

DISPERSION OF Pt/Al₂O₃ FOR TWO METHODS OF PRETREATMENTS OF CHLOROPLATINIC ACID AND THE INVESTIGATION OF THE SPECIES FORMED IN THESE PROCESSES

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ABSTRACT

H₂PtCl₆ was used for the preparation of Pt/Al₂O₃ by thermal treatment at 380°C then, reduction by hydrogen. Dispersion of Pt/Al₂O₃ was much higher when the pretreatment of H₂PtCl₆ was done in oxygen atmosphere at 380°C then in helium atmosphere.

The intermediates formed through the investigated thermal pretreatment processes were PtCl₄ and PtCl₂ at 260°C and 380°C respectively when helium was the atmosphere of pretreatment, while Pt(OH)Cl₃, PtOCl₂ and probably PtO₂ were obtained at the above temperature when oxygen was the atmosphere of the pretreatment.

Keywords: Dispersion, Pt/Al₂O₃, chloroplatinic acid.

INTRODUCTION

An extensive study to the preparation of Pt/Al₂O₃ catalyst was formerly investigated due to its vast usage in the hydrogenation processes¹⁴. Dispersion of the catalyst is of importance to catalyst efficiency. Dispersion of a catalyst is affected by many factors such as the method of pretreatment of the catalyst², namely the method of drying to remove water in the incipient wetness technique⁷, the temperature range at which thermal treatment was done, the atmosphere of the reactor and the type of the impregnated precursor¹². It was reported that H₂PtCl₆ undergoes ligand exchange with OH at different acidity and temperature lower than 150°C leading to the formation of a series of hydrolyzed species of H₂PtCl₆⁵⁻⁶.

In this study the Pt/Al₂O₃ was

Obtained by two methods of pretreatment. It is expected that the dispersion will differ according to the intermediates involved in each method. The methods of pretreatment are investigated here in order to find the pretreatment which gives the highest dispersed catalyst. Hydrogen chemisorption was used to estimate dispersion by the pulse dynamic method^{2,4}. Thermal gravimetric analysis was used for the investigation of the intermediates involved in the two different methods used for the catalyst preparation before reduction with hydrogen to get Pt/Al₂O₃.

EXPERIMENTAL

Chemicals : H₂PtCl₆ (99% purity, Aldrich)
Al₂O₃ (Surface Area 150 m²/g, high purity, Merck).
Apparatus : Thermal Gravimetric

Analyser (TGA) (Rheometric scientific STA 1500) and G.C 3400 (Varian).

Catalyst preparation: $\text{H}_2\text{PtCl}_6 \cdot \text{XH}_2\text{O} / \text{Al}_2\text{O}_3$ was prepared by the incipient wetness technique. The appropriate weight of $\text{H}_2\text{PtCl}_6 \cdot \text{XH}_2\text{O}$ required to prepare a catalyst having a nominal weight loading of 5w% Pt was dissolved in an amount of deionized water. The solution was added to the Al_2O_3 support in a drop wise manner to give a thin slurry. The resulting slurry was dried in vacuum for 24 h at 25°C.

Pretreatment Schedules :

Method 1: A portion (0.250 g) of the dried catalyst was heated in flowing O_2 in the reactor to 380°C (the assigned reduction temperature) for 60 min. followed by outgassing with He for 10min. then reduced by flowing H_2 for 2 h, outgassed with He for 1 h and then cooled to room temperature in flowing helium.

Method 2: Another portion of the dried catalyst was heated in flowing He (instead of O_2 in method 1) in the reactor to 380°C; the following steps were as in method 1.

Chemisorption measurements: Dispersion for each catalyst portion was measured using the pulse dynamic method for the pretreated sample in the glass micro reactor (6mm id silica, volume 4.4 mL). The chemisorption was performed by pulsing H_2 in to the He carrier gas. The H_2 was detected by a thermal conductivity detector of the G.C connected to a Varian integrator model 4290 Fig.1.

Thermal gravimetric analysis : 0.25 g of hydrated chloroplatinic acid was introduced into the furnace at room temperature A flow of 50 ml/min. of He or O_2 gas was used through a heating speed of 5°C/min. Mass loss graph was obtained for runs of O_2 and He at different temperature, Figures 2 and 3.

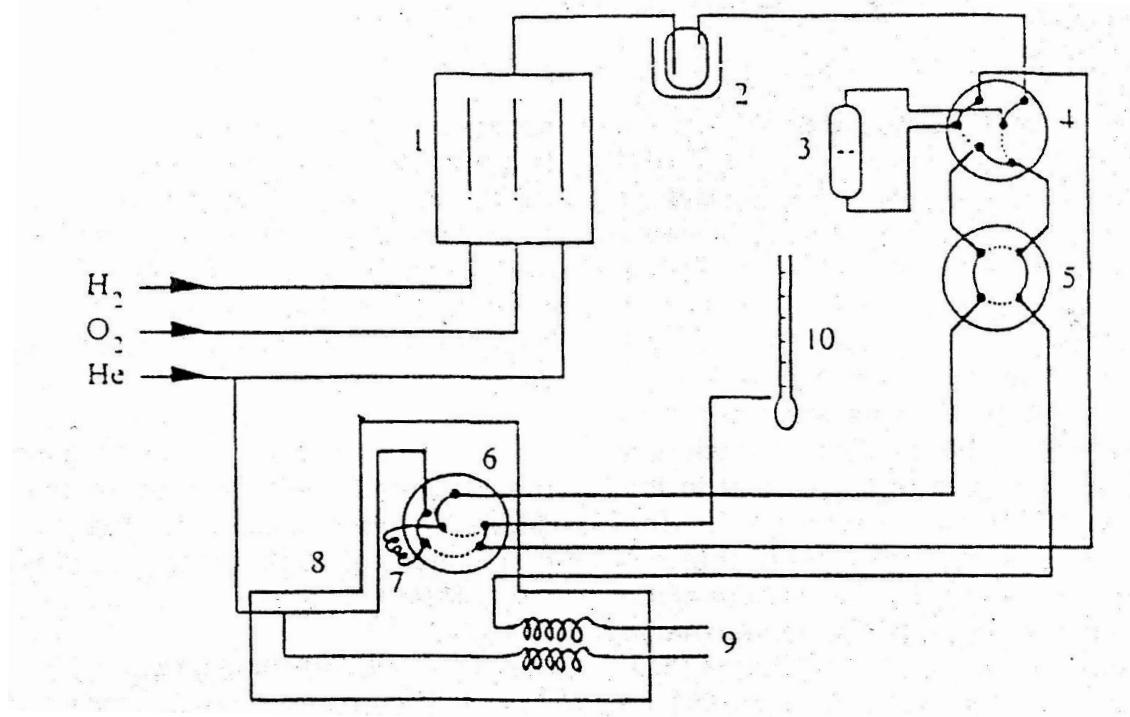


Figure 1: Flow System

1. Mass flow controller. 2. Saturator. 3. Micro reactor. 4. Six-port valve. 5. Four-port valve. 6. Sampling valve (six-port). 7. Sample loop. 8. Gas chromatograph. 9. Columns 10. Bubble flow meter.

RESULTS AND DISCUSSION

The dispersion values obtained are in average 92% for method 1 and 52% for method 2 (Table 1), on the assumption of 1:1 for H : Pt stoichiometry. The difference in dispersion for the two methods cannot be attributed to the readiness of the reduction of the metal chloride (PtCl_2 , PtCl_4) over the

metal oxide¹³, since it known that the chlorides of group VIII metals are easier to be reduced than their oxides¹⁴. Therefore, the difference in the dispersion must be attributed to the type and strength of adsorption and the mobility of the metal precursor surface species formed before complete reduction to the Pt metal. The calcined Pt-precursor species is thought to

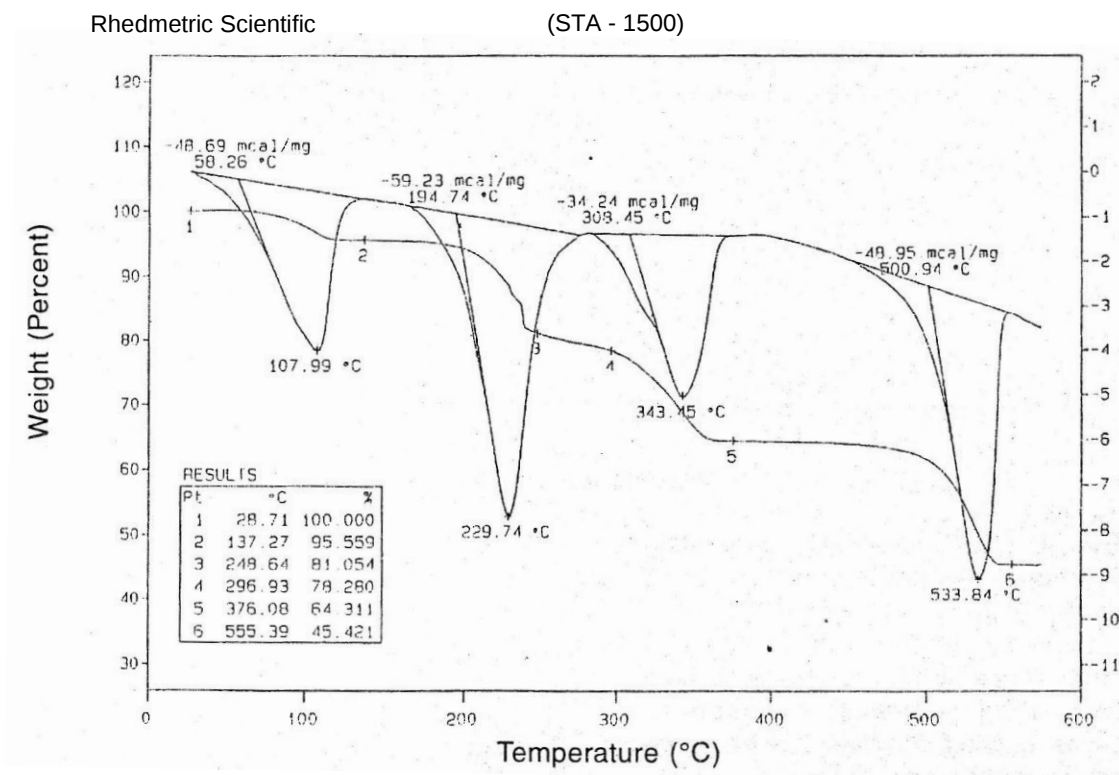
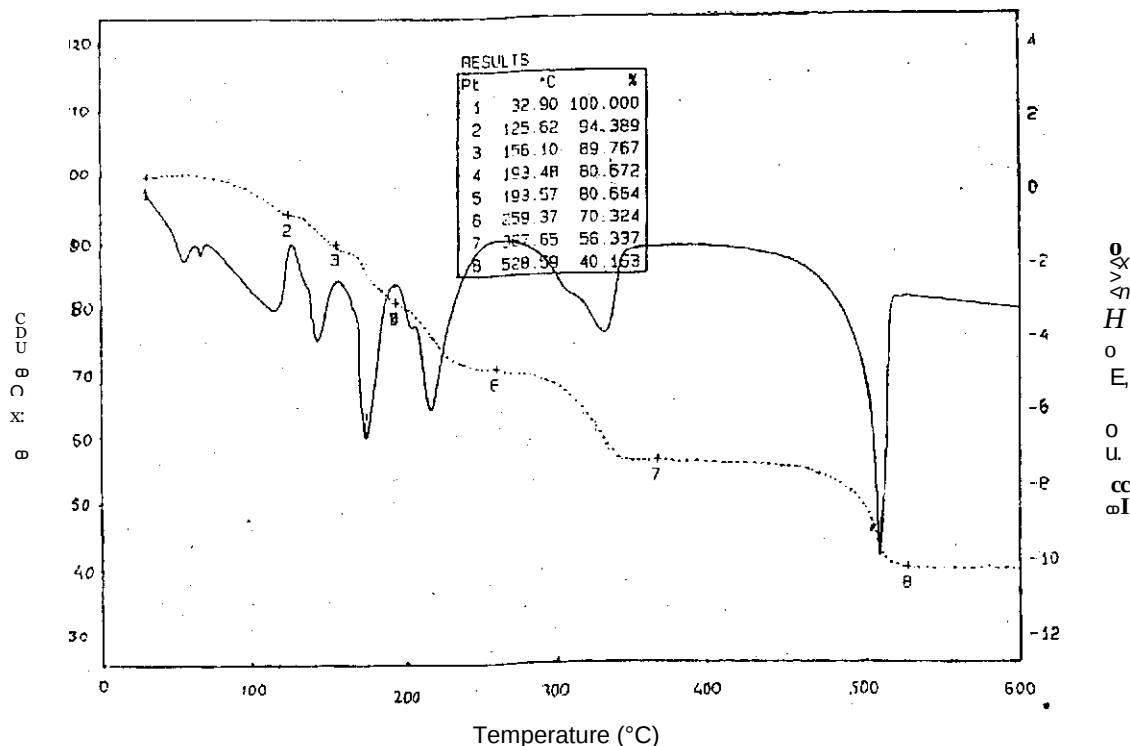


Fig. 2 : Thermal gravimetric graph of $\text{H}_2\text{PtCl}_6 \cdot \text{XH}_2\text{O}$, in Oxygen atmosphere

Table- 1: Dispersion, measured by the two used pretreatment methods

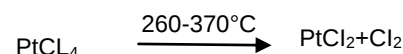
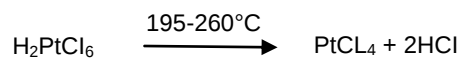
Run No.	% Dispersion by Method 2	% Dispersion by Method 1
1	50	90
2	55	93
3	58	95
4	53	91
5	54	92
Average	54	92.2

Fig. 3 : Thermal gravimetric graph of $\text{H}_2\text{PtCl}_6 \cdot \text{XH}_2\text{O}$, in helium atmosphere
Rheometric Scientific (STA - 1500)



be $\text{Pt}(\text{OH})\text{Cl}_3$, PtOCl_2 and PtO_2 , depending on the calcination temperature in the heating process of H_2PtCl_6 for the range $25\text{--}380^\circ\text{C}^{9-10}$. These species were found to be more mobile than those of metal chloride surface species formed in the He atmosphere through the heating process for the same temperature range⁷. The change in mobility causes more rich surface of Pt species when the oxychloroplatinurj Thtermediates are formed. The thermal gravimetric analysis (TGA) of the chloroplatinic acid (H_2PtCl_6) in He and O_2 atmospheres was carried out to realize that the above species are formed through the two methods of the catalyst pretreatment that led after hydrogenation to $\text{Pt}/\text{Al}_2\text{O}_3$, figures 2 and 3.

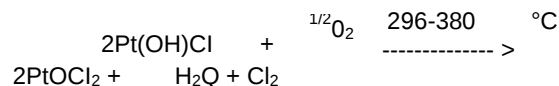
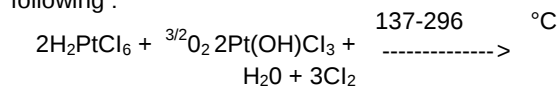
According to the results of TGA, recorded in Table 2 and 3, the decompositions in He atmosphere are as follows:



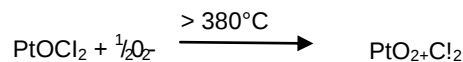
Hence, it is concluded that PtCl and PtCl_2

are the intermediates formed in method 2. Also the percentage of the predicted products in O

shown in Table 2, the led to the deduction of following :



The following also might occur at the end of the temperature rang9 $270\text{--}380^\circ\text{C}$



From these equations it is

Table- 2 : Predicted Products of H.PtCl₃ by thermal gravimetry when heated in O₂ atmosphere

Ratio	Theoretical % w	Experimental % w	Predicted Products
Pt(OH)Cl ₃	78	78.3	137-296°C
H ₂ PtCl ₆		= 81.6	2H ₂ PtCl ₆ + O ₂ → 2Pt(OH)Cl ₃ + H ₂ O
PtOCl ₂	88.6	95.56	
Pt(OH)Cl ₃		64.3	137-296°C
		81.7	2Pt(OH)Cl ₃ + 1/2 O ₂ → 2PtOCl ₂ + Cl ₂ + H ₂ O
		78.3	T > 380
			2PtOCl ₂ + O ₂ → 2PtO ₂ + 2Cl ₂

Table- 3 : Predicted Products of H.PtCl₃ by thermal gravimetry when heated in He atmosphere

Ratio	Theoretical % w	Experimental % w	Predicted Products
6H ₂ O	21	20	25-195°C
H ₂ PtCl ₆ .6H ₂ O			H ₂ PtCl ₆ .6H ₂ O → H ₂ PtCl ₆ + 6H ₂ O
			loss of water of crystallization
PtCl ₄	82.4	85	195-260°C
H ₂ PtCl ₆			H ₂ PtCl ₆ → PtCl ₄ + 2HCl
			decomposition of chloroplatinic acid
Cl ₂	21	22.7	260-367°C
PtCl ₄			PtCl ₄ → PtCl ₂ + Cl ₂
			decomposition of platinum tetrachloride
PtCl ₂	79	80	T < 380
PtCl ₄			noCl ₄ → PtCl ₂ + Cl ₂

The relative masses of the products at different temperature were taken from the TGA record listed in Fig.2 and 3.

The large difference between the theoretical and experimental is due to the formation of PtO₂ from PtOCl₂ at the temperature range 296-380°.

Concluded that Pt(OH)Cl₃, PtOCl₂ and PtO₂ are the intermediates formed in method 1.

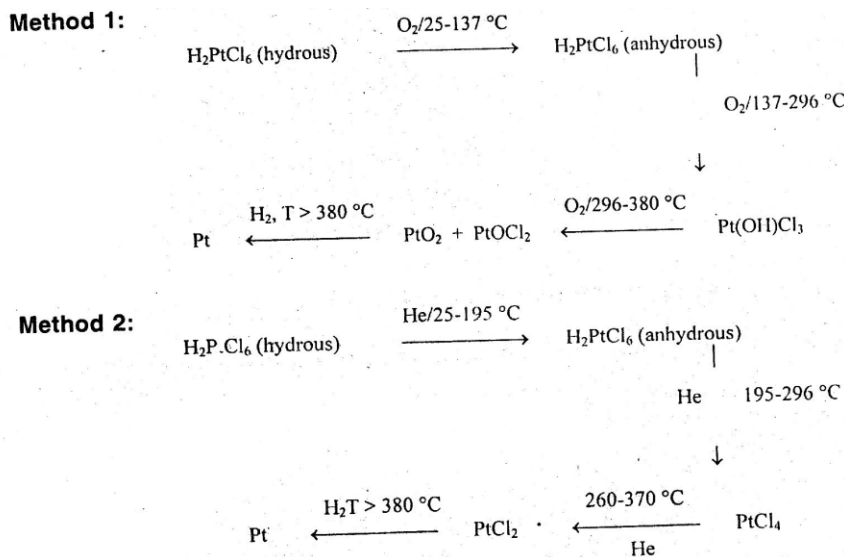
Recently, the results of temperature programmed reduction (TPR) and EXAFS studies by Choi *et al.*,¹⁵ had proved that catalysts prepared from Pt(II) precursors were less reduced than those prepared from Pt(IV). Therefore, the low values of dispersion obtained in this study are due to the strong adsorption (low mobility) and

the low reduction ability of the metal precursor surface species formed through the pretreatment of method 2. However, the high values of dispersion obtained in method 1 could be attributed to the formation of Pt(IV) chloroxygenated species which are more mobile than the PtCl₂ species⁷⁻¹⁰.

Heating 380 °C in method 2 will produce PtCl₂ which is known from above to be hardly reduced than PtCl₄. In method

1, PtOCl_2 and PtO_2 are formed which are pretreatments used in this study the following might be occurring :

In the two methods of the



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