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DIFFERENTIAL THERMAL ANALYSIS OF PtO_2/CARBON

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ABSTRACT

The reactions between Pt oxides and carbon black in helium and air were examined by DTA. The thermograms were dependent on the mode of sample preparation. 20 wt.% PtO_2 supported on carbon catalyst heated in He at 10°C min^{-1} produced an exotherm at approximately 400°C. Physical mixtures of PtO_2 and carbon only reacted at a higher temperature (approximately 550°C) in He where PtO_2 is thermally decomposed to Pt and O_2. In air, Pt catalyzed the oxidation of carbon in the 20 wt.% Pt supported on carbon sample. On the other hand, PtO_2 in the physical mixture did not appear to catalyze the oxidation of carbon in air. This difference in behavior is explained by assuming that atomic oxygen is produced in the supported catalyst sample which reacts at low temperature with carbon. In the physical mixture, thermal decomposition of PtO_2 yields molecular oxygen which reacts with carbon at a higher temperature than does atomic oxygen.

INTRODUCTION

There are many metals which catalyze the oxidation of carbon and as a result, numerous reports have appeared in the published literature on this subject[1-10]. From a technological point of view, carbon and carbon monoxide are important materials for reducing metal oxides to obtain high purity metals[11]. Thus, reactions between metal/metal oxides and carbon have also been extensively studied[12-15].

Highly dispersed Pt crystallites supported on metal oxides (SiO_2, Al_2O_3) and carbon are employed as industrial catalysts. A spent catalyst of Pt supported on SiO_2 or Al_2O_3 is regenerated by heating in air to oxidize carbonaceous species. The ignition temperature for the oxidation of carbon catalyzed by Pt was determined by l'Homme and Boudart[10]. From TG measurements, they were able to show the dependence of the ignition temperature on the oxygen partial pressure and the Pt concentration. The role of Pt in decreasing the ignition temperature of carbon was

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reported to be related to the ability of Pt to dissociate oxygen molecules to oxygen atoms which can then react with carbon in the vicinity of the Pt crystallite. The present paper describes the results of a DTA study on the reaction between Pt oxides and carbon. Weight loss measurements and X-ray diffraction analysis yielded supporting information to interpret the DTA data and to shed some light on the reaction mechanism. Furthermore, the present study complements the TG measurements on the Pt catalyzed ignition temperature of carbon reported by l'Homme and Boudart[10].

EXPERIMENTAL

Samples

Various Pt samples were examined by DTA and these are listed in Table 1. The 20 wt.% PtO_2 supported on carbon (Vulcan XC-72 obtained from Cabot Corp. was graphitized at 2700°C, BET nitrogen surface area 70 m^2g^{-1}) was prepared by impregnating the carbon with an aqueous solution of $Pt(NH_3)_2(NO_2)_2$ dissolved in dilute HNO_3. After evaporating the solution to dryness, the impregnated carbon was heat treated at 300°C for 2 h in flowing air in a tube furnace to thermally decompose the Pt salt. Due to the highly dispersed nature of Pt in the porous carbon structure, X-ray diffraction analysis showed only the presence of a broad diffraction peak profile with a *d*-spacing of approximately 2.64 Å. Based on data reported by Pearson[16], the diffraction peak is tentatively considered to be hexagonal PtO_2 [*d*-spacing of 2.67 Å for (100)]. The presence of an oxide of Pt is not unreasonable since the Pt salt was thermally decomposed in air.

Although the X-ray diffraction analysis of the Pt supported on carbon was interpreted on the basis of one diffraction peak, further evidence was obtained to support the presence of Pt oxide. A ESCA (Electron Spectroscopy for Chemical Analysis) Spectrometer (Hewlett-Packard) was used to determine the valence states of the Pt crystallites supported on graphitized carbon[17]. From the photoelectron spectra, only Pt^{4+} and to a smaller extent Pt^{2+} were detected which suggested that the Pt oxides, PtO and PtO_2, were present. The relative amounts of the two oxide

TABLE 1

X-RAY DIFFRACTION ANALYSIS OF Pt SAMPLES

Sample No.	*Catalyst*	*Treatment*	*Pt phases identified*
1	20% PtO_2/C	prepared by air decomposition of $Pt(NH_3)_2(NO_2)_2$ at 300°C, 2 h	PtO_2 (17 Å)
2	20% Pt/C	Sample 1, H_2 reduced 300°C, 2 h, followed by heat treatment in air, 335°C, 5340 min	Pt (70 Å)
3	Pt oxide	as received from Engelhard Industries	PtO_2 (115 Å) Pt (1500 Å)

species are not known but the presence of the bulk phase oxide PtO has been open to question[18]. For purposes of analyzing the DTA data we will not consider PtO as being present in significant amounts.

Pt black (BET nitrogen surface area 30.5 m^2g^{-1} Pt) and Pt oxide were obtained from Engelhard Industries. X-ray diffraction analysis (see Table 1) indicated[16] the Pt oxide contained a mixture of large Pt crystallites as well as hexagonal PtO_2. Commercial Pt oxide used by Muller and Roy[18] in their investigations on the thermal stability of PtO_2 contained the same mixture.

Physical mixtures of Engelhard Pt oxide and graphitized carbon were prepared by grinding together the appropriate amounts of the powders with a mortar and pestle. Samples were prepared with weight fractions of carbon from 0.05 to 0.91.

X-ray diffraction analysis

X-ray diffraction analysis was employed to identify the phase composition of the Pt samples prior to and after programmed thermal analysis. A recording X-ray diffractometer with Cu X-rays and a scintillation counter was used. The powder samples were carefully pressed by hand into a glass sample holder without using any binder material. A scan rate of 1 deg min^{-1} was used throughout.

DTA

DTA studies were conducted with a DuPont Model 990 Thermal Analysis System coupled to a 1200°C DTA cell. A description of the DTA cell is given elsewhere[19]. The gas flow was set at 100 cm^3 min^{-1} and in the upward direction past the sample as shown schematically by Miller and Wood[19]. Depending on the experiment, He or air was used. Copper turnings heated to 350°C were employed to remove any residual O_2 impurity and a drying trap was used to remove water present in the He gas streams. In general, either Pt foil annealed to 1200°C for 2 h in flowing H_2 or graphitized carbon black was used as the reference material. Preliminary experiments indicated that a more stable baseline was obtained if graphitized carbon or Pt foil was used as the reference material rather than Al_2O_3. Typically, the sample was 5–20 mg. The weight change of the sample was measured on an analytical balance to ± 0.1 mg.

The following procedure was adopted for the DTA experiments. The sample was weighed and then placed in the DTA module. For thermal analysis of the Pt sample in an inert environment, He was passed through the DTA cell for 60 min prior to the programmed temperature increase. Preliminary experiments verified that 60 min was sufficient to remove oxygen originally present in the porous samples. If air was used, the linear heat rate was initiated immediately after the steady state gas flow was established. After heating the sample in He to the maximum temperature desired, the furnace was turned off and the sample was cooled to room temperature in flowing He. The sample was then weighed. A linear heating rate of 10°C min^{-1} was used throughout.

There is an influence of the mode of sample packing on the reaction between carbon and an oxidant, as observed in the case of $KClO_4/C$[15] but we have not investigated these effects. To avoid differences in packing on the thermograms, each sample was prepared in the same manner. After weighing the sample in the alumina crucible, the crucible was gently tapped to settle the powder. No attempt was made to compress the sample by mechanical means since the small sample sizes were not convenient for handling.

Since the sample sizes used in the DTA experiments were not convenient for X-ray analysis, a second set of experiments was performed on larger samples simulating the DTA conditions. These samples were prepared in a tube furnace which was programmed with a linear heating rate (10°C min^{-1}) similar to the DTA experiments. When the temperature reached the same upper limit as the corresponding DTA experiment, the tube furnace was shut off and allowed to cool at the natural rate in a flowing stream of helium.

Discussion of Results

Figure 1 shows the thermogram obtained with 20 wt.% PtO_2/C prepared by the thermal decomposition in air of $Pt(NH_3)_2(NO_2)_2$ impregnated into carbon. An exotherm is clearly evident at approximately 400°C which is missing on the second heating cycle. Since these results were obtained in oxygen-free He, the exotherm was interpreted to arise from the heat produced by the overall reactions

$$PtO_2 + 2C \rightarrow Pt + 2CO \qquad (1)$$

and/or

$$PtO_2 + C \rightarrow Pt + CO_2 \qquad (2)$$

X-ray diffraction analysis of 20 wt.% PtO_2/C after heating in He to the temperature limit shown in Fig. 1 indicated Pt (crystallite size from X-ray line broadening of 75 Å) was present, as required by eqns (1) and (2). Further evidence to indicate that the

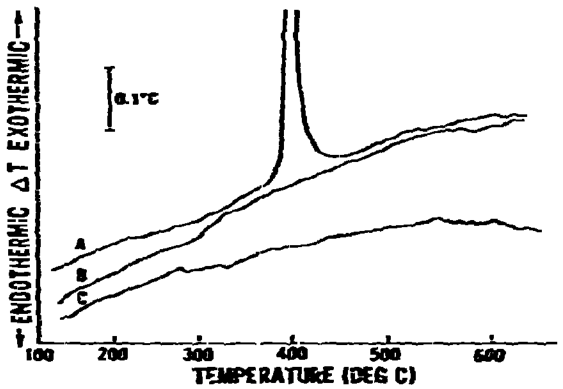

Fig. 1. DTA of 20% PtO_2 supported on carbon catalyst. 10°C min^{-1}, He. A, initial sample; B, second heat cycle of initial sample; C, initial sample exposed to H_2 at room temperature for 40 min. before heating in He.

overall reaction involved PtO_2 and C is suggested by the DTA curve (Fig. 1) obtained after the catalyst was initially treated with H_2 at room temperature. Hydrogen rapidly reduced PtO_2 to Pt at room temperature and the subsequent DTA curve in He indicated that the exotherm observed in the presence of PtO_2 was absent. From the weight loss of the sample after heat treatment in He, we were able to deduce the overall reaction which can explain the observed exotherm in Fig. 1. A weight loss of 0.4 mg was measured which agrees with the calculated weight loss of 0.4 mg for the stoichiometry of eqn (1) and on this basis it was concluded that the reaction forming CO predominated during the linear programmed heating of 20% PtO_2/C in He. Admittedly, a small amount of CO_2 could be formed according to eqn (2) but the relative amounts of CO and CO_2 can only be obtained by analysis of the evolved gas composition. Since there was present excess carbon with a high surface area, it does not seem unreasonable to expect that the reduction of PtO_2 would proceed to form CO as the predominant gaseous product. This subject will be discussed in more detail later in the paper.

Carbons generally contain surface oxygen groups in the form of carbonyl, carboxyl, lactone, phenol, etc. The relative amounts of these organic functional groups depend on the carbon and the pretreatment involved during carbon manufacturing. Carbon surface oxides will desorb during heat treatment in vacuum[20] or inert environments[21]. The concentration of oxygen associated with graphitized Vulcan XC-72 was measured[22] and was found to be very low (0.11 wt.%). Preliminary DTA studies of the graphitized carbon used in the present investigation indicated that the

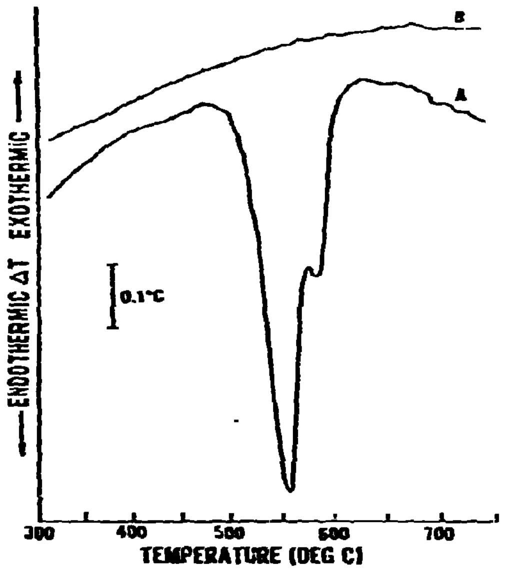

Fig. 2. DTA of commercial PtO_2. 10°C min^{-1}, He. A, initial sample; B, second heat cycle of initial sample.

thermal desorption of carbon surface oxides could not be detected, and therefore, would not alter the interpretations discussed here.

For the DTA study of the reaction between physical mixtures of PtO_2 and carbon, a commercial PtO_2 was used without further purification. The DTA curve obtained on Engelhard PtO_2 in He is shown in Fig. 2. There were observed two successive endotherms which do not appear on the second heating cycle. X-ray diffraction analysis of PtO_2 heat-treated to 750°C in He showed only Pt was present and with the weight loss measurements, the decomposition reaction giving rise to the endotherms can be represented by

$$PtO_2 \rightarrow Pt + O_2 \tag{3}$$

The origin of the double endotherms was not examined.

Physical mixtures containing various weight ratios of Engelhard PtO_2 and graphitized carbon black were examined by DTA in flowing He (Fig. 3). An endo-

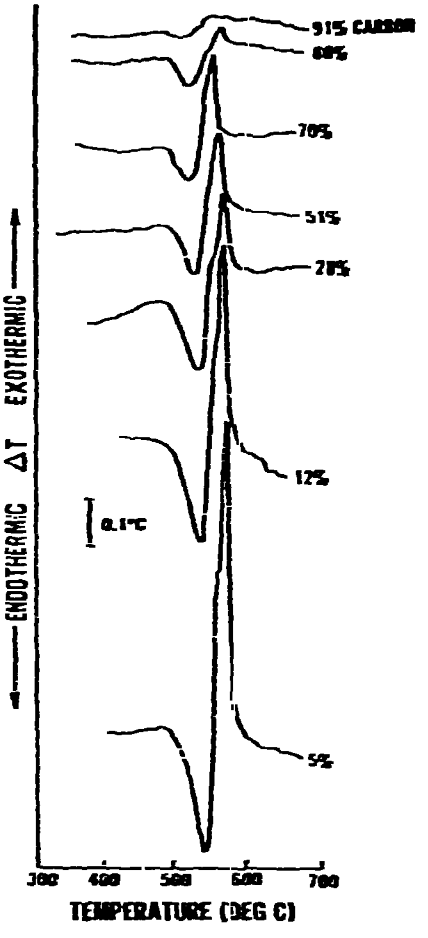

Fig. 3. DTA of PtO_2 and carbon physical mixtures. 10°C min^{-1}, He.

therm appears at approximately 550°C followed by an exotherm. In general, as the fractional amount of PtO_2 was increased, the peak height of the exotherm became progressively higher relative to the peak height of the endotherm. The DTA curves for the physical mixture of PtO_2 and carbon can be interpreted as follows. When the linearly programmed temperature reaches about 500°C, the PtO_2 undergoes thermal decomposition with the evolution of oxygen according to eqn (3). This is followed by the exothermic reaction between carbon and oxygen:

$$2C + O_2 \rightarrow 2CO \tag{4}$$

and/or

$$C + O_2 \rightarrow CO_2 \tag{5}$$

When the oxygen supply is depleted after all the PtO_2 has decomposed, the carbon oxidation reaction ceases. The heat liberated by the carbon oxidation reaction must be greater than the heat required to decompose PtO_2 in order to yield the net exothermic DTA peaks shown in Fig. 3.

By controlling the oxygen supply through the changes in the ratio of PtO_2 to carbon, we can show a qualitative difference in the stoichiometry of the reaction between carbon and oxygen. The gaseous species formed during the linear programmed heat treatment of PtO_2/C mixtures can be ascertained from weight-loss measurements of the samples and the stoichiometry of the reaction sequence given by eqns (3) to (5). These results are summarized in Table 2 for the physical mixtures examined by DTA. When the relative amount of carbon is large, the weight-loss measurements agree with the stoichiometric equation indicating CO is produced during carbon oxidation. On the other hand, when the relative amount of carbon is small, then the stoichiometric equation for CO_2 formation agrees with the weight-loss measurements. These results are in accord with the well-known observation that the oxidation of carbon

TABLE 2

DETERMINATION OF GASEOUS PRODUCTS FROM THE WEIGHT-LOSS MEASUREMENTS OF PtO_2/C PHYSICAL MIXTURES

Sample heated at 10°C min^{-1} in flowing He.

Physical mixture (wt. % C)	*Sample weight-loss measured (mg)*	*Sample weight-loss calculated for the stoichiometry of*	
		Eqn (4) (mg)	*Eqn (5) (mg)*
91	0.1	0.1	0.1
80	0.4	0.4	0.3
70	0.8	0.7	0.6
51	0.7	1.0	0.8
28	1.0	1.3	1.0
12	1.6	2.0	1.6
5	2.2	2.8	2.2

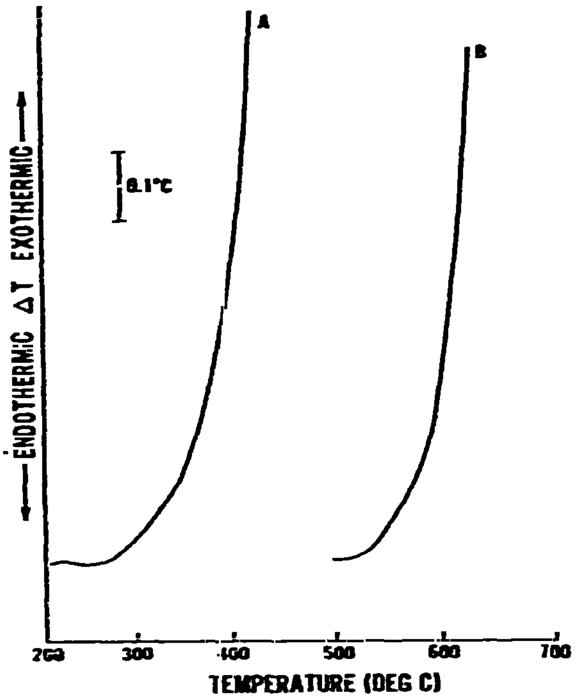

Fig. 4. DTA showing the onset of carbon oxidation in air. 10°C min^{-1}. A, 20% Pt supported on graphitized carbon black; B, graphitized carbon black.

in an excess of oxygen yields CO_2 (eqn (5)) while in the presence of insufficient oxygen, CO is produced (eqn (4)).

By examining the Pt catalyzed oxidation of carbon using DTA, we can gain further insight into the reaction mechanism of the PtO_2 and carbon physical mixtures. Figure 4 shows the DTA curves for the air oxidation of carbon without Pt and the carbon support in the 20% Pt on carbon catalyst (Sample No. 1 initially reduced in H_2 at 300°C for 2 h). The results presented in Fig. 4 agree qualitatively with the TG data presented by l'Homme and Boudart[10] on the ignition temperature of Pt catalyzed carbon (Spheron 6) in various partial pressures of oxygen. The catalytic influence of Pt in lowering the oxidation temperature of carbon in air is markedly noticeable. In fact, the catalyzed oxidation of carbon in air occurred in the same temperature range (300–400°C) as the exothermic reaction observed with PtO_2/C catalysts (Fig. 1 and 6) in He. Similarly, the oxidation of pure carbon in air occurred near the same temperature as the oxidation of carbon in PtO_2/C mixtures was observed (Fig. 3).

The air oxidation of a physical mixture of 28% PtO_2/C yielded the DTA curve shown in Fig. 5. The rapid temperature increase of the physical mixture due to the oxidation of carbon occurred at approximately the same temperature as observed with pure carbon. Furthermore, physical mixtures of PtO_2 and carbon showed a similar temperature for carbon oxidation when heated in He. Also included in Fig. 5 is the DTA curve for PtO_2 decomposition in air. The presence of 0.2 atm partial

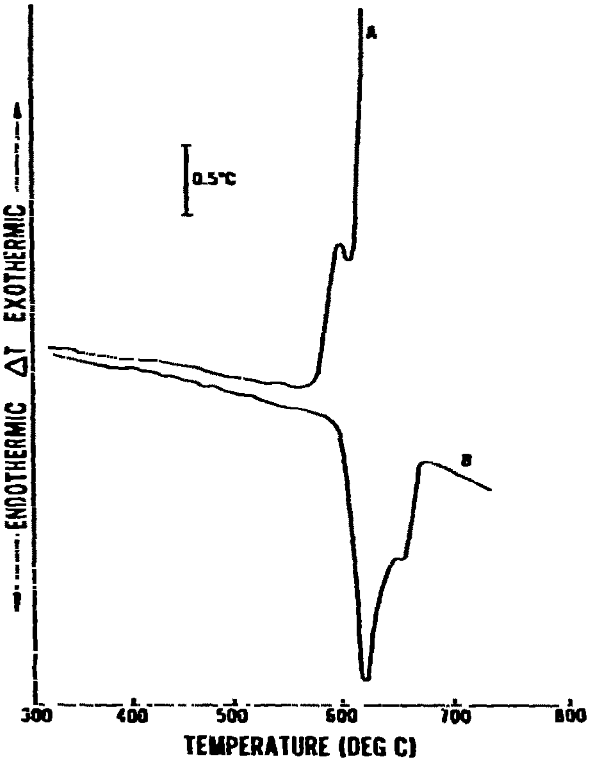

Fig. 5. DTA of PtO_2 and physical mixture of PtO_2 and carbon in air. 10°C min^{-1}. A, 28% C/PtO_2; B, PtO_2.

pressure of O_2 has the effect of increasing the temperature at which PtO_2 decomposes but the results are qualitatively the same as the DTA curve for PtO_2 in He (Fig. 2). Moreover, the DTA results for the thermal decomposition of PtO_2 in air are in agreement with the TG data of Hoekstra and Siegel[23] who reported that a loss of trace amounts of oxygen occurred at about 350°C but the main decomposition reaction occurred at 600–680°C.

The DTA study of the Pt-catalyzed oxidation of carbon in air supports the interpretations presented earlier. The Pt acts as a site for O_2 dissociation and supplies oxygen atoms which then migrated to the carbon and react. According to l'Homme and Boudart[10] the rate of oxidation of carbon at low temperatures is limited by surface migration of adsorbed oxygen atoms supplied by Pt. It would appear, therefore, that in order for the oxygen atoms generated at the Pt surface to react with carbon, there must be contact at the Pt/C interface. Supported Pt on carbon catalysts evidently provides a Pt/C interface where adsorbed oxygen atoms generated on the Pt can react with carbon in the local vicinity. On the other hand, physical mixtures of PtO_2 and carbon may provide poor physical contact between the two components, so the oxygen atoms associated with Pt cannot react with carbon at low temperatures. The only way for oxygen to react with carbon in the physical mixtures is by the transport of oxygen through the gas phase after thermal decomposition of PtO_2.

The temperature of carbon oxidation under these conditions is then dictated by the temperature of decomposition of PtO_2.

If one discards the argument that the contact between PtO_2 and carbon in the physical mixture is poor, then another interpretation is necessary to explain the observed results. An alternative explanation for the absence of catalytic oxidation of carbon by Pt in the physical mixture might lie in the presence of Pt oxides which have different thermal stabilities toward dissociation to Pt and oxygen atoms. Accepting the model proposed by l'Homme and Boudart[10], the oxygen atoms generated at the Pt surface react with the carbon at low temperature. Presumably, if the thermal stability of Pt oxide is increased, as noted by the higher temperature necessary for dissociation to Pt and oxygen atoms, then the catalytic oxidation of carbon must occur at a higher temperature. However, in the absence of additional information on the thermal properties of PtO_2 prepared by various techniques, we can only speculate as to the validity of this interpretation.

Heat treatment of 20% Pt/C (Sample 2) in air at 335°C for various times caused a measurable change in the DTA curves for the samples in He (see Fig. 6). As the heat treatment times increased, the peak temperature of the exotherm associated with the heat of reaction described by eqn. (1) became progressively higher. Although the X-ray diffraction analyses did not show the presence of bulk PtO_2, we presume that longer heating times in air resulted in the formation of Pt oxides which have different thermal properties from surface Pt oxides. Furthermore, the fact that the peak temperature of the exotherms increased with heat treatment suggested an increase in the thermal stability of the Pt oxide. Finally, the catalyst prepared by the

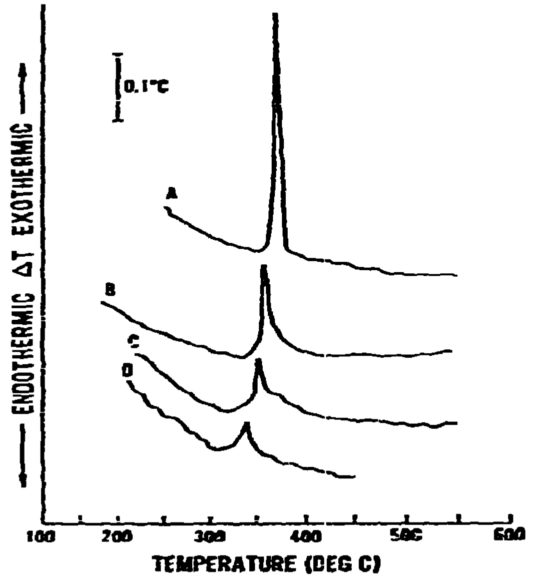

Fig. 6. Influence of heat-treatment on the DTA of 20% PtO_2 supported on carbon catalysts. Samples heated in air at 335°C for various times. 10°C min^{-1}, He. A, 5340; B, 1250; C, 60; D, 10 min.

thermal decomposition of $Pt(NH_3)_2(NO_2)_2$ consisted of PtO_2 that yielded an exotherm in He with a peak temperature substantially higher than observed with the sample in Fig. 6, further supporting the concept of the presence of Pt oxides exhibiting different thermal properties which are dependent on the mode of preparation or previous history of the sample.

The stoichiometry of the overall reaction between PtO_2 and carbon in He can be represented by eqns (1) and (2) for both the supported catalyst and the physical mixture. What appears different is that the former sample undergoes an exothermic reaction at approximately 400°C while the latter sample undergoes an exothermic reaction at approximately 550°C. How can these observations be rationalized? The catalytic influence of Pt in lowering the oxidation temperature of carbon (Fig. 4) was explained by assuming that the atomic oxygen generated on the Pt surface reacted with carbon. Atomic oxygen is a stronger oxidizing agent than molecular oxygen and hence, carbon can be oxidized at a lower temperature in the presence of Pt. The exotherms observed in the vicinity of 350–400°C in Figs. 1 and 6 are attributed to the oxidation of carbon by atomic oxygen initially associated with the Pt crystallites and the reactions can be represented by

$$PtO_2 \rightarrow Pt + 2O \qquad (6)$$

$$O + C \rightarrow CO \qquad (7)$$

When the commercial PtO_2 (Sample 3) is heated in He, the oxygen associated with the Pt is evolved as molecular O_2 and therefore, PtO_2 and carbon physical mixtures exhibit exotherms at temperatures where carbon and molecular oxygen react, namely about 550°C in air.

CONCLUSION

The exothermic reactions between carbon and Pt oxides appear to be strongly dependent on the mode of sample preparation and the previous history of the sample. Based on the observations of the catalytic oxidation of carbon by Pt in air, we suggest that the exotherm observed on the Pt/C supported catalyst in He is due to the reaction between atomic oxygen and carbon. Physical mixtures of PtO_2/C exhibit exotherms in He and air at higher temperatures and the exothermic reaction is attributed to the oxidation of carbon by molecular oxygen. The interpretation of the results presented here are based on DTA to monitor the temperature at which Pt oxides and carbon undergo reaction. Considering the limitations of DTA for examining powder samples, the conclusions are presented with caution and are in need of confirmation by other experimental studies.

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REFERENCES

1 L. F. Jones, D. Dollimore and T. Nicklin, *Thermal Analysis*, Vol. 2, *Proceedings of the Third International Conference*, 1972, p. 67.
2 F. S. Feates, P. S. Harris and B. G. Reuben, *J. Chem. Soc. Faraday Trans. I*, 70 (1974) 2011.
3 D. W. McKee, *Carbon*, 8 (1970) 131.
4 G. A. l'Homme, M. Boudart and L. D'Or, *Acad. R. Belg. Bull. Cl. Sci.*, 52 (1966) 1249.
5 E. T. Turkdogan and J. V. Vinters, *Carbon*, 10 (1972) 97.
6 E. A. Heintz and W. E. Parker, *Carbon*, 4 (1966) 473.
7 G. R. Hennig, *J. Inorg. Nucl. Chem.*, 24 (1962) 1129.
8 G. Harker, *Proc. Fourth Conf. Carbon*, Pergamon, London, 1960, p. 125.
9 R. J. M. Griffiths and E. L. Evans, *J. Catal.*, 36 (1975) 413.
10 G. A. l'Homme and M. Boudart, *Eleventh International Symposium on Combustion* held at the Combustion Institute, Pittsburgh, Pa., 1967, p. 197.
11 A. S. Dorling, *Metallurgica*, 64 (1961) 71.
12 A. S. Dorling, *Metallurgica*, 64 (1961) 7.
13 Z. G. Szabo and M. Gabor, in J. S. Anderson, M. W. Roberts and F. S. Stone (Eds.), *Reactivity of Solids*, Chapman and Hall, London, 1972, p. 796.
14 T. P. Herbell, in W. E. Kuhn (Ed.), *Fine Particles, Second International Conference*, The Electrochemical Society, Princeton, N. J., 1974, p. 269.
15 S. Patai and E. Hoffmann, *J. Am. Chem. Soc.*, 72 (1950) 5098.
16 W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2, Pergamon Press, Oxford, 1967, p. 478.
17 P. N. Ross and K. Kinoshita, unpublished data.
18 O. Muller and R. Roy, *J. Less Common Metals*, 16 (1968) 129.
19 G. W. Miller and J. L. Wood, *J. Therm. Anal.*, 7 (1970) 71.
20 R. B. Anderson and P. H. Emmett, *J. Phys. Chem.*, 56 (1952) 753.
21 M. T. Coltharp and N. Hackerman, *J. Phys. Chem.*, 72 (1968) 1171.
22 K. Kinoshita and J. A. S. Bett, in C. S. Tedmon (Ed.), *Corrosion Problems in Energy Conversion and Generation*, The Electrochemical Society, Princeton, N. J., 1974, p. 43.
23 H. R. Hoekstra and S. Siegel, *Inorg. Chem.*, 7 (1968) 141.