	% <sup>a</sup>	H/Pt	$d$ (nm)	% <sup>a</sup>
623	12	0.228	4.7	0	—	—	—
623	12	0.226	4.8	2.1	0.454	2.4	0
623	12	0.215	5.0	6.4	0.453	2.4	0
673	12	0.195	5.5	17.0	0.431	2.5	4.2
723	12	0.175	6.2	31.9	0.404	2.7	12.5
773	12	0.142	7.6	61.7	0.397	2.7	12.5
773	16	0.139	7.8	66.0	—	—	—
773	20	0.137	7.9	68.1	—	—	—
773	24	—	—	—	0.375	2.9	20.8
773	36	0.097	11.1	136.2	0.341	3.2	33.3

<sup>a</sup> Percentage of particle size increase.

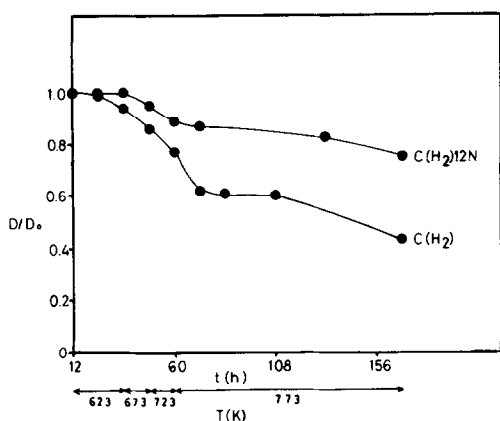


FIG. 6. Effect of different sintering treatments on the dispersion of the catalysts  $C(H_2)$  and  $C(H_2)_{12N}$ .

ferent temperatures studied. This behavior, which can be explained only on the basis of a carbon-platinum interaction, indicates that the oxidized support enhances the thermal stability of platinum.

According to Bett *et al.* (29), in a study of the growth of platinum particles supported on a graphitized carbon black, the rate-limiting step of the sintering process is the migration rate of the particles through the support. It is clear from Fig. 6 that the ease of migration of Pt particles is significantly less for carbon containing oxygen surface groups. The migration of Pt in the absence of these groups is pronounced. Since at the sintering temperatures the  $CO_2$  complexes are almost eliminated this confirms that the interactions of Pt particles with CO complex are important in restricting the migration of Pt and thus hindering the sintering.

#### CONCLUSIONS

It has been shown that the oxygen surface groups of the carbon support play an important role in the properties of the platinum catalysts prepared:

(a) The dispersion increases with the amount of surface groups; there are two possible explanations for this effect:

—the treatment with  $H_2O_2$  increases the number of acidic groups of the carbon

support, thus decreasing its hydrophobicity and making the surface more accessible to the metal precursor during the impregnation step.  $CO_2$  complex, basically carboxylic groups, may be the most important groups in this step since they are the strongest acid groups.

—the increase in the number of oxygen surface groups may produce an increase in the interaction of the metal precursor or the metal particles with the support, thus increasing the dispersion. The more stable groups, CO complex, could be implied in this effect.

(b) The sintering resistance increase noticeably with the content of CO complex; the migration of the Pt is prevented because of the enhanced interaction with the carbon surface.

These results indicate that a deeper knowledge of the chemical nature of the carbon support is needed in carbon-supported catalyst since its effect on the final properties may be at least as important as other more studied factors such as surface area, porosity, and preparation method.

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