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Properties of Platinum Catalysts Supported on Carbon Blacks

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Chemical and gas-plasma treatments were used to modify chemical/physical properties of carbon black powder commonly used to support platinum catalysts. Altered catalyst-carbon interactions affect catalyst-particle size, which can, in turn, affect catalyst activity and subsequent catalyst life. We have demonstrated that particle size of deposited platinum on carbon can be changed by carbon black pre-treatments. These modifications can be easily applied to carbon blacks used in fuel cells, high powered batteries, and a variety of chemical reactions where noble metal catalysts are supported on high surface area carbon blacks.

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ABSTRACT

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INTRODUCTION

Carbon black is a widely used support for heterogeneous electrocatalysts due to its high surface area, porosity, stability in a variety of liquid media, and good electrical conductivity. Catalytic activity of high area carbon-supported platinum (and its alloys) has been of great interest in fuel cell applications for both oxygen reduction and methanol oxidation. One important criteria is how Pt ion precursors are initially loaded, supported and subsequently reduced. Typically, Pt based solutions are mixed with, and allowed to either adsorb on, or chemically bind to, carbon black powder. Platinum ions are then reduced to metallic Pt by adding liquid or gaseous reducing agents. Since interactions between carbon surface properties and precursor Pt ions affect the initial fixation and subsequent reducibility of metal ions, it is expected that changing preparative conditions of carbon black (which affect chemical structure, surface area, porosity, and surface composition) will play significant roles in deciding loadings, dispersion, morphology, chemical and electronic properties, and ultimate catalytic properties of dispersed Pt particles. Presently, clear correlations between these properties and carbon black surface functional groups are not quantitatively known.

As discussed by Kinoshita [1], activated carbon blacks contain appreciable amounts of combined oxygen and hydrogen which give rise to various surface complexes. Electrochemical and catalytic properties of carbon blacks strongly depend on chemical species present on carbon surfaces, and how, and in what quantities, they are bound there. Oxygen based functional groups such as quinones (>C=O), hydroxyl and/or phenols (-OH), and carboxyl (-COOH), can increase final Pt metal uptake by serving as adsorption sites and can also increase metal dispersion by enhancing sintering resistance to subsequent thermal treatment. It is therefore of interest to precisely understand interactions between Pt metal complexes and carbon surface groups.

It is possible to alter concentrations of specific carbon surface groups, or to create new surface functional entities such as carboxyl, hydroxyl or quinone groups, via chemical or thermal treatments. By introducing appropriate identifiable electroactive functional groups, carbon black can be made either hydrophobic or hydrophilic. Numerous studies, intended to understand the influence of catalyst particle size on catalyst activity, have resulted in differing (and often contradictory) results. Bregoli [2] found that smaller Pt crystallites had greater specific catalyst activity for oxygen reduction in acid electrolytes. Giordano et al.[3], who carefully studied effects of Pt particle size on oxygen reduction in phosphoric acid fuel cells did not find such a correlation, but concluded that Pt utilization was linearly related to electrode hydrophobicity-hydrophilicity.

Peuckert et al.[4] showed that 30-40 Ådiameter Pt particles gave the highest Pt activity for oxygen reduction and found that various chemical groups, tethered to carbon surfaces, also decisively affected catalyst dispersion. Watanabe et al. [5] found that oxygen reduction, in both sulfuric and phosphoric acid, was not directly dependent on Pt crystallite dimensions, but, rather, on Pt inter-crystallite distances on carbon supports.

Effects of various oxygen containing surface groups and their concentration on carbon black supports have been correlated to subsequent Pt dispersion and activity. Hillenbrand and Lacksonen [6, 7] found significantly decreased activity of Pt-on-carbon anodes if the carbon black was heated at 1000°C in nitrogen before applying Pt. If the carbon was reoxidized (with CO_2 at 1000°C) before applying Pt, full Pt activity was obtained. Out of this work came the realization that chemical variations of carbon surfaces had large effects on Pt catalyst activity and that interactions between carbon supports and Pt catalyst play important roles. Prado-Burguette et al. [8] studied effects of various oxygen containing surface groups on subsequent Pt dispersion and found that increased oxygen surface groups on carbon supports resulted in better Pt dispersion. Carbon-oxygen complexes (phenolic hydroxyl or quinonic groups on carbon black), which form Pt-O complexes during heat treatment, were found to be very effective anchoring sites in preventing Pt. agglomeration.

Drazic and Adzic [9] studied different surface treatments of carbon black used as Pt supports for hydrogen electrodes and found that HC1 treated carbon blacks improved Pt catalyst performance in acid solutions. Antonucci et al. [10] reported that for Pt adsorbed on carbon blacks, as oxygen containing groups on carbon surfaces increased, Pt surface areas decreased. Functional groups on carbon support affected the electronic nature of Pt states. Pt binding energy shifts, measured by XPS, correlated with oxygen containing functional groups on carbon black. In this report, we modified, characterized and evaluated physical and chemical properties of Pt supported on various pretreated carbon black powder.

EXPERIMENTAL

Vulcan XC-72 (Cabot, Bilerica, MA), with 300 Å average particle size, was treated at room temperature with either acid, base, or one of three separate gas plasma treatments. For acid or base treatment, carbon powders were well mixed with either hydrochloric acid or sodium hydroxide, filtered, rinsed copiously with distilled water, and dried in a vacuum oven. Gas plasma treatment has been thoroughly reviewed by Liston [11]. Dry carbon black powder, in an open tray, was placed in Gasonics/IPC (Fort Washington, PA) Model 4107 barrel plasma etcher.

The chamber was then evacuated, and backfilled at low gas flow rates with either oxygen, ammonia, or CF_4, and operated at 300 millitorr gas pressure and 250 watts of rf power for 16 minutes. Computer controlled valves allowed slow evacuation and filling of the chamber which prevented the extremely fluffy carbon black powder from scattering.

Single point BET surface area measurements were performed on these carbons by using 30% N_2/70% He. Carbon pH was measured in a carbon-water slurry. Platinum was impregnated on carbon black supports by mixing 4 g carbon, 2.65 g of hexachloroplatinic acid (H_2PtC1_6), and 300 ml of distilled water. The solution was mixed well under constant stirring and heating, and adjusted to pH 7. Absorbed Pt ions were then reduced to metal by in-situ reduction with formaldehyde at 90-100°C.

Platinized carbon was filtered, rinsed with hot water and dried overnight under dynamic vacuum at 80°C to yield 20% Pt on carbon by weight. Although chloroplatinic acid could also have been reduced to Pt metal by passing argon over chloroplatinic acid soaked carbon samples at 500°C, it would have required an extra washing to remove residual chloride and was therefore not used.

X-ray diffraction, used to determine particle size of deposited Pt crystallites in carbon black, was carried out in a Phillips diffractormeter using Cu Kα radiation. Based on the (111) Pt peak width, Pt particle size, d, was calculated by the Scherer formula.

$$\beta_{1/2} = 0.9\lambda/d\ (\cos\theta/2)$$

where $\beta_{1/2}$ is the x-ray diffraction bandwidth (in radians) at half height, and θ is the maximum peak position (approximately 40° for Pt metal).

RESULTS AND DISCUSSION

Table 1 lists surface area, pH, ESR spin intensities and particle size of Pt supported on carbon black that had previously undergone various chemical and gas-plasma treatment. Changes of more than 3 pH units after nitric acid and CF_4 gas-plasma treatment indicated that carbon black had become considerably more acidic. Gas-plasma treatment causes minimal changes in physical properties since BET surface areas of baseline and gas-plasma treated carbon blacks were not significantly different.

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF TREATED CARBON BLACKS

	TREATMENT					
	NONE	ACID	BASE	CF_4	O_2	NH_3
pH	6.5	3.2	6.2	3.3	4.2	6.5
surface area m^2/g	197	--	--	195	192	190
ESR Spin Intensity	1.0	--	--	1.1	1.3	0.7
Pt particle size, Å	74	72	61	59	74	69

Electron Spin Residents Spectra

Unpaired electrons in carbon (electrons not involved in chemical bond formation) are sensitive probes of their microscopic environment and can provide information on surface chemical processes. ESR linewidths were not significantly different for baseline, CF_4 and NH_3 treated carbons (55.1, 54.3 and 53.5 Gauss, respectively), while linewidths of O_2 treated carbon were only slightly narrower (48.6 Gauss). The relative spin number in NH_3 plasma treated carbon black samples was $\leq$70% of the number of spins in either baseline, CF_4 or O_2 plasma treated carbon black samples. Reduced spin concentrations may be due to less broken bonds at carbon edge sites.

Platinum Particle Size

Particle sizes of Pt crystals on carbon blacks varied with carbon black pretreatment. While average particle size of Pt dispersed on baseline carbon was 74 Å, smaller particle sizes were obtained when Pt was dispersed on base treated (59 Å), or CF_4 gas-plasma treated carbon (61 Å). Smaller Pt particle sizes imply higher catalyst surface areas and better catalytic activity.

CONCLUSION

Modifying electrocatalyst-carbon support interactions by altering carbon chemistries can beneficially affect platinum electrocatalytic activity.

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