JOURNAL OF CATALYSIS 67, 287–295 (1981)

Temperature-Programmed Reduction and Cyclic Voltammetry of Pt/Carbon-Fibre Paper Catalysts For Methanol Electrooxidation

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Received February 11, 1980

Temperature-programmed reduction (TPR) and cyclic voltammetry (CV) studies of platinum catalysts supported on pyrographite-coated carbon-fibre paper, and prepared by either ion exchange or impregnation, clearly demonstrate the nature of the interactions between the platinum species and the support. After drying the above catalysts at 120°C, the ion-exchanged preparation exhibits the stronger interaction with the carbon support, as might be expected since a chemical interaction with carbon surface groups is known to occur in such catalysts. The presence of a fraction of bulk $Pt(NH_3)_4(OH)_2$ impregnating salt in the impregnated catalyst has been detected using TPR. After air activation at 300°C, subambient reduction peaks were observed and the strength of binding of Pt in the ion-exchanged catalyst was reflected by its increased difficulty of reduction in comparison with that of the impregnated catalyst. The stoichiometry of reduction in ion-exchanged catalysts corresponds to $Pt^{2+} \rightarrow Pt^0$ in both dried and activated catalysts, with a small amount of Pt^{4+} present in the latter. Upon activation the impregnated catalyst showed the presence of some Pt metal, which was thought to arise from the decomposition of the fraction of bulk $Pt(NH_3)_4(OH)_2$ in the dried catalyst. Activation of ion-exchanged catalysts at temperatures higher than 300°C led to a progressive weakening of the Pt-support interaction and consequent smaller Pt surface areas. Activation at 500°C in air produced Pt metal exclusively and very low Pt surface areas. The strong interaction between Pt and the carbon support upon activation of the ion-exchanged catalyst at 300°C is thought to be the origin of the large metal surface area and the high catalytic activity for methanol electrooxidation found upon reduction.

INTRODUCTION

Recently we reported (*1*) the methanol electrooxidation activity of various platinum catalysts supported on pyrographite-coated carbon-fibre paper (PGCFP). It was shown that the most active catalysts were those prepared by the ion exchange of surface oxide groups on the preoxidised carbon by cationic platinum salts, followed by decomposition of the salt in air at 300°C. Catalysts prepared by simple impregnation of the untreated carbon paper with the same salt had much lower catalytic activities. The ion-exchange technique led, as might be expected, to much greater platinum metal surface areas than did the impregnation technique, and certainly this factor contributed to the higher activity of the activated, reduced ion-exchanged catalysts. It was also speculated that in the ion-exchanged catalyst a strong interaction took place between the platinum species and the surface of the carbon-paper, leading to a modification of the platinum properties and, as a consequence, improved catalytic activity.

We have now characterised the catalysts discussed above at each stage of their preparation, i.e., after drying followed by air activation and after reduction, using temperature-programmed reduction (TPR) and the electrochemical technique, cyclic voltammetry (CV). These techniques have been shown to provide similar information on the nature of catalysts (*2*), TPR being a bulk technique and CV a surface technique for monitoring the first few atomic layers of the catalyst. Information can be obtained on metal surface area, the valency of metal species and metal/support interactions. This paper describes the results and conclu-

0021-9517/81/020287-09$02.00/0

sions arising from the application of these techniques to the platinum/carbon-fibre paper catalyst system.

EXPERIMENTAL

CATALYST PREPARATION

The carbon support used was a cellulose-based carbon-fibre paper obtained from Stonehart Associates, Inc. The paper was 0.2 mm thick and the BET surface area about 1 m^2 g^{-1}. Prior to its use as a support, a layer of pyrographite was deposited on the paper by pyrolysis of a 0.5% CH_4/99.5% v/v N_2 mixture at 1250°C. The thickness of the pyrographite layer on the fibres was about 2.7 μm.

Impregnated catalysts were prepared by contacting the PGCFP for 15 min with an aqueous solution of $Pt(NH_3)_4(OH)_2$ of concentration 5 mg Pt ml^{-1}. The solution was then decanted and the resultant wet PGCFP dried at 120°C in air. For the ion-exchanged catalysts, the PGCFP was first electrochemically oxidised at 2 mA cm^{-2} current density in 1% HNO_3 electrolyte for 90 min and then washed with distilled water. The oxidised PGCFP was then contacted with an aqueous 5 mg Pt ml^{-1} solution of $Pt(NH_3)_4(OH)_2$ for 24 h during which time the ion exchange took place. The exchanged catalyst was then washed thoroughly with distilled water to remove uncomplexed Pt species, and dried at 120°C in air. In both cases the dried catalysts were activated in air at 300°C to decompose the ammoniated platinum species. Reduced catalysts were prepared after air activation by electrochemical reduction. Some studies were also carried out on samples activated in air at 400, 450, and 500°C.

CATALYST CHARACTERIZATION

Temperature-Programmed Reduction (TPR)

The TPR technique has been described in detail in a number of recent publications (*2–4*), and the setup and instrumentation used here are described in those publications. However, in the course of this investigation, it was found necessary to extend the operating temperature range to subambient temperatures and this was achieved by using a Stanton Redcroft Model 681 linear temperature programmer equipped with a liquid nitrogen cooling system. This enabled the temperature to be varied linearly between −160 and +500°C. The heating rates in all experiments were 6°C min^{-1} and the flow rate of the 5% H_2/95% v/v N_2 reducing gas was 600 ml h^{-1}. The system was calibrated by injecting known amounts of hydrogen into a calibration loop at the end of each run.

Cyclic Voltammetry (CV)

Cyclic voltammetry was carried out in a conventional three-armed cell, comprising a working (test) electrode, bubbling H_2 reference electrode, and platinum gauze counter electrode compartment. The electrolyte used was 3 M H_2SO_4 at 25°C. The potential of the electrode was controlled using a PAR Model 173 potentiostat in combination with a PAR Model 175 waveform generator; the CV profiles were displayed on a Bryans Model 26000 x–y recorder. The voltage sweep rate used in all experiments was 50 mV s^{-1}. The sweeps were generally run between 0 and 1.6 V, the starting potential for all experiments being 0.7 V to avoid any prior reduction of the platinum species in the air-activated catalysts.

Platinum surface areas were determined coulometrically from the hydrogen desorption area of the anodic cyclic voltammetric sweep (0.05–0.4 V) assuming 210 μC for desorption of hydrogen from 1 cm^2 platinum (*5*).

Catalyst Analysis

The catalysts were analysed by first extracting the noble metal from the carbon support with boiling *aqua regia*. The resultant aqueous solutions were analysed by atomic absorption spectrophotometry using a Perkin–Elmer Model 560 spectrophotometer.

RESULTS AND DISCUSSION

The TPR profiles of the catalysts dried at 120°C are shown in Fig. 1, together with the TPR of the unsupported $Pt(NH_3)_4(OH)_2$ salt after drying at 120°C. The unsupported salt reduces in a single peak with maximum at 147°C and a hydrogen uptake corresponding to that required for reduction of Pt^{2+} to Pt^0 (Table 1). The impregnated catalyst shows two reduction peaks, one at 148°C and a second more intense peak at 168°C. The peak at 148°C presumably arises from some bulk $Pt(NH_3)_4(OH)_2$ present in the pores of the impregnated catalyst, whilst the peak at 168°C arises from $Pt(NH_3)_4(OH)_2$ involved in an interaction with the support. Again, the uptake of hydrogen corresponded to a two-electron reduction. The ion-exchanged catalyst on the other hand shows a single reduction peak at 196°C, with the higher temperature reflecting the increased bonding strength between the catonic Pt species and the acidic surface of the oxidised support.

The H_2 uptake in this sample was slightly higher than that expected for the reduction of Pt^{2+} (Table 1). It is possible that this arises from some H_2 uptake by the carbon, presumably in the reduction of surface groups adjacent to the reduced Pt formed during the electrochemical oxidation of the support. The asymmetry of the reduction peak probably reflects this occurrence. From previous photoelectron spectroscopic studies (*6*), we have established that in dried samples of the catalysts the Pt species is in the divalent state. Thus the TPR results indicate that in dried impregnated samples a significant amount of bulk $Pt(NH_3)_4(OH)_2$ exists together with the main fraction of $Pt(NH_3)_4(OH)_2$ which is involved in an interaction with the carbon, rendering the reduction more difficult. The dried ion-exchanged catalyst clearly shows the homogeneity of the preparation as only one TPR peak is observed—the washing step has presumably removed uncomplexed bulk $Pt(NH_3)_4(OH)_2$. More important, the position of the TPR peak maximum at 196°C, some 28°C higher than that of the impregnated catalyst and 50°C higher than that of unsupported $Pt(NH_3)_4(OH)_2$, reflects the chemical bond that exists between the $Pt(NH_3)_4{}^{2+}$ cations and the acidic

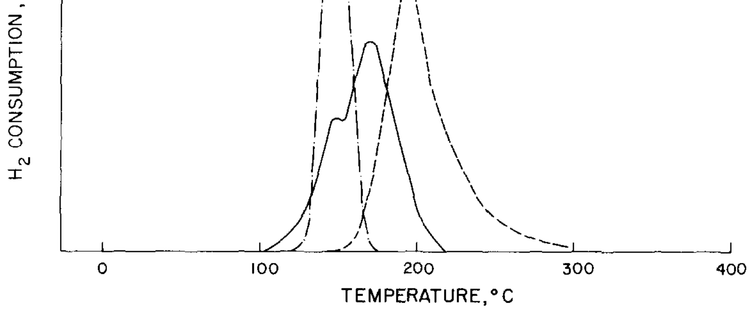

FIG. 1. TPR profiles of catalysts dried at 120°C.

TABLE 1

Theoretical and Measured Hydrogen Consumptions for the Reduction of Pt^{2+} in 120°C Dried Catalysts[a]

	Pt/H_2 mole ratio	
	Theoretical	Experimental
Unsupported	1.0	1.10
Impregnated	1.0	1.15
Ion exchanged	1.0	1.37

[a] Calculated by comparison of the area of the reduction peak with the area of a peak produced by the injection of a known volume of hydrogen.

surface oxides of the carbon-paper support.

The same samples were characterised after activation at 300°C. The TPR profiles are shown in Fig. 2. Hydrogen consumptions during TPR are compared with the theoretical values for reduction of Pt^{2+} and Pt^{4+} in Table 2. The TPR profiles showed no reduction peaks in any of the samples studied above room temperature. In Fig. 2 it can be seen that the impregnated catalyst reduces in a peak at −97°C with a weaker peak at −78°C, whilst the ion-exchanged catalyst reduces in a single peak at −56°C with a very weak high-temperature shoulder. The unsupported $Pt(NH_3)_4(OH)_2$ activated in air at 300°C shows no reduction peaks below room temperature and was shown by X-ray powder diffraction and cyclic voltammetry to consist of platinum metal after the air activation. An inspection of Table 2 shows that the H_2 uptake for the ion-exchanged catalyst is slightly higher than that expected for reduction of Pt^{2+} to Pt^0 and is in agreement with earlier photoelectron spectroscopic studies (*6*) which showed the presence of a small fraction of Pt^{4+} in addition to Pt^{2+}. However, the impregnated catalyst shows a H_2 uptake that is considerably lower than that expected for a reduction of Pt^{2+} to Pt^0. As discussed earlier, the impregnated catalyst contains a species similar to bulk $Pt(NH_3)_4(OH)_2$ that, as mentioned above, reverts to Pt^0 on air activation. Thus, in the air-activated impregnated catalyst it was suspected that some Pt^0 was present and this was confirmed by X-ray powder diffraction. No Pt^0 was detected by X-ray diffraction in the ion-exchanged catalyst.

The oxidised Pt species in the air-activated impregnated catalyst is clearly easier to reduce than that of the ion-exchanged catalyst and again we think this reflects the increased strength of the bond between the Pt^{2+} and the oxidised carbon surface in the case of the ion-exchanged

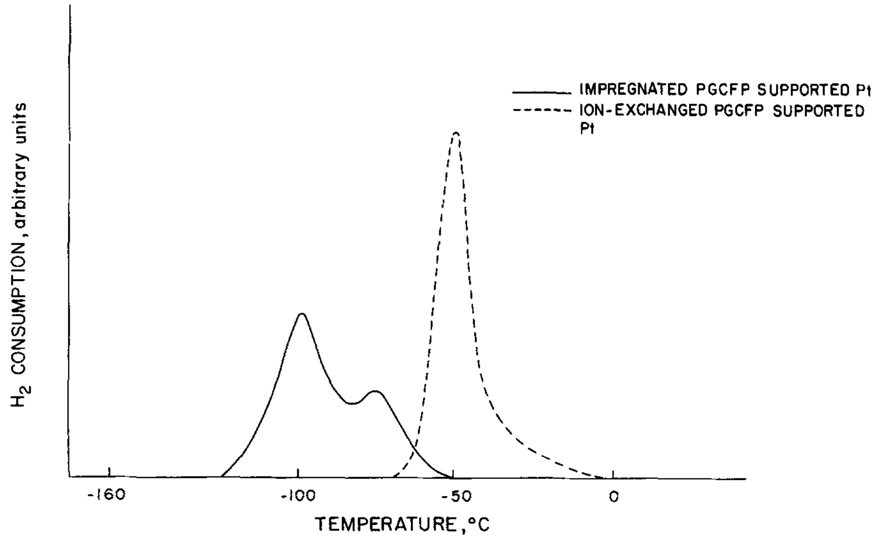

FIG. 2. TPR profiles of catalysts activated in air at 300°C.

TABLE 2

Theoretical and Measured Hydrogen Consumptions for the Reduction of Pt^{2+} and Pt^{4+} in 300°C Air-Activated Catalysts

	Pt/H_2 mole ratio		
	Theoretical		Experimental
	Pt^{2+}	Pt^{4+}	
Impregnated	1.0	2.0	0.36
Ion exchanged	1.0	2.0	1.24

catalyst. The temperatures of reduction in both catalysts are remarkably low and, in fact, are the lowest recorded peaks ever found using TPR. The differences in reduction characteristics can be accounted for by invoking arguments of differing metal dispersion, since in the impregnated catalyst the metal is rather poorly dispersed (<30 m^2 g^{-1}), whilst in the ion-exchanged catalyst the metal area is >80 m^2 g^{-1}. However, the effect of metal/support interaction may play a significant role. A more plausible interpretation, however, is that the reducibility is influenced by the extent of a metal/support interaction, perhaps allied with a metal dispersion effect. In the Pt/Al_2O_3 system, where the Pt surface area is >250 m^2 g^{-1}, a mild reoxidation of the reduced catalyst at, say, 150°C produces PtO species on the Al_2O_3 surface and this is thought to be involved in a strong interaction with the Al_2O_3 (*7*). Here the TPR spectrum shows a single reduction peak at room temperature. The Pt is even better dispersed than with the ion-exchanged carbon-supported catalyst, and a strong interaction with the support makes the Pt reducibility more difficult. Thus, the trend in reducibility goes from impregnated to ion-exchanged to Al_2O_3-supported Pt and reflects the increased dispersion *and* increased metal/support interaction. At this time it is impossible to unequivocally infer which of these two phenomena plays the dominant role.

The cyclic voltammetric results for the air-activated impregnated and ion-exchanged catalysts are shown in Figs. 3 and 4. It can be seen that on the first cycle from 0.7 to 1.6 and back to 0.0 V there is little or no evidence of the typical oxygen chemisorption and reduction phenomena associated with Pt metal until potentials of less than 0.35 V are reached on the cathodic sweep. This is as might be expected since the 300°C air activation was thought to

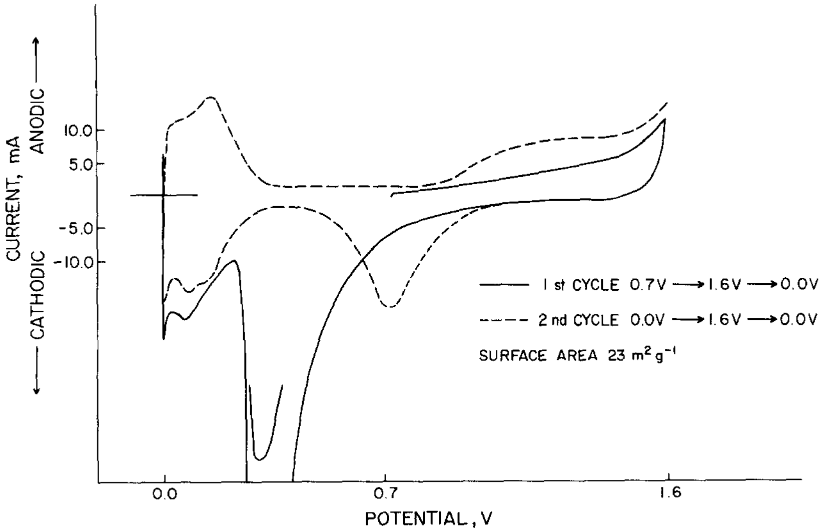

FIG. 3. Cyclic voltammogram of a Pt-impregnated air-activated catalyst.

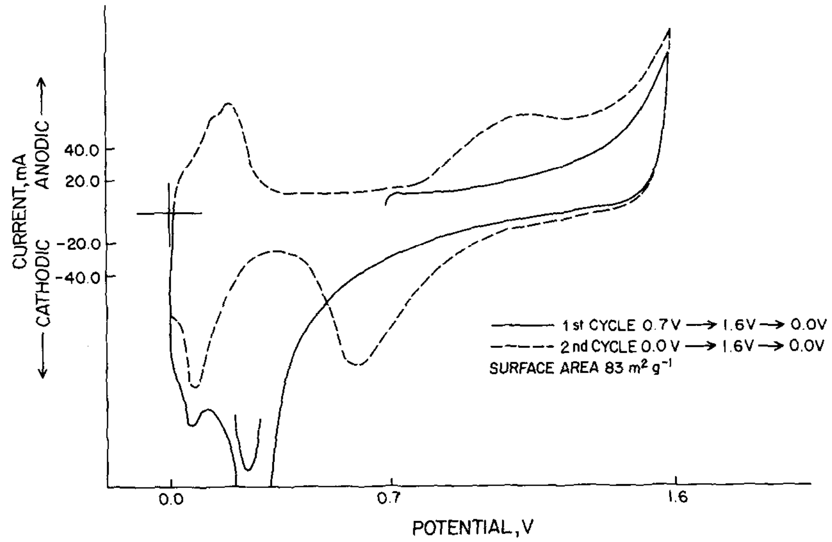

FIG. 4. Cyclic voltammogram of a Pt ion-exchanged air-activated catalyst.

produce a Pt oxide phase on the carbon surface. However, at 0.31 V in the impregnated catalysts (Fig. 3) and at 0.24 V in the ion-exchanged catalyst (Fig. 4) cathodic peaks are observed and these clearly arise from the cathodic reduction of the oxide formed upon air activation:

$$PtO + 2H^+ + 2e \rightarrow Pt + H_2O.$$

The reduction peaks are immediately followed by the peaks arising from the electrosorption of hydrogen (cathodic 0.35–0.0 V), desorption of H_2 on the anodic sweep 0.0–0.35 V), chemisorption of O_2 (anodic >0.8 V) and finally reduction of surface Pt oxide species (cathodic <0.75 V).

The oxide formed upon air activation and subsequently electroreduced as outlined above is clearly different from that formed on Pt at high potentials (<1.6 V) during cyclic voltammetric measurements. The surface oxide formed electrochemically at potentials up to 1.6 V is reduced on the cathodic sweep, usually between 0.55 and 0.75 V depending on the catalyst, whereas the oxide formed during air activation is reduced as mentioned above at 0.24 and 0.31 V, respectively, depending on the catalyst. There has been considerable controversy regarding the nature of the oxide film formed electrochemically on Pt. Some studies (*8*) claim that the layer is simply chemisorbed oxygen, whereas oxygen atom penetration studies (*9*) suggest that oxide formation actually takes place. However, it is clear that the oxygen species formed electrochemically is more easily reduced than that formed by air activation.

It is interesting to compare the CV results with the TPR results. TPR showed that the air-activated ion-exchanged catalyst was more difficult to reduce than the impregnated catalyst and in CV a similar situation existed. The analogies between CV and TPR have been alluded to previously (*2*).

Also, some CV runs were carried out in the presence of methanol to check on the presence of Pt^0 in the 300°C air-activated catalysts. Indeed, as suspected on the basis of the TPR, CV, and X-ray diffraction results, the impregnated catalyst after air activation showed a methanol electrooxidation peak prior to the reduction of the Pt species (Fig. 5), thus showing that Pt^0 was present in that species, though clearly in a very poor dispersion, judging from the low currents involved. The ion-exchanged catalyst on the other hand showed no evidence for methanol electrooxidation until the Pt

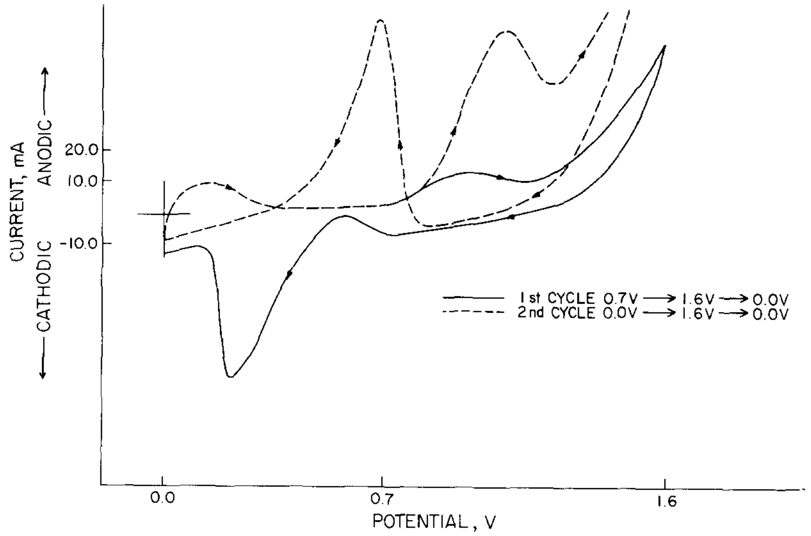

FIG. 5. Cyclic voltammogram of impregnated air-activated Pt catalyst in presence of 1 *M* MeOH.

species was reduced on the cathodic sweep (Fig. 6), again confirming the TPR and X-ray diffraction data. Methanol is not oxidised on Pt oxide except at very high anodic potentials.

An inspection of Figs. 3 and 4 upon completion of the first cycle reveals the surface characteristics of the reduced catalysts. It is quite apparent from the charge involved in H_2 desorption that the Pt area in the ion-exchanged catalyst after air activation is much greater than that of the impregnated catalyst. This greater surface area probably originates from the strong chemical interaction between oxidised Pt and the oxide-covered surface of the carbon, and reduction of such a species produces very small crystallites of platinum. The impregnated Pt catalyst, where bulk $Pt(NH_3)_4(OH)_2$ was shown to be present

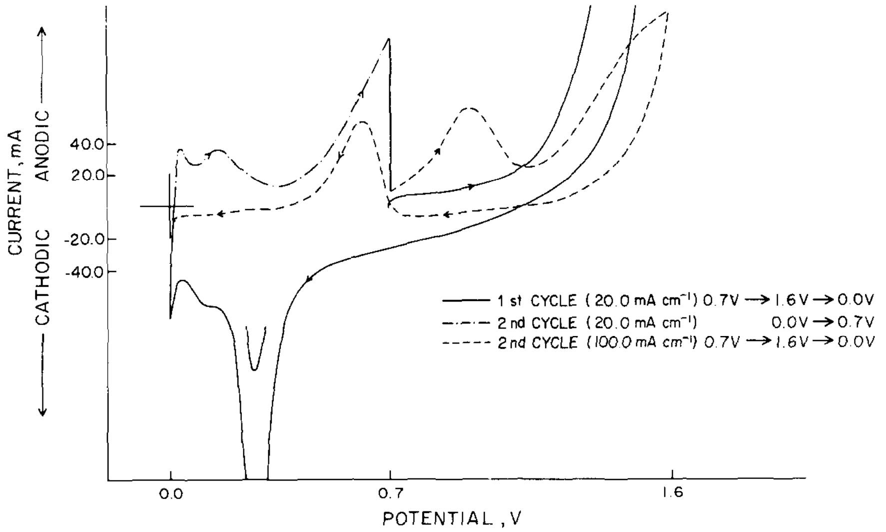

FIG. 6. Cyclic voltammogram of Pt ion-exchanged air-activated catalyst in presence of 1 *M* MeOH.

and where the remainder of the Pt species was involved in a much weaker interaction with the carbon surface, contains a much more poorly dispersed Pt species after reduction and in addition contains the Pt^0 species formed upon air activation at 300°. Thus we can see how the metal oxide/carbon support interaction can account for an improved metal dispersion. If we look at the H_2 chemisorption and oxide reduction characteristics of the reduced catalysts (Figs. 3 and 4) it is clear that the ion-exchanged catalyst shows quite different chemisorption characteristics; e.g., the oxide reduction peak is shifted in a cathodic direction in the ion-exchanged catalyst.

To study the effect of higher activation temperatures on the condition of the ion-exchanged catalysts a series of the dried catalysts were heated in air at 400, 450 and 500°C. The TPR and CV results are given in Table 3. It can be seen that the effect of increased temperature of activation is (a) to decrease the Pt metal surface area, (b) to facilitate the reduction of the oxidised species formed, and (c) to produce increasing amounts of Pt^0 with increasing temperature. The Pt/carbon chemical interaction is presumably weakened as the temperature increases as a result perhaps of the changes occurring on the carbon surface as the temperature rises. As the Pt/carbon interaction is weakened, then the sintering rate of the Pt species will grow. This will be reflected in a decreased area of the Pt species after reduction and also in a shift in the reduction of the oxidised Pt species to lower temperature (TPR) and to more anodic potentials (CV). The decreased metal/support interaction and/or the increased metal crystallite size is also reflected in the potential of the surface oxide reduction peak in CV, which shifts from 0.6 V at 300°C activation to 0.72 V after 500°C activation. As pointed out above, Pt^0 species is formed above 400°C as evidenced by the decreased H_2 uptake in TPR and the appearance of weak peaks in the CV profile of the oxidised catalyst attributable to metallic Pt. At 500°C activation temperatures there was no oxidised Pt species detectable (no reduction peaks in TPR) and the whole of the Pt inventory was present at Pt^0. Previous thermal analysis studies (*10*) have shown that the decomposition of surface groups on the carbon to form CO and CO_2 begins above 400°C and is catalysed by the presence of Pt. It is conceivable that this process is responsible for the reduction of the Pt to the zero-valent state.

CONCLUSIONS

It has been clearly demonstrated using TPR and CV that the preparation of platinum on carbon-fibre paper catalysts by ion-exchange of acidic surface oxide groups on the preoxidised carbon by cationic Pt species results in a chemical interaction between the Pt and the carbon that is much stronger than that obtained by simple impregnation of the untreated carbon. A

TABLE 3

Influence of Activation Temperature on Properties of PGCFP-Supported Pt Catalysts Prepared by Ion-Exchange Technique

Activation temperature (°C)	Oxide reduction peak potential (CV) (V)	Electrochemically formed surface oxide reduction peak potential (V)	Stoicheiometry of platinum reduction (TPR), Pt/H_2 mole ratio	Pt surface area ($m^2\ g^{-1}$)
300	0.24	0.60	1.25	86.0
400	0.27	0.68	0.76	55.0
500	—	0.72	0.00	12.0

result of this interaction is that the Pt metal species formed upon reduction of the air-activated catalysts is much more finely dispersed than in the ion-exchanged catalyst. In addition, the ion-exchanged material upon air activation at 300°C of the dried catalyst produces an oxidised Pt metal precursor that is also strongly interacting with the support. Conversely, air activation at 300°C of the dried impregnated catalyst led to a much more weakly bound Pt species, and, in addition, to significant amounts of Pt metal that was very poorly dispersed. The ion-exchange procedure thus stabilises the Pt species such that decomposition to the metal during air activation does not occur significantly until activation temperatures in excess of 400°C are attained.

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