Carbon as a Support for Catalysts

I. Effect of Surface Heterogeneity of Carbon on Dispersion of Platinum

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Differences in the degree of dispersion of platinum supported on a graphitized carbon black, subjected to varying levels of carbon burn-off in air, have been found. Dispersion increases with the extent of prior gasification of the carbon support. This increase cannot be explained in terms of total surface area increase of the carbon support as a result of gasification. Rather gasification increases the surface heterogeneity of the carbon support, which in turn increases the potential energy barrier for the diffusion of platinum species across the carbon surface during sample preparation which uses temperatures up to 500°C.

INTRODUCTION

Noble metal catalysts supported on carbons are used in several industrial chemical processes. Since activity and selectivity of a catalyst depend on its degree of dispersion, that is the ratio of surface metal atoms to the total number of metal atoms, various studies have been reported in the literature regarding the determination of surface areas of metals supported on carbons (1–3). Activated carbons, because of their large internal surface area (1000–1200 m²/g), are often used as catalyst supports. However, such carbons are invariably associated with mineral impurities which may act as dissociating centers for hydrogen and oxygen during catalytic reactions and, in some cases, may act as catalyst poisons. There is thus need to use relatively pure carbons as catalyst supports. In catalysis, it is generally desirable to have a high degree of dispersion of the catalyst on the support. Bartholomew and Boudart (4)

have shown that upon activation of Graphon, a graphitized carbon black which has a highly homogeneous surface (5) and is devoid of essentially all impurities, there is a significant increase in the degree of dispersion of supported platinum over that found on the original Graphon. Therefore, a systematic investigation of the changes in the dispersion of platinum as a function of activation of a relatively pure carbon support appears desirable. This paper describes the results of such a study.

EXPERIMENTAL METHODS

Materials

The carbon support was prepared by the graphitization of a furnace carbon black Vulcan 3 manufactured by the Cabot Corp. The carbon black had an arithmetic mean diameter of 235 Å. Surface areas from its particle size distribution and N_2 adsorption were 74 and 77 m²/g, respectively, indicating that the carbon is essentially nonporous. The carbon black was graphitized at 2800°C using the following heating

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cycle: room temperature to 2000°C in 4 hr in an argon purge, 2000–2800°C in 3 hr in a chlorine–argon purge, hold at 2800–2810°C for 1 hr in a chlorine–argon purge and cool down to room temperature in 3 days in an argon atmosphere before exposure to air. Chlorine was used to volatilize most of the inorganic impurities as chlorides. The graphitized sample is referred to as V3G in the text.

Twenty gram portions of V3G were activated at 500°C in a flow of dry air to 3.7, 8.0, 21.4, and 48.9% carbon burn-off in the manner described elsewhere (6).

Preparation of Platinum Supported on Carbon V3G

The experimental procedure for the preparation of supported platinum was essentially the same as used by Bartholomew and Boudart (4). Briefly, the procedure consisted of impregnating the carbon with chloroplatinic acid dissolved in a 4 to 1 vol mixture of benzene and absolute ethanol (50 ml of mixture/g of catalyst). The suspension was mechanically stirred and evaporated to near dryness at room temperature by bubbling N_2 through the suspension for about 70 hr. After further drying the sample in a vacuum oven at 70°C over night, it was reduced in flowing ultrapure hydrogen (20–30 ml/min) at 500°C for 10 hr.

Determination of Surface Area of Platinum

The specific surface area of platinum was determined by using the titration technique suggested by Benson and Boudart (7). For this purpose, a 2–3 g portion of the reduced sample was oxidized with ultrapure O_2 at ambient temperature. The amount of hydrogen adsorbed on the oxidized sample was determined at 30°C in a volumetric adsorption apparatus described by Benson and Boudart (7). The following stoichiometry was used to determine the number of platinum atoms at the surface (7):

$$Pt(O) + 1.5H_2 \rightarrow Pt(H) + H_2O.$$
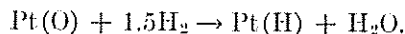
In order to use the above stoichiometry, it is essential that water vapor released during the titration be completely adsorbed by the support. When alumina or silica is used as the metal support, the evolved water can be readily adsorbed by the support. However, it is doubtful if it can be completely adsorbed by the V3G support. It is known (8) that the gasification of a graphitized carbon black increases the total (BET) surface area (TSA) as well as the active surface area (ASA); that is, the concentration of carbon sites at the edges of the crystallites. The relative increase in ASA for a given level of burn-off is far in excess of the increase in TSA. During gasification and subsequent cooling to room temperature in air, ASA is covered with oxygen complexes (8). Walker and Janov (6) have shown that these complexes can preferentially adsorb a monolayer of water, each hydrogen in the adsorbed water molecule hydrogen-bonding to a chemisorbed oxygen atom. Assuming that the increase in ASA for V3G for a given burn-off is of about the same magnitude as for the graphitized carbon black, Graphon, used by Walker and Janov (6), it was calculated that none of the V3G samples used as a support in the present study would have sufficient capacity to completely adsorb water released during titration of the catalyst. Since treatment of oxygenated carbons in H_2 at 500°C (during reduction of the catalyst) leads to the elimination of appreciable amounts of oxygen complexes (9), the adsorption capacity of various V3G samples for water vapor will be further reduced after the reduction step. Therefore, in order to ensure that all the evolved water vapor is adsorbed, 0.5 g Drierite was mixed with the supported Pt–C sample before titration.

Physical adsorption of hydrogen on the carbon support itself was determined for each burn-off sample up to 400 Torr—the maximum pressure used for the titration of the catalyst. This adsorption, which followed Henry's law, was subtracted from the total amount of hydrogen consumed.

Adsorption of hydrogen on Drierite was undetectable.

Surface Area of Carbons

Total surface area of various V3G samples was determined by N_2 adsorption at 77°K, using the BET equation.

RESULTS AND DISCUSSION

Total surface areas of V3G samples activated to different levels of burn-off, as well as surface area and degree of dispersion of platinum for 1.0%, by weight, loading on various supported samples, are given in Table 1. It is seen that surface area and degree of dispersion of platinum increase with increasing activation of the support. The extent of platinum dispersion increases from 16% from the unactivated V3G to 55% for the 48.9% burn-off sample, while surface area of the platinum for the corresponding samples increases progressively with increasing burn-off. It is interesting to note that while there is a twofold increase in the surface area of V3G upon activation to 48.9% burn-off, the degree of dispersion of platinum increases almost 3.5-fold.

It may be argued that for the same catalyst loading an increase in the surface area of the support upon activation decreases the amount of platinum per unit area of the support, thus leading to an increase in the degree of dispersion. In order to examine this possibility, the dependence

TABLE 1

Effect of Burn-off on Surface Area and Degree of Dispersion of Platinum Supported on Various V3G Samples

Burn-off (%)	Surface area		Degree of dispersion of Pt (%)
	V3G (m²/g)	Pt (m²/g Pt)	
0.0	56	41	16
3.7	67	45	17
8.0	70	47	18
21.4	87	69	26
48.9	110	145	55

of degree of dispersion on catalyst loading per unit area of the support was studied before and after activation of V3G to 48.9 burn-off. The results are given in Table 2. The mean diameter of platinum particles and the number of surface platinum atoms per unit area of the support are also included in Table 2. It is seen that for the unactivated sample there is a strong dependence of degree of dispersion on the catalyst loading. For instance, it increases from 16% for 1.0% platinum loading to 27% for 0.3% loading. In contrast, for the activated sample, there is no change in the degree of dispersion upon increasing the catalyst loading from 0.3 to 1.0%. Considering the results for samples 2 and 4 in Table 2, it is seen that for the same catalyst loading per unit area of support the degree of dispersion on the activated

TABLE 2

Effect of Catalyst Loading on Degree of Dispersion, Mean Particle Diameter and Number of Platinum Atoms on the Surface

Sample No.	Burn-off (%)	Pt content		Degree of dispersion (%)	Mean diam of Pt particle (Å)	No. surface Pt atoms/m² of support ×10⁻¹⁶
		Wt%	mg/m² V3G			
1	0.0	1.0	0.178	16	68	8.7
2	0.0	0.5	0.089	26	41	7.1
3	0.0	0.3	0.053	27	39	4.4
4	48.9	1.0	0.091	55	19	15.0
5	48.9	0.3	0.027	55	19	4.6

sample is twice as much as that on the un-activated sample. Furthermore, in the case of samples 3 and 4, even though the activated sample has almost double the catalyst loading per unit area compared to that on the unactivated V3G sample, the degree of dispersion on the latter is half as much as that on the activated sample. It is significant that for 1.0% platinum loading on the unactivated and on the 48.9% burn-off V3G samples, the number of surface platinum atoms per unit area of the support is increased by 72% by activation of the support.

Since a higher degree of dispersion of platinum supported on the activated V3G samples cannot be explained in terms of total surface area increase of the support, another explanation for the observed behavior should be sought. It is known (8, 10) that in the case of relatively homogeneous graphitized carbon blacks, surface heterogeneity can be introduced and increased by carbon gasification. The increase in surface heterogeneity is due to an increase in the width and depth of crystallite boundaries and enlargement of the diameter and depth of point defects in the basal plane of the crystallite. It is possible that the observed increase in the degree of dispersion with increasing burn-off of the support is due to an accompanying increase in surface heterogeneity of the substrate.

Flynn and Wanke (11) have recently shown from an electron microscopy study that, during reduction of a platinum catalyst supported on alumina, agglomeration of particles starts at as low a temperature as 300°C and becomes significant at 500°C. Two models have been proposed to explain the particle size changes during sintering. Ruckenstein and Pulvermarcher (12) postulated crystallite migration as a sintering mechanism, while Flynn and Wanke (13) attributed it to the loss of atoms or molecular metal species from the crystallites, followed by surface diffusion and recapture by other crystallites. Some of the observed experimental facts cannot be explained by

the former mechanism (11). Flynn and Wanke (13) suggested that the migrating atoms may be considered as a two-dimensional gas. During the reduction of the catalyst at 500°C, surface heterogeneities on the support can provide potential energy barriers to the diffusion of the "two-dimensional gas" across the surface, thus hindering particle growth. Obviously, the greater the surface heterogeneity the greater will be the magnitude and/or frequency of the potential energy barriers. Taken in the context of the present study, the greater the extent of gasification of the carbon, the smaller will be the particle size of the supported platinum and, hence, the greater will be the degree of its dispersion for a given catalyst loading, as is observed. To the authors' knowledge, this is the first direct and systematic approach where the effect of surface heterogeneity of support on degree of dispersion of metals has been reported. It is noted that Mahajan and Walker (14) have previously reported that the two-dimensional critical temperature of adsorbed xenon decreases significantly and continuously as the extent of surface heterogeneity of graphitized carbon blacks is increased upon gasification. They have attributed this decrease to an increase in the magnitude of the potential energy barrier for the translation of xenon across the surface.

The mechanism suggested above receives support from the model developed by Phillips et al. (15) for morphological changes occurring in gold particles (diameter less than 100 Å) on amorphous carbon. They consider a random distribution of preferred trapping sites on the heterogeneous surface of amorphous carbon. These trapping sites act as two-dimensional potential wells. Metallic particles will escape from these sites only if their thermal energy is greater than the energy of the potential well.

It was mentioned above that during gasification and subsequent cooling of the carbon in air, its ASA is covered with oxygen complexes. The presence of these

complexes may affect both the chloro-platinic acid uptake as well as its mobility during the early stages of the reduction process. This may eventually affect the degree of dispersion of reduced platinum. In order to see if such is the case, two portions of the 21.4% burn-off V3G sample were impregnated with the same amount of chloroplatinic acid (1.0% platinum loading). One portion was associated with oxygen complexes while the second portion was treated with H_2 at 950°C to remove the oxygen complexes (16). Following this treatment, the sample was cooled in H_2. Under these conditions, ASA will be covered with chemisorbed hydrogen. Since hydrogen is chemisorbed essentially at the same sites as oxygen (17), subsequent exposure of the treated sample to air during impregnation is not expected to result in chemisorption of oxygen (18). Following impregnation, the two samples were reduced in H_2 in the usual manner. The degree of dispersion of platinum supported on the oxidized and oxygen-free carbons was found to be 26 and 27%, respectively. This shows that under the present experimental conditions, the presence (or absence) of oxygen complexes has little or no effect on the degree of dispersion of platinum.

In order to see if there is any effect of solvent used for impregnation on the degree of dispersion of platinum, the 48.9% burn-off V3G sample was impregnated with chloroplatinic acid (1.0% platinum loading) dissolved in distilled water. The suspension was dried in a vacuum oven at 110°C. This method has been used for the preparation of platinum catalysts supported on alumina (11). The degree of dispersion of platinum was found to be 24% compared to 55% obtained for the same catalyst loading when impregnation is carried out in a benzene–ethanol mixture. The mechanism of impregnation and the changes undergone by adsorbed chloroplatinic acid during reduction are speculative. However, it is reasonable to assume that a more uniform

distribution of chloroplatinic acid on the substrate will give a higher degree of dispersion of platinum. The observed marked difference in the degree of dispersion when impregnation is carried out in aqueous and nonaqueous media suggests that chloroplatinic acid is adsorbed more uniformly from a benzene–ethanol mixture than from an aqueous solution. Since the dielectric constant of the benzene–ethanol mixture is much less than that of water, it is likely that chloroplatinic acid is present essentially as undissociated molecules in the former media, while in the aqueous solution it is strongly ionized, platinum being present in the form of an anion $[PtCl_4]^{2-}$. Therefore, it is expected that chloroplatinic acid will be adsorbed non-specifically, molecularly and uniformly from a benzene–ethanol mixture. Since carbons are poor adsorbents for anions (19), it is likely that chloroplatinic acid from an aqueous solution is adsorbed nonuniformly on the support; that is, it may be adsorbed as agglomerates in the form of islands or clusters giving rise to a broad distribution of particle sizes. Such a distribution is more conducive to particle growth during sintering (11).

It is known that following activation of a graphitized carbon in air or oxygen, the edge sites are covered with oxygen complexes. These complexes are predominantly carbonyl groups. It may be agreed that the CO-complex present on the carbon surface after burn-off and chlorine, which may be present either from the chlorine–argon purge (used during the graphitization process) or from impregnation with chloroplatinic acid, could react during heat treatment in hydrogen to form phosgene. It is well known that platinum is very volatile in the presence of phosgene and other carbonyl chlorides and that a vapor phase redistribution of platinum can be obtained in the presence of phosgene. It is also possible to remove platinum from catalyst surfaces by extended exposure to phosgene. However, in the present study formation

of phosgene seems to be unlikely for the following reasons.

It has been shown elsewhere in this paper that the degree of dispersion of platinum for a given catalyst loading on a given activated V3G sample is the same whether the carbon is initially associated with oxygen complexes or whether, following activation, it is treated with H_2 at 950°C to remove the oxygen complexes. To the authors' knowledge, no known heteroatom functional groups present on carbon surfaces are thermally stable up to 2800°C, the temperature seen by V3G during its preparation. However, if any chlorine was retained on the V3G surface after the chlorine–argon purge, then it would have been completely desorbed as HCl during heat treatment in H_2 at 950°C (used for removing oxygen complexes). In this context, Puri (20) has previously shown that chemisorbed chlorine can be quantitatively removed as HCl upon treatment with H_2 at as low a temperature as 700°C. The fact that the degree of dispersion of platinum for a given catalyst loading is the same whether or not the activated V3G sample contains adsorbed CO or Cl_2 suggests that phosgene is not formed during the catalyst preparation.

We do not know for certain if any chlorine is fixed on the carbon surface during impregnation with chloroplatinic acid or upon subsequent heat treatment of the impregnated samples. Puri (20) has shown that in the case of carbons which are initially deficient in carbon–hydrogen surface complexes (such as graphitized V3G) most of the chlorine that can be chemisorbed on the carbon surface remains intact even after prolonged outgassing at 1200°C. Taken in the context of the present study, this means that any chlorine chemisorbed on the carbon surface during impregnation will not be desorbed as Cl_2 during subsequent treatment with H_2 (reduction step) although it may be evolved as HCl. Furthermore, Puri (20) has shown that

while the CO-complex on a carbon surface is desorbed almost completely on heat treatment in vacuum at 1000°C, it is completely eliminated in H_2 at much lower temperatures. This suggests that the CO-complex is not desorbed as such in H_2; probably it comes off as CH_4 and/or H_2O. In the light of the above discussion, it is concluded that in the present study there is little possibility of the formation of phosgene.

Spillover of dissociated hydrogen away from platinum onto adjacent active sites on the carbon support has been reported previously (2, 21). It may be argued that an increase in ASA of the V3G carbon support upon gasification will increase the extent of spillover, thus giving a higher apparent degree of dispersion of platinum. However, it is concluded that negligible spillover occurred in the present study for the following reasons:

i. Hydrogen spillover has not been reported during titration of the carbon supported catalyst at ambient temperatures (4), although its occurrence has been observed at 250°C and above (2, 21).

ii. During reduction of the catalyst at 500°C, the ASA of the carbon support will be largely occupied by hydrogen (17). Since chemisorbed hydrogen will not be displaced by oxygen during the oxidation of the catalyst at room temperature (18), uptake of hydrogen, if any, on the carbon support during the titration of the catalyst will be negligible.

iii. When 48.9% burn-off V3G sample, prior to impregnation, is heated in H_2 at 950°C and subsequently cooled in H_2, the ASA will be completely covered with hydrogen. If any hydrogen spillover were occurring, the calculated degree of dispersion of platinum supported on the H_2-treated carbon should have been less than on the V3G sample associated with oxygen complexes. However, the degree of dispersion of platinum on both the samples was shown earlier to be the same.

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