PREPARATION AND CHARACTERIZATION OF Pt-BLACK FOR ANODIC HYDROCARBON OXIDATION

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A. Introduction

The work presented here is part of a wider study to develop a correlation between the physical characteristics of Pt-black and its activity for the anodic oxidation of saturated hydrocarbons. Since the physical characteristics of a black should be a function of its preparation, some emphasis has been placed on studying a preparative method in order to obtain Pt-black of varying characteristics. Because of the technical importance of Pt-black and the scarcity of information on its preparation available in the recent literature, this phase of the study is of interest on its own.

B. The Formaldehyde Reduction of Pt-black

Of the many reductions proposed and used to prepare Pt-black, one of the most widely studied reactions concerns the reduction of a chloroplatinic salt with formaldehyde in a basic medium.

The over-all reaction is mainly a combination of the following reactions:

$$PtCl_6^{2-} + 2\,HCHO + 6\,OH^- \rightarrow Pt + 2\,HCOO^- + 4\,H_2O + 6\,Cl^-$$

and

$$PtCl_6^{2-} + HCHO + 6\,OH^- \rightarrow Pt + CO_3^{2-} + 4\,H_2O + 6\,Cl^-$$

with one or the other being more dominant according to the preparation conditions[1].

This system was selected for our study because it is the best known process and because it offers the possibility of separating the initial nucleation and the subsequent growth of the nuclei to a well defined precipitate of Pt-black. Furthermore, the growth stage can be considered to occur as a mixed electrode process. According to this latter mechanism, the initial nucleation is followed by an electrochemical deposition of Pt coupled with an anodic oxidation of formaldehyde. Although both electrode processes occur on the same particle simultaneously and at the same rate, they are essentially independent of each other. The principle is illustrated in Fig. 1 which shows the individual i(E)-curves obtained for the anodic

oxidation of formaldehyde and the cathodic electrodeposition of Pt from a chloroplatinic salt, both in acid and in basic electrolyte on a Pt-microelectrode. From these curves it can be concluded that a mixed electrode reaction is only possible in basic solution since the anodic reaction occurs at lower potential than the cathodic reaction. This is not the case in acid medium, agreeing with the observation that, although thermodynamically possible, a chloroplatinic salt is not reduced by formaldehyde in acid medium even over extended periods of time.

Figure 2 shows the change in potential of a Pt-microelectrode vs. RHE immersed in a solution of chloroplatinic acid and formaldehyde after the addition of NaOH. The absolute value of potential should indicate the potential of the particles formed during reaction. An interesting observation from this experiment is that the potential of the microelectrode changes slowly during a period of time which coincides with the induction time of the reaction, i.e. time between mixing of the reactants and visual observation of precipitation. Simultaneously with the observed blackening of the solution, the potential drops steeply to remain at about +100 mv (vs. rev. H_2-electrode in same solution) during the reaction. The fact that the potential always remains positive with respect to the hydrogen electrode indicates that hydrogen evolution, which is thermodynamically possible, does not occur under these conditions.

In considering the precipitation of Pt-black as a mixed electrode process, it is tempting to use criteria similar to those used in electrodeposition of powders[2] for predicting the effect of reaction parameters. The major difference is that the current would be supplied by the formaldehyde oxidation, and would vary according to the reversibility of the reaction and the concentration of formaldehyde. Thus, by extension of the experience on electrodeposition of powders, factors favoring deposition of Pt at conditions closer to the diffusion limiting transport should tend to give finer particles.

On the other hand, the nucleation process (i.e. the formation of a cluster of a few atoms without metallic properties) has to occur by a mechanism different from the electrochemical mechanism. In addition, heterogeneous nucleation in the walls of the vessels and on impurity particles is also possible.

A phenomenon related to the nucleation process is the formation of a bright mirror on the solution surface and walls of the container. Under some conditions, in absence of stirring the formation of the mirror on the surface can be observed before any reaction appears in the bulk solution. The reaction (characterized by blackening of the solution) progresses slowly down from this surface mirror into the solution as a very well defined layer, which can reach a thickness of up to several centimeters before complete mixing occurs. This observation indicates a dendritic growth on the mirror with possible detachment of crystals that serve as secondary nuclei.

In order to obtain active materials, the formation of this mirror is to be avoided since after drying, platelets of very low BET surface area are formed. In general, the longer the induction time, the larger the amount of mirror material will be formed.

Another difficulty when studying the effect of preparation parameters involves transformations occurring after preparation, such as agglomeration and recrystallization. These factors are affected by the gas bubbled during preparation, by the presence of protective colloids and ions, and by the adsorption of intermediates of HCHO oxidation and/or of its polymerization products, etc.

Finally, in an actual preparation drastic changes of parameters occur (especially, for example, the concentration of $PtCl_6^{2-}$) as the reaction progresses which results in the formation of black under varying conditions.

C. Physical Characterization and Determination of Electrochemical Activity

In order to study the effect of the parameters on the precipitation process, many preparations with different reaction conditions were made, and the resulting materials were characterized using the BET surface area, pore size distribution, bulk density, electron microscope shadowgraphy, selected area electron diffraction and X-ray diffraction. The last method was an extension of the method of Warren and Averbach (3); the technique utilized a Fourier analysis of the diffraction intensity data to provide information on the average crystallite size. In addition, strain and resulting stored energy, stacking and twinning fault probability are separated. The combined use of these methods allows characterization of the crystallites, the elementary particles, and the agglomerates which form a black (4).

The activity of the prepared blacks for the anodic oxidation of propane at 150°C in 85% H_3PO_4 was measured, using a Pt-Teflon structure (5, 6) and the floating electrode technique (7). In addition to the conventional over-all activity determination, a nonsteady-state method has been developed to determine the intrinsic activity of the black in the Pt-Teflon structure (8).

From these measurements the current at a potential of 400 mv vs. rev. H_2 (i_{400}) and the value of the current peak (Ep) were used as parameters characterizing the activity.

D. Results on Pt Preparation

Separation of nucleation and growth phases. After preliminary experiments which showed poor reproducibility, attention was directed to the separation of the nucleation and growth stages of the process. This was accomplished (1) by adding Na_2CO_3 to a solution of $PtCl_6^{2-}$ and HCHO to raise the pH to ~ 9 where the mixed electro-growth process is insignificant, (2) by allowing the resulting solution to nucleate for a predetermined time, and (3) by adding this mixture to the NaOH solution. The number of nuclei per unit volume of solution was varied by changing the nucleation time and the portion of $PtCl_6^{2-}$-HCHO solution submitted to this process. This procedure was derived from that of Turkevich, Hillier, and Stevenson (9) for the precipitation of gold. Two fast-addition funnels were used to insure quick mixing of reactants in order to achieve the desired initial concentrations. The apparatus is shown in Fig. 3.

The effect of nuclei concentration on crystallite size for experiments performed with the same reactant concentrations, the same sequences of addition, the same temperatures, etc., but with varying nucleation times, is indicated in Table I.

TABLE I

Black #	Time (min)	Average Crystallite Size (Å) 111	200	220	311
73-44	1	87	75	82	77
73-45	3	70	62	75	70
73-46	10	72	60	67	63

The black produced from the 1 minute nucleation time had the largest crystallite size, while the materials produced from the 3 and 10 minute nucleation have approximately the same size. Since crystallite size is inversely related to the number of nuclei present at the beginning of the growth stage of the preparation, these results indicate that after 1 minute nuclei are still forming and by 3 minutes the formation of nuclei has reached a steady state condition.

In additional preparations the relative number of nuclei/unit volume was changed by reducing the volume of the nucleating solution without changing the concentrations, as mentioned above, at a constant time of 10 minutes and at constant concentration of the final reacting solution. Comparing solutions with the number of nuclei in the ratio 1; 1/2; 1/4; 1/8, the most active material was that corresponding to 1/4 ratio.

Effect of order of addition. Adding HCHO to a premixed solution of $PtCl_6^{2-}$ and NaOH resulted in inactive catalysts with surface areas varying between 2.6 and 7 m^2/g when using high NaOH conc = 5 M (Table II). An example of the electron microscope pattern of these preparations is given in Fig. 4 which shows very large spherical particles. Selected area electron diffraction of individual particles shows that they are polycrystalline. In contrast, a material obtained by adding the mixture of $PtCl_6^{2-}$ and HCHO to 5 M NaOH at the same temperature, concentration, etc., shows a lace-like structure (Fig. 5) made of single crystals and high over-all activity. In experiment #73-25, nucleation time was not controlled.

TABLE II

High NaOH Concentration (NaOH-5.0M)
(All Concentration Refer to Electrogrowth Phase)

a) HCHO added to $PtCl_6^{2-}$/NaOH mixture

Black #	$PtCl_6^{2-}$ Conc. (M)	HCHO Conc. (M)	BET (m^2/g)	Electrochemical Activity i_{400} ma/cm^2	i_p ma/cm^2
73-26	0.25	1.50	3.0	Inactive	------
73-30	0.25	1.50	5.0	Inactive	------
73-31	0.25	1.50	6.9	Inactive	------
73-32	0.25	1.50	4.1	Inactive	------
73-35	0.05	1.50	2.5	Inactive	------
b) $PtCl_6^{2-}$/HCHO mixture added to NaOH					
73-25	0.25	1.50	31.7	58	235
73-58	0.13	0.39	25.2	72	107
73-56	0.06	0.19	22.2	28	52

Effect of reactant concentrations. The higher concentration of HCHO during the growth produced a faster reaction rate and consequently a smaller particle size. When the molar ratio of HCHO to $PtCl_6^{2-}$ was equal to or lower than unity, long induction times were found which resulted in extensive mirror formation during preparations at or below room temperature. It was apparent from the stoichiometry of the reaction that the reduction requires at least a 2 to 1 molar ratio of HCHO to $PtCl_6^{2-}$; however, preparations were made a ratio of unity or lower in order to study the relation between low HCHO concentration and mirror formation. At high temperatures, the induction time was considerably shorter, but the same mirror product was obtained. However, at molar ratios of HCHO to $PtCl_6^{2-}$ $\geq$ 3, there was no appreciable effect contributable to the HCHO concentration.

Therefore, working at molar ratios of HCHO to $PtCl_6^{2-} \geq 3$, blacks were prepared either at different $PtCl_6^{2-}$ concentrations or at various NaOH concentrations in the growth stage while keeping constant the temperature, nucleation time, and the concentration of $PtCl_6^{2-}$ and HCHO in the nucleation stage. Rather than attempt to determine the effect of varying the concentration of the $PtCl_6^{2-}$ or NaOH separately, the results are better presented in the form of the molar ratios. Plotting the current/geometric cm^2 at 400 mv of the various blacks as determined in the over-all activity against the molar ratio of $[NaOH]/[PtCl_6^{2-}]$, there is an apparent optimum ratio of ~ 25:1 (Fig. 6). Above and below this value, activity falls off.

In particular, the active materials formed at molar ratios of HCHO to $PtCl_6^{2-}$ of 11 and 25 were obtained from reasonably reproducible preparations from an electrochemical activity standpoint. X-ray diffraction data on identical preparations 73-60, 61, and 62 (molar ratio of 11) gives very good agreement on crystallite size (Table III)

TABLE III

Black	Average Crystallite Size (Å)				Electrochemical Activity	
	111	200	220	311	i_{400} ma/cm^2	i_p ma/cm^2
73-60	51	53	52	49	102	147
73-61	51	50	50	48	70	143
73-62	55	50	52	51	67	105

Effect of temperature. The only apparent effect of temperature was to increase the rate of reaction. Many early investigators[10] emphasize the need to prepare the blacks at low temperatures to avoid formation of resinous material (probably polymers of HCHO) and formation of mirror. Attempts to reproduce Willstatter preparation at 5°C, with special precautions to avoid local heating, failed to produce a black of higher activity than those prepared at high temperatures. Since the more active blacks obtained in the present work were prepared at 80-90 C, it is tempting to conclude that higher temperature is beneficial insofar as it accelerates the reaction, decreasing the induction time, and possible mirror formation.

Effect of oxygen. It has been claimed that adsorbed oxygen plays an important role in the catalytic activity of platinum black in the sense that materials freed of oxygen were generally inactive[11]. To test this, a series of identical preparations were made under O_2 and N_2. The bubbling of oxygen through the reaction solution was useful in coagulating the resulting colloid solutions of platinum. As to their effect on BET area or electrochemical activity, no clear difference could be detected between black produced under O_2 or under N_2.

The beneficial effect mentioned in the literature may be related to the slower sintering rate of platinum when covered with oxygen, reported by McKee[12], or to a cleaning by oxidation of chemisorbed intermediates of the HCHO oxidation.

E. Relation Between Structure and Activity

In general, the over-all activity per unit weight is high in blacks having agglomerates of high internal porosity and relatively large particle size. This may be a pure structural effect confirming those electrode models in which electrolytic transport to the reaction site through the flooded agglomerates is postulated[13, 14]. Surface areas larger than $\sim 15\ m^2/g$ are necessary to obtain high activity; above this value no correlation between activity and surface area was found.

A somewhat surprising result is that a black with low stored energy produced higher over-all activity than the blacks with considerably more stored energy. Preliminary measurements show a similar effect on intrinsic activity. Work is continuing to define better the properties of the black and to relate these properties to the structure after electrode manufacture.

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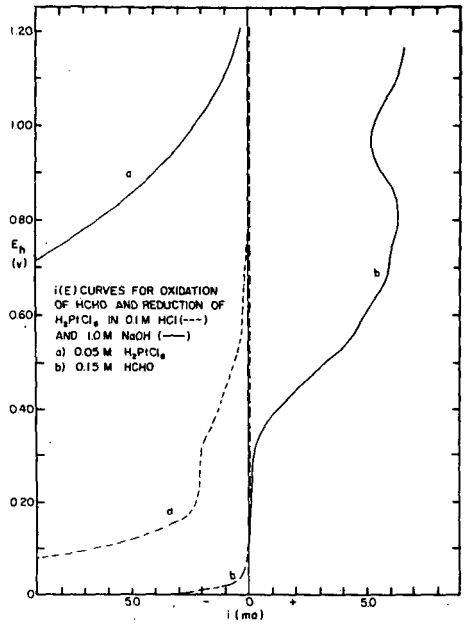

Fig. 1 i(E) curves

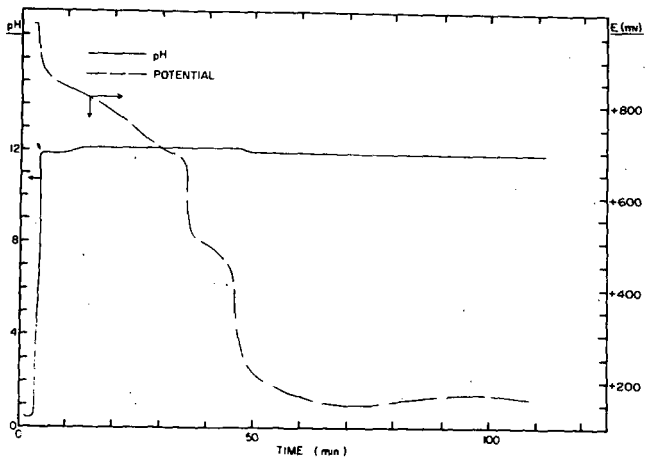

Fig. 2 Variation of potential with time

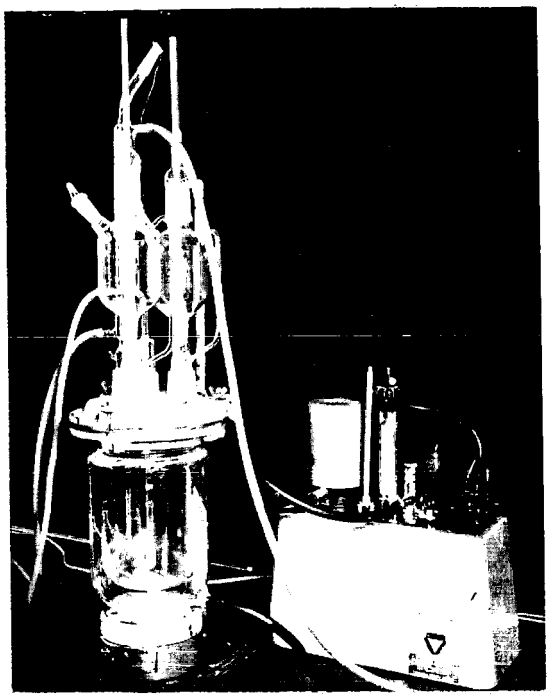

Fig. 3 Apparatus for preparation of Pt blacks

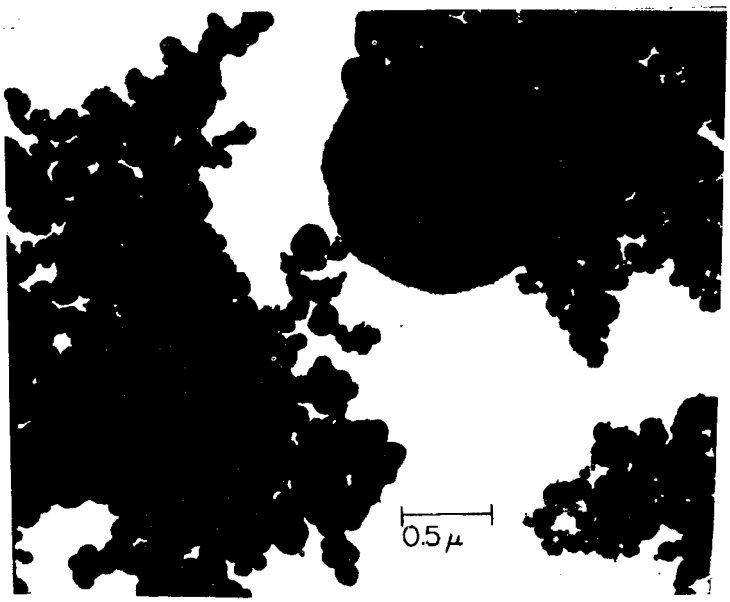

Fig. 4 Pt black, 73-26

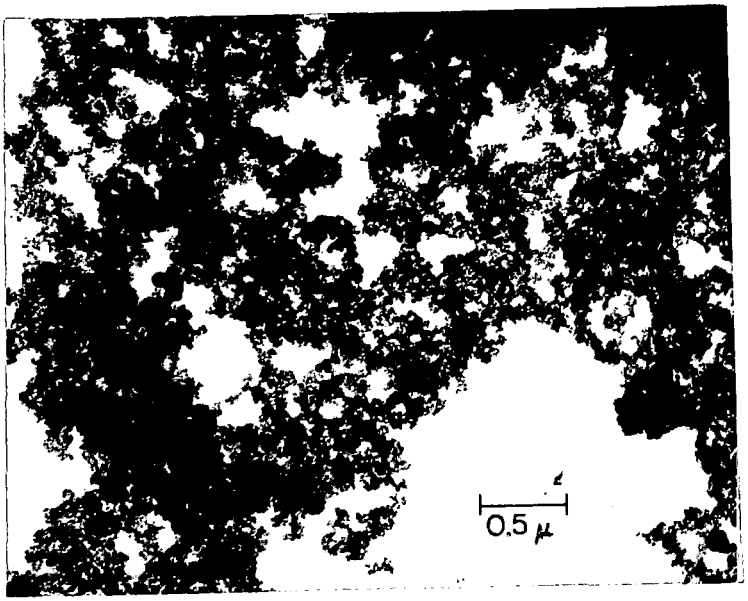

Fig. 5 Pt black, 73-58

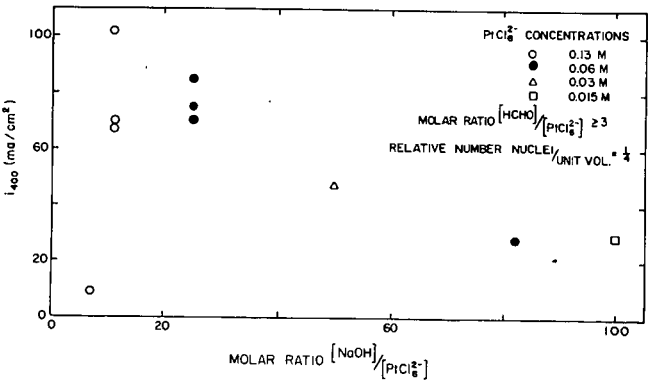

Fig. 6 Activity as a function of molar ratio