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Platinum Catalyzed Decomposition of Activated Carbon: 1. Initial Studies

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Abstract

Carbon is an important support for heterogeneous catalysts, such as platinum supported on activated carbon (AC). An important property of these catalysts is that they decompose upon heating in air. Consequently, Pt/AC catalysts can be used in applications requiring rapid decomposition of a material, leaving little residue. This report describes the catalytic effects of platinum on carbon decomposition in an attempt to maximize decomposition rates. Catalysts were prepared by impregnating the AC with two different Pt precursors, $Pt(NH_3)_4(NO_3)_2$ and H_2PtCl_6. Some catalysts were treated in flowing N_2 or H_2 at elevated temperatures to decompose the Pt precursor. The catalysts were analyzed for weight loss in air at temperatures ranging from 375 to 450 °C, using thermogravimetric analysis (TGA). The following results were obtained: (1) Pt/AC decomposes much faster than pure carbon; (2) treatment of the as-prepared 1% Pt/AC samples in N_2 or H_2 enhances decomposition; (3) autocatalytic behavior is observed for 1% Pt/AC samples at temperatures ≥ 425 °C; (4) oxygen is needed for decomposition to occur. Overall, the Pt/AC catalyst with the highest activity was impregnated with H_2PtCl_6 dissolved in acetone, and then treated in H_2. However, further research and development should produce a more active Pt/AC material.

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Introduction

Carbon is an important support material used in many heterogeneous catalysis applications [1]. One form of carbon that is especially applicable in heterogeneous catalysis is activated carbon. Activated carbon (AC) is carbon that has been treated either physically by steam and carbon dioxide, or chemically using an activating agent at elevated temperatures. The treatment results in a carbonaceous material that has a very high surface area (800-1200 m^2/g) and pore volume [2,3,4]. AC is an excellent catalyst support because of its high surface area and pore volume, stability in acidic and basic environments, inertness, and cost effectiveness [1,4].

A variety of metal catalysts, such as noble metals (Pt, Pd, Rh) and base metals (Sn, Fe, Mn, Co, Ni), have been used as active catalyst phases via dispersion on active carbon supports [1,2]. The four primary methods of metal impregnation are: wet impregnation, ion exchange, precipitation, and chemical vapor deposition [2]. Of all the methods, wet impregnation is the most common. Most applications of AC-supported precious metal catalysts involve fine chemical synthesis. Some of these applications include: selective hydrogenation, alcohol synthesis from aldehydes and ketones, amine synthesis from aliphatic and aromatic nitriles, and selective fatty acid saturation [4]. Although fine chemical synthesis is often performed using very controlled environments, many other catalytic reactions are performed at high temperatures in oxidizing or reducing environments.

Given its extensive applications in catalytic processes, it is important to determine under what conditions carbon-supported metal catalysts are viable. One setback of these catalysts is that, at temperatures >100 °C, in oxygen-rich environments such as air, combustion occurs resulting in carbon gasification. Furthermore, when carbon is impregnated with metals such as platinum, combustion is greatly enhanced due to surface reactions that are facilitated by the dispersed platinum phase. An article by Moulijn and Kapteijn discusses the mechanisms and kinetics of metal catalyzed carbon decomposition [5]. Conversely, there is an advantage to gasification taking place in that dispersed metal catalysts such as platinum can be easily recovered in a cost-effective process [4]. The combustion reaction is shown in Figure 1.

$$C_{(graphite)} + O_2(g) \xrightarrow[\triangle]{Pt} CO_2(g)$$
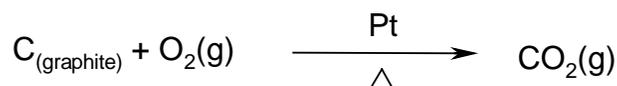
Figure 1: Gasification of graphitic carbon in the presence of oxygen and heat to form gaseous carbon dioxide.

Gasification of carbon will also take place in hydrogen to form methane in a similar reaction to that shown in Figure 1 [1,5].

The aim of this study is twofold. The primary goal is to develop a material that, when heated in air, will decompose rapidly and leave little or no residue. Materials with these characteristics would greatly aid metal recovery techniques used in conjunction with spent carbon-supported precious metal catalysts. However, this type of material cannot be developed without a thorough understanding of the decomposition behavior of carbon. This leads to the second goal of the project: studying the survivability of carbon-supported platinum catalysts in oxidizing environments.

Both of these goals will be accomplished by preparing carbon-supported platinum catalysts and subjecting them to thermal decomposition. The catalysts will be made with different platinum precursors and will be exposed to various treatments. Decomposition studies will be made using thermogravimetric analysis in order to evaluate the rate and extent of carbon decomposition.

Experimental

Sample Preparation

Wet Impregnation Technique
   Wet impregnation involves filling the pore volume of the carbon support with a solution of the desired metal [2,4,6-10]. The two most common types of platinum precursors are chloroplatinic acid (H_2PtCl_6) and platinum ammonium complexes such as $Pt(NH_3)_4(NO_3)_2$ and $Pt(NH_3)_4Cl_2$. After impregnation, the catalysts are dried and used in the as-prepared form or treated in nitrogen or hydrogen at elevated temperatures [2,4,7,10].

Preparation of Pt/AC from Pt(NH₃)₄(NO₃)₂
   Activated Carbon (AC) was obtained from Fisher Scientific with nominal impurities of acid-soluble substances $\leq 3.5\%$, and residue on ignition $\leq 4.0\%$. Surface area, pore volume, and average pore diameter was obtained using a Quantachrome Autosorb-6 Automated Gas Sorption System. The respective results are 818 m^2/g, 0.97 cc/g, and 4.7 nm. Pt/AC samples with Pt loadings of 1 and 2 wt. % were prepared using wet impregnation with tetraammineplatinum (II) nitrate ($Pt(NH_3)_4(NO_3)_2$), which was obtained from Alfa Aesar. The $Pt(NH_3)_4(NO_3)_2$ was dissolved in the minimum amount of deionized (DI) water necessary to wet the AC; this was found to be 2.2 mL DI water / 1 g AC. Appropriate stoichiometric amounts of the $Pt(NH_3)_4(NO_3)_2$ precursor were used to prepare the 1 and 2 wt. % samples. A paste initially formed, which was then thoroughly mixed with a spatula in a Petri dish and dried overnight in an oven at 100 °C in air.

Preparation of Pt/AC from H₂PtCl₆

A second method of Pt impregnation was developed using a solution of chloroplatinic acid (H_2PtCl_6) in water as the platinum precursor. The same Fisher Scientific carbon was used as the AC source. The H_2PtCl_6 solution was dissolved in the minimum amount of DI water, acetone, or methanol needed to wet the carbon. A stoichiometric amount of the H_2PtCl_6 precursor was used to prepare a 1 wt. % sample. A paste initially formed, which was then thoroughly mixed with a spatula in a Petri dish and dried overnight in an oven at 100 °C in air.

Sample Treatment

Treatment in Nitrogen

The as-dried samples impregnated with $Pt(NH_3)_4(NO_3)_2$ were heat treated in flowing N_2 to decompose the $Pt(NH_3)_4(NO_3)_2$ complex. The samples were placed in a 5 mm inner diameter quartz tube and heated in flowing nitrogen in a tube furnace. The samples were heated to 300 ºC for 1 h in 100% N_2, with a flow of 20 standard cubic centimeters per minute (sccm).

Treatment in Hydrogen

The as-dried samples impregnated with H_2PtCl_6 were heat treated in flowing H_2 using a Coutler Omnisorp series 100 CX chemisorption apparatus to decompose the H_2PtCl_6 complex. The samples were first purged with He for 30 min and then reduced in H_2 at 400 ºC for 3 h.

Sample Analysis

Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was used to analyze carbon decomposition. A TA Instruments model STD 2960 simultaneous DTA-TGA instrument was used. Approximately 15 mg of sample was placed in an alumina crucible. Dry air (~20% O_2) was fed into the instrument at a rate of 95 sccm. The temperature was ramped at 20 ºC/min up to the desired set point temperature and then held for 500 min. The set point ranged between 375 ºC and 450 ºC. All samples were analyzed using the TGA, and repeat measurements were taken to ensure reproducibility. Sample analysis consisted of monitoring weight loss and temperature difference as a function of time at a given temperature set point.

Results and Discussion

A complete list of TGA results providing preparation method, preparation date, treatment, and wt. % remaining at 300 min is given in Appendix I.

Pure Carbon

To obtain baseline data, the pure Fisher AC was analyzed for decomposition in the TGA. These results are shown in Figure 2 and Table 1. Decomposition rates were calculated by measuring the slope between 100 and 300 min. As expected, the TGA curves show that increasing the set point temperature correlates with increases in the rate and extent of decomposition.
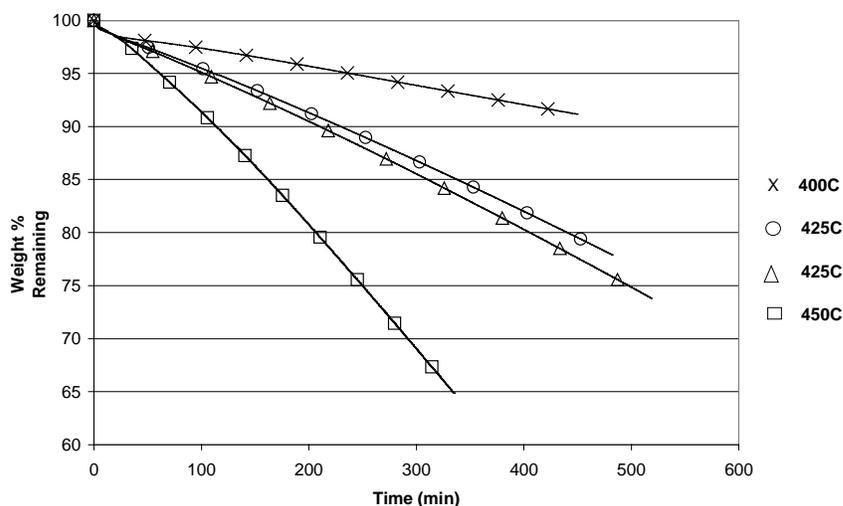
Figure 2: Temperature dependent decomposition of pure activated carbon.

Set Point (°C)	Rate (% decomposition / min)
400	0.0173
425	0.0492
425	0.0448
450	0.108

Table 1: Average decomposition rates of pure carbon at temperatures between 400 and 450 °C.

As shown in Figure 2, the wt. % remaining as a function of time is relatively linear. Table 1 also shows that decomposition rates are reproducible. For the repeat measurements at 425 °C, there is only a 1-2% difference in weight after 300 min and a

very small difference in rate. Hereafter, 300 min will be used as a standard time for comparison of the extent of decomposition for different samples.

Effect of Platinum Loading

The catalytic effect of platinum impregnated with the $Pt(NH_3)_4(NO_3)_2$ precursor is shown in Figure 3. The TGA curves show that impregnating the AC with platinum greatly enhances the decomposition rate and that higher Pt loading results in higher activity.
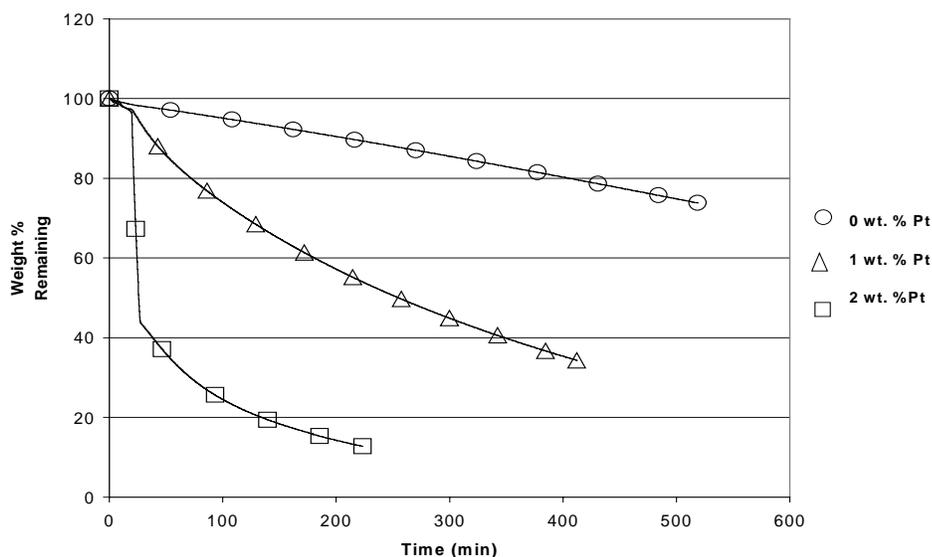
Figure 3: Effect of platinum loading on the decomposition of as-prepared platinum impregnated active carbon at 425 °C.

These findings are consistent with the hypothesis that platinum particles chemisorb oxygen, which facilitates the combustion of carbon. Increasing the platinum content leads to an increased exposure of carbon to platinum. Higher platinum loading also leads to autocatalytic behavior that can be seen by the rapid weight loss of the 2% Pt sample in Figure 3. Autocatalysis occurs because carbon decomposition is accompanied by an exothermic reaction that causes the sample temperature to significantly increase above the set point.

Differential thermal analysis (DTA) curves of the samples in Figure 3 are shown in Figure 4. Clearly, increased amounts of dispersed Pt leads to an exothermic reaction. At 20 min, which corresponds to a temperature of 400 °C, an exothermic reaction is observed for the Pt/AC samples, while none is observed for the pure carbon. A common occurrence with all samples is that the observed temperature difference correlates directly with the decomposition rate. From an application point of view autocatalytic behavior is

desirable because it results in rapid carbon gasification. However, a problem occurs when attempting to quantify TGA results where autocatalytic behavior takes place because the results are less reproducible. Autocatalytic behavior is significantly affected by the sample size and the packing of the sample in the sample holder. Reproducible packing is very difficult to achieve because of the extremely low density of the AC. For this reason, most samples were analyzed at temperatures where autocatalytic behavior was not observed.
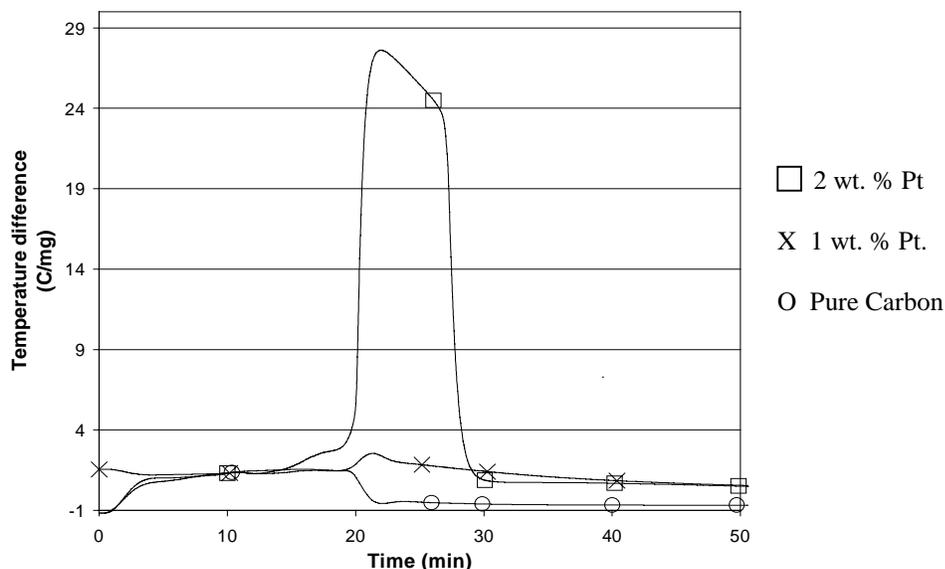
Figure 4: DTA curves of the samples in Figure 3 showing the temperature differences of samples due to exothermic reactions.

Effect of Treatment: Pt(NH$_3$)$_4$(NO$_3$)$_2$ Impregnation

The samples impregnated with Pt(NH$_3$)$_4$(NO$_3$)$_2$ were prepared by dissolving Pt(NH$_3$)$_4$(NO$_3$)$_2$ in water. The polar nature of water, however, does not allow for easy wetting of the non-polar AC. Dissolving Pt(NH$_3$)$_4$(NO$_3$)$_2$ in less polar solvents was attempted but not successful due to the ionic nature of the Pt(NH$_3$)$_4$(NO$_3$)$_2$ complex.

For samples prepared using water as a solvent, TGA results show a 1% weight loss at approximately 250 °C that is due to the decomposition of the Pt(NH$_3$)$_4$(NO$_3$)$_2$ precursor. Consequently, to decompose the precursor prior to TGA experiments, the Pt/AC was treated in flowing N$_2$ at 300 °C. Post-treatment results show no weight loss at 250 °C, demonstrating that the precursor was completely decomposed. The N$_2$ treatment resulted in a higher extent of decomposition as shown in Figure 5. Similar results were seen when the samples were analyzed at 425 °C (see Figure 3 and Appendix I). These data suggest that decomposing the precursor in N$_2$ better disperses the platinum.
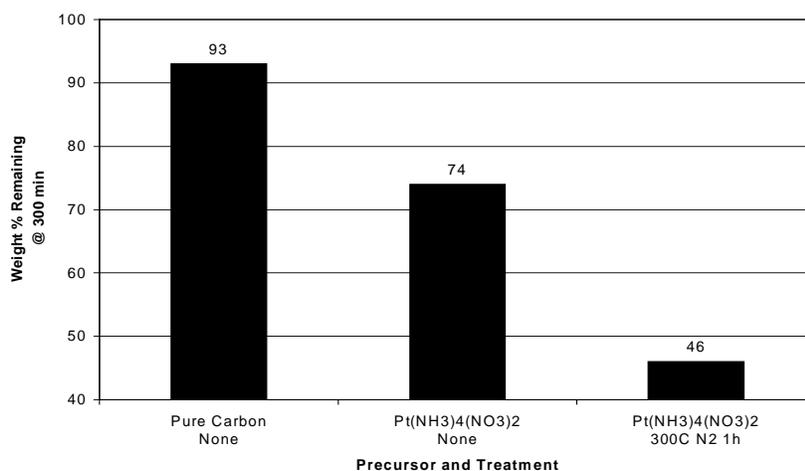
Figure 5: Effect of precursor and treatment on decomposition at 400 °C.

Effect of Treatment: H$_2$PtCl$_6$ Impregnation

Samples were impregnated with H$_2$PtCl$_6$, using water, acetone, and methanol as solvents (the aqueous H$_2$PtCl$_6$ solution is miscible in all three solvents). TGA results of the untreated samples show a very low extent of decomposition as seen in Figure 6 (no treatment is designated as "None").
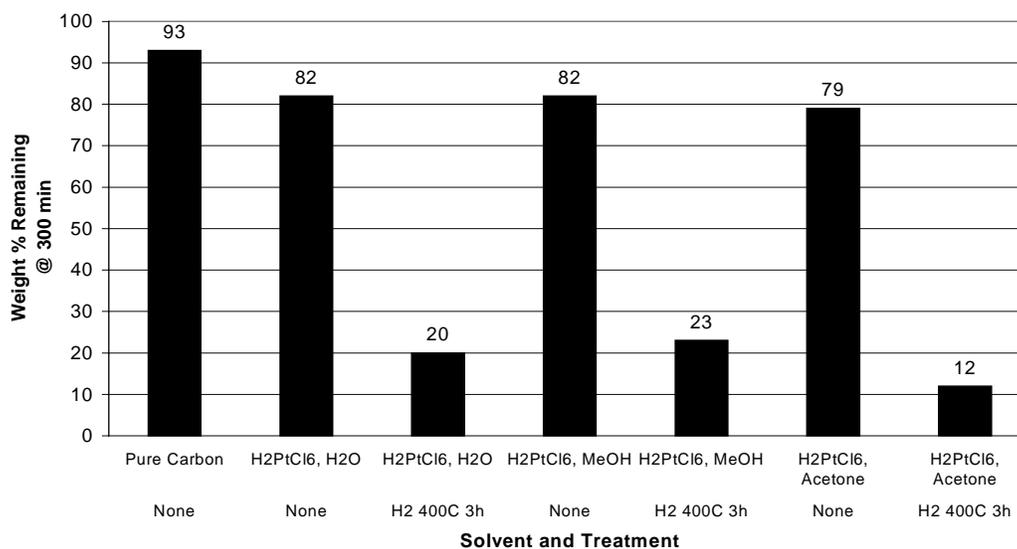
Figure 6: Effect of solvent and treatment on the decomposition of 1 wt. % H$_2$PtCl$_6$ samples at 425 °C.

These untreated samples are only slightly more active than the pure carbon. Treatment was attempted for the H_2PtCl_6 impregnated samples just as the $Pt(NH_3)_4(NO_3)_2$ impregnated samples by exposing the Pt/AC sample to flowing N_2 at 300 °C. This treatment did not result in any improvements, as the precursor was not decomposed. However, after the samples were reduced in hydrogen at 400 °C, decomposition of the H_2PtCl_6 precursor (producing HCl) was complete, and significant changes were observed. H_2PtCl_6 must be treated in H_2 because while the $Pt(NH_3)_4(NO_3)_2$ complex can be decomposed and reduced in an inert environment at elevated temperatures, the H_2PtCl_6 complex requires a more reducing environment for precursor decomposition and formation of metallic Pt. The TGA results at 425 °C for this sample show a very high decomposition rate that is accompanied by autocatalytic behavior. Similar results were observed for the H_2PtCl_6 impregnated samples made with the three different solvents, with acetone showing a somewhat higher extent of decomposition. Figure 6 shows that the extent of decomposition at 300 min is approximately 4 times greater for the treated samples than the untreated ones.

Since autocatalytic behavior was observed at 425 °C for the reduced samples, TGA experiments were also performed with these samples at 400 °C in an effort to better quantify the results. These results appear in Figure 7. Again, the acetone solvent produced a higher extent of decomposition relative to the methanol or water solvents.
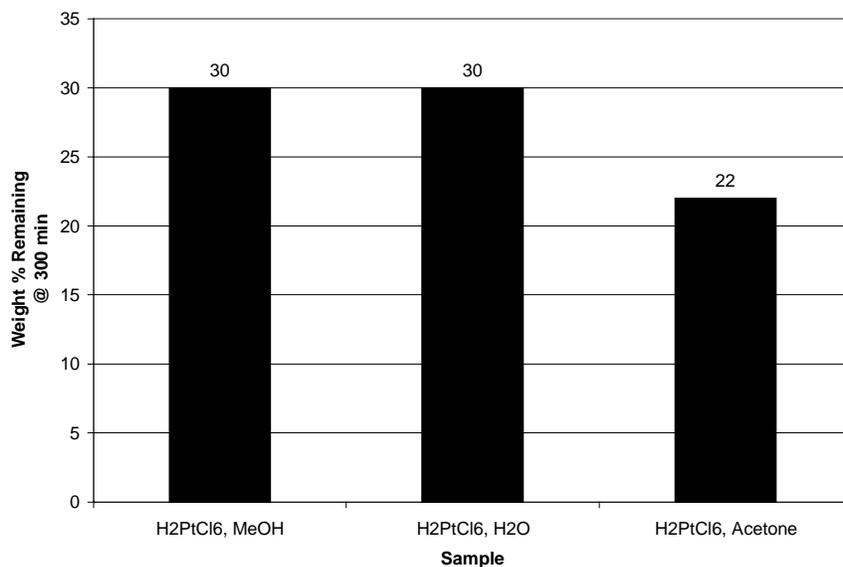
Figure 7: Consumption of hydrogen reduced 1% Pt/AC H_2PtCl_6 impregnated samples at 400 °C.

Table 2, which displays calculated decomposition rates between 100 and 300 min, shows that decomposition rates for the platinum dispersed samples exceed those for pure carbon by more than an order of magnitude. Results also show that water and methanol give approximately the same rate and extent of decomposition, while acetone gives a somewhat higher rate and extent of decomposition.

Sample	Rate (% decomposition / min)
Pure Carbon	0.0173
1% Pt/C (methanol)	0.258
1% Pt/C (water)	0.255
1% Pt/C (acetone)	0.293

Table 2: Average decomposition rates of hydrogen reduced 1% Pt/AC H_2PtCl_6 impregnated samples at 400 °C.

This result agrees with a review by Rodriguez-Reinoso, which states that less polar solvents, like acetone, wet carbon much better than polar solvents, such as water and methanol [1]. The acetone wets the entire porous carbon particle distributing platinum throughout the internal particle structure. Polar solvents, on the other hand, only wet the surface of carbon granules, and do not allow platinum to reach the center of the porous particle. These results would lead one to believe that significant differences should be observed between the different solvents, when in fact, the differences are not very significant. The reasoning behind this phenomena is consistent with a shrinking core model. We propose that these relatively minor differences occur because the carbon is constantly decomposing and exposing new surfaces. Thus, the platinum that was initially on the surface of the porous carbon particle will eventually reach the original center of the particle structure.

Effect of Oxygen

All the previous TGA data was taken while flowing 95 sccm of dry air into the TGA furnace. A test was performed to determine if decomposition would occur in the absence of oxygen. Figure 8 compares the decomposition of a 1% Pt/AC sample in argon and air environments.
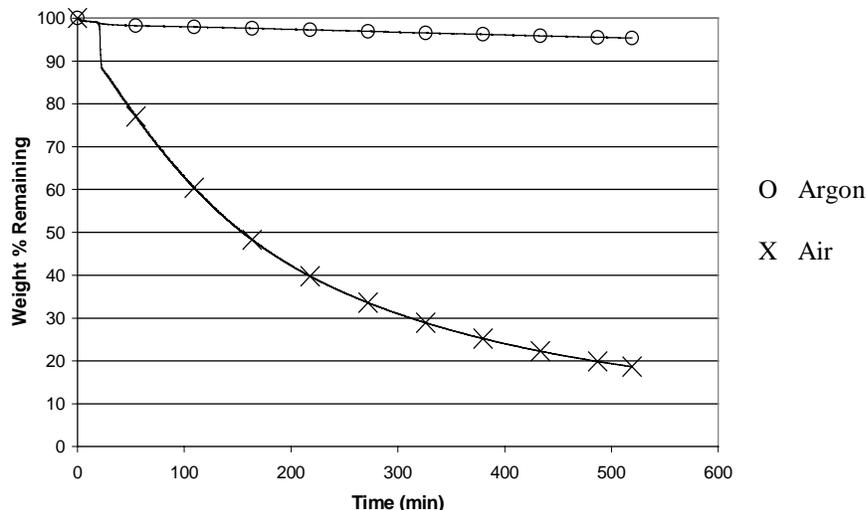

Figure 8: Decomposition of 1% Pt/AC samples in air and argon.

This experiment was performed on a $Pt(NH_3)_4(NO_3)_2$ impregnated, nitrogen treated sample, at a set point of 425 °C. The TGA results clearly show that oxygen is needed for

decomposition to occur. In the absence of oxygen, decomposition results in a 3% weight loss at 300 min, while in air there is a 70% weight loss. It is expected that similar results would be observed for pure AC samples. This result is significant in that is consistent with the previously proposed combustion mechanism.

Conclusions

Our findings show that platinum supported on AC is a viable material for enabling carbon decomposition in air. Upon heating, the Pt/AC material decomposes rapidly and reproducibly, and shows a high extent of decomposition. It can be concluded that AC impregnated with platinum decomposes much faster than pure AC. Higher platinum loadings result in faster decomposition and lead to less reproducible autocatalytic behavior at higher temperatures. Based on cost limitations and acceptable residue contents, platinum contents of 1 or 2 wt. % appear to give the best performance. Furthermore, the AC can be impregnated with either $Pt(NH_3)_4(NO_3)_2$ or H_2PtCl_6 to produce viable results, although data shows that H_2PtCl_6 impregnation gives more complete decomposition than impregnation with $Pt(NH_3)_4(NO_3)_2$. Improvements in decomposition efficiency result when the $Pt(NH_3)_4(NO_3)_2$ impregnated samples are treated in nitrogen and when the H_2PtCl_6 impregnated samples are reduced in hydrogen. H_2PtCl_6 impregnated samples prepared with acetone as the solvent and reduced in hydrogen had the highest activity of all the experimental samples. Finally, it was shown that the Pt/AC samples must be in an oxidizing environment for decomposition to take place—a result that is consistent with a combustion mechanism.

Recommendations for Future Work

These catalysts appear to be excellent materials for the desired application. Listed here are a number of future experiments that should be performed to complete this work. First, we will subject AC to oxidative environments with H_2O_2 or HNO_3 to make the AC more hydrophilic, facilitating better impregnation with polar solvents like water. Second, we will granulate Pt/AC samples in an attempt to improve the reproducibility of sample packing, as well as TGA results. Third, we will further vary reaction temperature and platinum loading to give a more comprehensive understanding of decomposition characteristics. Fourth, we will use other methods of preparation, utilizing different platinum precursors and other metals. Fifth, we will analyze samples for metal dispersion, surface area, and reduction characteristics. Finally, we will evaluate commercially-prepared Pt/AC catalysts to see how they compare with the results shown herein.

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Appendix I

Pure Carbon

Source	Analysis Temp (C)	Treatment	Weight % @ 300min
Fisher	400	None	93
Fisher	425	None	87
Fisher	425	None	86
Fisher	450	None	68

1% Pt/C 400C

Prep. Method	Prep. Date	Treatment	Weight % @ 300min
Pt(NH3)4(NO3)2	12/18/2000	None	75
Pt(NH3)4(NO3)2	12/18/2000	None	73
Pt(NH3)4(NO3)2	04/03/2001	None	75
Pt(NH3)4(NO3)2	04/03/2001	None	74
Pt(NH3)4(NO3)2	04/03/2001	300C N2 1h	46
Pt(NH3)4(NO3)2	04/03/2001	300C N2 1h	47
H2PtCl6, MeOH	02/27/2001	H2 400C 3h	30
H2PtCl6, H2O	02/27/2001	H2 400C 3h	30
H2PtCl6, Acetone	02/27/2001	H2 400C 3h	22

1%Pt/C 425C

Prep. Method	Prep. Date	Treatment	Weight % @ 300min	
H2PtCl6, Acetone	02/27/2001	None		79
H2PtCl6, Acetone	02/27/2001	None		79
H2PtCl6, Acetone	02/27/2001	H2 400C 3h		12
H2PtCl6, H2O	02/22/2001	None		80
H2PtCl6, H2O	02/22/2001	None		82
H2PtCl6, H2O	02/27/2001	H2 400C 3h		20
H2PtCl6, MeOH	02/27/2001	None		82
H2PtCl6, MeOH	02/27/2001	H2 400C 3h		23
Pt(NH3)4(NO3)2	12/18/2000	None		43
Pt(NH3)4(NO3)2	01/18/2001	None		33
Pt(NH3)4(NO3)2	01/18/2001	None		42
Pt(NH3)4(NO3)2	01/18/2001	None		37
Pt(NH3)4(NO3)2	01/18/2001	None		43
Pt(NH3)4(NO3)2	01/18/2001	None		31
Pt(NH3)4(NO3)2	02/01/2001	None		45
Pt(NH3)4(NO3)2	02/01/2001	None		45
Pt(NH3)4(NO3)2	02/08/2001	300C N2 1h	Argon,	96.5
Pt(NH3)4(NO3)2	02/08/2001	300C N2 1h		10
Pt(NH3)4(NO3)2	02/08/2001	300C N2 1h		30

2% Pt/C

Prep. Method	Analysis Temp (C)	Prep. Date	Treatment	Weight % @ 300min
Pt(NH3)4(NO3)2	375	02/08/2001	None	53
Pt(NH3)4(NO3)2	400	12/23/2001	None	19
Pt(NH3)4(NO3)2	425	12/23/2001	None	13
Pt(NH3)4(NO3)2	450	12/23/2001	None	3

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