

## Recovery of Platinum and Rejuvenation of Alumina From Spent Reforming Catalyst, $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$

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### Abstract

Recovery of platinum from spent naphtha reforming catalyst ( $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ ) which contain 0.30 wt % of Pt was conducted using two methods, the first one was treatment of the spent catalyst with aqua regia whereas the second one involved chlorination of the spent catalyst. The results show that the chlorination method is more efficient than the acid treatment one as 93 % platinum can be recovered, in addition to reserving the  $\gamma\text{-Al}_2\text{O}_3$  skeletal structure from serious changes. The recovered platinum was converted to hexachloroplatinic acid, a material that can be used to prepare the catalyst again by impregnation method using either new alumina or certain proportion of it and recovered one.

**Keywords:** Catalyst, Recovery, Pt, Alumina

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### 1- INTRODUCTION

Catalysts are widely used in different processes related to petroleum and petrochemical industries [1]. Usually the activity of these catalysts decreases after some operations. This is related to different factors like coke formation on the active sites of the catalyst. In order to increase the activity, the catalyst should be regenerated and in order to regenerate the catalyst, it is usually heated to a high temperature and in the presence of a oxygen containing gas. The regeneration of the catalyst generally increases its activity to the level of a new catalyst. But after some operation, reduction has no effect on the activity and the catalyst should be replaced by a new one and the spent one need processing.

Processing of spent catalysts for winning their metal values [2] except for some noble metals based systems was in its infancy even fifty years ago. Most frequently used metals in the catalysts are critical ones such as cobalt, nickel, molybdenum, vanadium, copper, zinc etc in addition to noble metals. However there have been discouraging factors in the way of taking up the processing of spent catalysts for metals values. Some of these are:

- 1-Source raw materials are spread over a wide area
  - 2-Transportation problems
  - 3-Uncertain availability as life of catalysts varies.
  - 4-Non-availability of standard processes for treating spent catalyst (unlike those of ores).
- In spite of these factors, there are always some driving forces for the recovery of metals from spent catalysts. Some of these factors are:
- 1- Conservation of natural resources.
  - 2-Lower cost of recovered metals compared to virgin metals.
  - 3- Non-availability of the metals indigenously.
  - 4- Higher disposal cost due to anti-pollution regulations.
  - 5-Shortage of disposal sites
  - 6- Minimizing environmental pollution.

Platinum, rhenium, and other noble metals are the most essential active parts of aromatization, reforming, and dehydrogenation catalysts [3] and very year, oil and petrochemical industries expel a great amount of such spent catalysts.

Since the general introduction in the late 1960s of gold-palladium catchment gauze to recover platinum lost from the catalysts of ammonia oxidation plants [4] and their incorporation into an efficient, reliable process in the mid 1970, their application become widespread.

There are some methods for recovery of platinum, rhenium and other noble metals from catalysts [5-14]. One effective method for recovery of Pt and Re from spent catalysts containing these metals or from solutions containing the ions of these metals, is using appropriate ion exchange resins [5, 7, 9, 10, 13] where the noble metals are separated from the other impurities in solution in the columns containing ion exchange resins [7]. One invention method is directed to a method for recovering precious metals such as platinum, palladium, rhodium, gold and rhenium using a leaching solution comprising allergen salts and sulfuric acid and/or ammonium salts (15).

A new process called AquaCat for the recovery of precious metals from spent heterogeneous and homogeneous catalysts [16] is described which involves supercritical water oxidation during which the carbonaceous materials is converted into less noxious compounds, leaving the precious metals as their oxides.

During recovery of the noble metals, platinum and rhenium from the spent aromatization catalyst of naphtha using anion exchange resins, the catalyst is solved in a mixture of sulphuric acid and aqua regia, and the produced solution is passed through the columns which contain the ion exchange resins. The platinum and rhenium that exist in the solution are adsorbed on the resin, then the resin is washed by the means of a suitable acid and platinum and rhenium are desorbed from resin. The different parameters which affect the process of desorption and adsorption are also considered and the best condition for the maximum efficiency is determined. The efficiency has been 100% in the adsorption process and over 95 % in the desorption process.

In new method [17] of recovery two products are manufactured – precious metal and sodium aluminate. Thus there is some constant profitability connected with the processing of spent aluminum oxide to raw material of catalyst industry – sodium aluminate.

Recovery of these metals was the goal of research focused on developing a simple and economical separation and recovery method using electrochemical technology [18]. An electrochemical cell essentially uses a current carrying solution and two electrodes at which oxidation and reduction processes occur as current flows [19]. These results showed that up to 80% of the platinum group metals could be recovered in this manner from spent catalysts. Also, it was discovered that the leaching solution could be reused and recycled back into the process after electrochemical deposition of the platinum group metals has occurred.

This paper focus on studying the separation of platinum from spent reforming catalyst using aqua regia and chlorination methods and evaluating the reuse of produced alumina.

## **2. EXPERIMENTAL**

### **2.1 Materials**

Spent catalyst, Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ammonium chloride, hydrochloric acid, potassium chloride, ammonium hydroxide, sodium bromate, sodium acetate, sodium sulfide, hexachloroplatinic acid, nitrogen gas, carbon tetrachloride, nitric acid, formic acid, all are of analytical grade.

### **2.2 Pretreatment of Catalysts**

The spent catalyst was first sieved to isolate the powder and use the uncrushed complete extrudates only in chlorination method while the whole catalyst can be used in aqua regia extraction. It is washed if necessary with distilled water and dried in an oven for four hours at 120 °C in order to remove the volatile matter that may be present and adsorbed on its surface and may cause problems. It was then heated gradually to a temperature of 450 °C and calcined for another four hours at this temperature in order to get rid of any existed coke.

### **2.3 Recovery of Platinum With Aqua Regia**

It is well known that platinum metal is insoluble in mineral acids and hence the aqua regia is nearly the only acid for its dissolution. A previously sieved from powder/or not weight and calcined sample, 100

gm was mixed with aqua regia solution 200 ml and then heated to 90 °C and left for two hour at this temperature.

The resulted acid solution was mixed with hydrochloric acid solution and heated several times at 90°C in order to dissociate the nitric acid and get rid of nitrogen oxides. This process was repeated several times with the addition of hydrochloric acid and distilled water until yellow nitrous oxides evolution ceased and the platinum solution formed is free of mineral acids and it is in the form of hexachloroplatinic acid solution with some dissolved aluminum salts resulted from the dissolution of alumina in acid media. This solution is difficult to deal with to precipitate hexachloroplatinate because the extraction causes disintegration of alumina structures to fine particles which need to be separated prior to any treatments.

## 2.4 Recovery of Platinum Using Chlorination Method

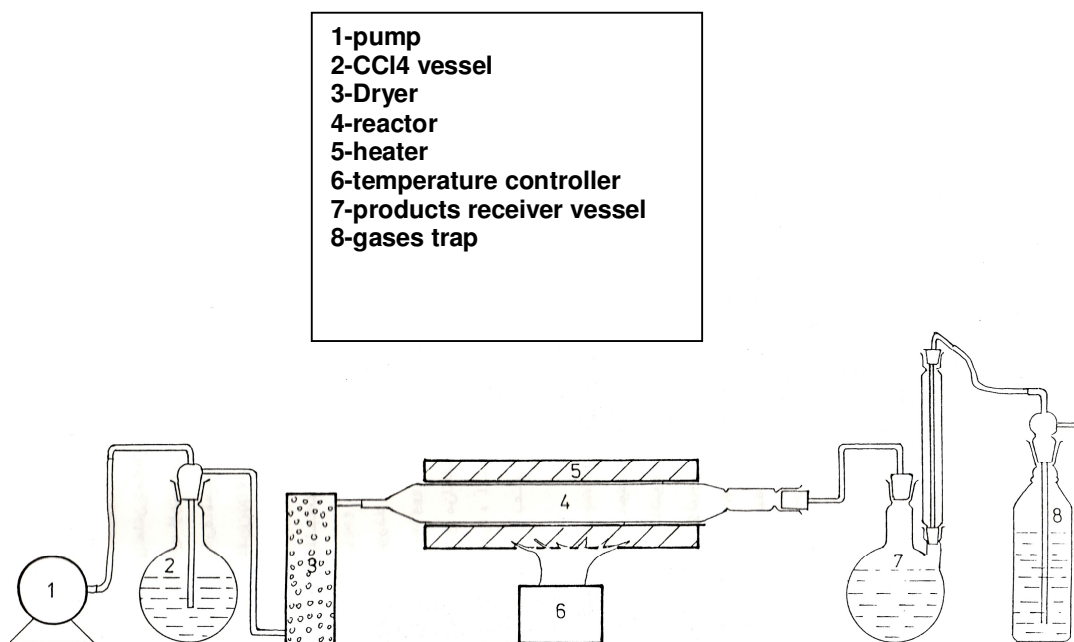
It is well known that platinum form volatile chlorides when exposed to chlorine gas at high temperatures, so chlorination process was used as new method to separate platinum from spent catalysts.

### 2.4.1 Description of the Chlorination Unit

The schematic representation of chlorination unit used is demonstrated in fig.1. The unit composed simply of chlorine gas source, chlorination reactor and product collection parts. Chlorine gas was generated from dissociation of carbon tetrachloride vapor placed in flask 2 after being mixed with compressed dry air and enter the heated furnace (5). The reactor (4) was quartz tube of 30 cm length and 2 cm diameter inserted in a heat controlled (6) tubular furnace.

Products collection unit is basically a round bottom flask (7) attached to the reactor where the liquid and solid particles are trapped in and the vapor one was passed to water condenser to be cooled and collected while the otherwise are finally sent to trap (8) filled with acidified water.

**FIGURE 1:** The schematic representation of chlorination unit



## **2.4.2 Chlorination Process**

50gm of catalyst extrudates (0.3% pt) previously sieved from powder was placed and fixed as a bed in the middle of the quartz tubular reactor between two pieces of glass wools to avoid its movements. The reactor was heated to a temperature of 200 °C and then air saturated with carbon tetrachloride vapor was passed through the reactor at flow rate of 100 liter/hour and the temperature raised gradually. At the beginning white vapor of carbon tetrachloride appears which is then turned deep and brown-greenish at about 250 °C and finally turned to yellow-orange one at 350 °C.

At a temperature of 350 °C carbon tetrachloride dissociates liberating chlorine gas which is reacted with platinum of catalyst forming its chlorides; this was continued for 3-4 hours. The apparatus was left to cool for three hours and then the condenser and flask were rinsed with acidified water and the liquid being mixed with the trap solution. This wash up liquid was concentrated and converted to hexachloroplatinic acid by treating and heating it with aqua regia and hydrochloric acid followed by distilled water.

## **2.5 Precipitation Methods**

### **2.5.1 Precipitation of Platinum as Ammonium Hexachloroplatinate**

By concentrating the free powder extracts to a level that aluminum is not precipitated and then with the addition of saturated ammonium chloride solution platinum was precipitated as ammonium hexachloroplatinate. The formed precipitate, was washed, filtered, dried and weight as so or converted to platinum metal after heating in a furnace at 700 °C for four hours.

### **2.5.2 Precipitation of Aluminum as Hydroxide Prior to Platinum**

This was done by treating the aluminum and platinum containing solution with ammonium hydroxide solution, the bulky aluminum hydroxide precipitate was filtered, washed and the filtrate was used to precipitate platinum as in 2.5.1.

### **2.5.3 Precipitation of Platinum as Platinum Sulfide**

The platinum was precipitated as sulfide by the addition of sodium sulfide with slight heating. The formed black precipitate was washed, filtered and dried and can be converted to platinum metal after heating to 700 °C

### **2.5.4 Precipitation of Platinum as Potassium Hexachloroplatinate**

Platinum was precipitated by the addition of saturated potassium chloride solution with slight heating. The formed yellow crystals precipitate was washed filtered and dried and from the weight platinum can be quantitatively determined.

### **2.5.5 Precipitation of Platinum as Metal**

This was done by treating the platinum containing solution with sodium acetate/formic acid solution, 3 %. The platinum reduced to free metal precipitate which is filtered, washed and the weight can be determined.

## **2.6 Treatment of Alumina**

The remaining alumina after platinum separation was sieved from powder which is very little indeed and washed with distilled water several times to get rid of acids present and dried at 120 °C for three hours and calcined at 400 °C for four hours to get rid off chlorine present and to adjust its acidity.

## **2.7 Catalyst Analysis and Characterization**

Pt and Al were determined by standard atomic absorption methods, Surface area are measured by using BET method [20] and the apparatus used was CarloEraba Sorptomic Series 1800, pore volumes and densities were determined by the liquid impregnation methods [21]. Hardness was determined with the ERWEKA TBH28 hardness meter [22]. The Bulk density is determined by placing a weight catalyst in a graduated cylinder then shake it by hand on the table or by vibrator and read the volume of it and then calculate the density i.e. it is the packing or load density of the reactor.

### 3. RESULTS AND DISCUSSION

#### 3.1 Results of Extraction With Aqua Regia

The observation of extracts obtained and the remaining alumina showed that an appreciable amount of aluminum oxide in the catalyst was dissolved or crushed to fine suspended particles even at different temperatures and time. This led us to follow different routes to deal with the platinum extract obtained.

The precipitation of platinum as ammonium hexachloroplatinate gave a higher precipitate than the theoretical value and the reason is due the precipitation of some impurities or co-precipitation of aluminum as well. The quantitative determination of the amount of precipitate determined as potassium hexachloroplatinate using 25 gm of spent catalyst with 0.3% wt platinum is:

Weight of potassium hexachloroplatinate obtained experimentally = 0.262 gm  
Weight of platinum in potassium hexachloroplatinate experimentally = 0.105 gm  
Weight of platinum in potassium hexachloroplatinate theoretically = 0.075 gm

On the other hand the precipitation of aluminum as hydroxide prior to platinum show that the formed precipitate was very massive and bulky and requires a large amount of solution for precipitating, washing and filtrations process in addition to long time required. The resulted precipitate obtained from the extract showed that platinum weight obtained is 0.0525 gm which less than the theoretical one and even constitutes 70 % of it because some of platinum was adhered and withdrawn with the gelatinous aluminum hydroxide precipitate.

In order to avoid what was mention above; the platinum was precipitated as platinum sulfide by the addition of sodium sulfide with slight heating as its hydrolysis liberates hydrogen sulfide as precipitating agent. The formed black precipitate was washed, filtered and dried and can be weight as so or converted either to platinum metal after heating to 700°C or to hexachloroplatinic acid by the addition of HCl solution and heating it in aqua regia or using oxidizing agent such as hydrogen peroxide and HCl. It was reconverted also to ammonium hexachloroplatinate by ammonium chloride solution treating.

To calculate the extraction efficiency a catalyst sample with higher platinum content, 1.13 % wt was prepared by liquid impregnation technique and 10 gm of it was used in extraction and precipitation as platinum sulfide which is then converted to ammonium hexachloroplatinate. Quantitative determination as potassium hexachloroplatinate is given:

Weight of platinum sulfide formed experimentally = 0.117 gm  
Weight of ammonium hexachloroplatinate formed experimentally = 0.200 gm  
Weight of potassium hexachloroplatinate formed experimentally = 0.219 gm  
Platinum in potassium hexachloroplatinate formed experimentally = 0.088 gm  
Theoretical weight of platinum in hexachloroplatinate = 0.113 gm  
Extraction efficiency = 78%

Where extraction efficiency calculated as a percent ratio between the experimental and theoretical values of 78 %. This low extraction efficiency together with problems associated with the presence of aluminum in the extract which complicate the procedure of separation necessitated enforced us to think about another and more useful way to do so.

#### 3.2 Results of Platinum Separation by Chlorination Method

Some unsuccessful experiments were done using stainless steel reactor as a results of its corrosion with hydrochloric acid resulted from the reaction of water vapor and chlorine gas. This was observed by the formation of brown color iron compounds in the extract, so quartz reactor was used instead.

The chlorination products (using 50 gm of spent catalyst of 0.3 % pt) are platinum chlorides mixture and to deal with, it was converted to stable platinum (IV) hexachloroplatinic acid by concentrating the chlorinated solution and heating it in aqua regia, using oxidizing agent such as hydrogen peroxide and HCl. The acid was separated and purified by recrystallization weighing 0.370 gm.

Ammonium hexachloroplatinate precipitate was produced from the acid by using saturated ammonium chloride solution, the precipitate was then filtered, washed, dried and weight as ammonium hexachloroplatinate of 0.317 gm.

Platinum was precipitated as platinum sulfide by the addition of sodium sulfide with slight heating as it hydrolysis liberated hydrogen sulfide as precipitating agent. The formed black precipitate was washed, filtered and dried with the weight yield be 0.185 gm

Finally the platonic acid solution was treated with sodium acetate/formic acid solution, 3 %, where the platinum was reduced to free metal precipitate which is filtered, washed and weight determined was 0.139 gm. platinum metal was also produced by the ordinary calcinations mentioned before.

Efficiency of precipitation was calculated by precipitating it with potassium chloride and using 32 gm of prepared catalyst that contain 0.65% pt:

Weight of potassium hexachloroplatinate obtained experimentally = 0.482 gm

Weight of platinum in hexachloroplatinate obtained experimentally = 0.193 gm

Theoretical weight of platinum in hexachloroplatinate = 0.208 gm

Extraction efficiency = 93 %.

So we can finally conclude that chlorination process is more effective than the aqua regia with respect to extracted platinum being 93% compared to 78 % in aqua regia route and also the alumina left after platinum separation reserve its physical properties as in table (1) in contrast to the aqua regia method in which some of alumina was destroyed [17] and converted to aluminates which need more process to be useful. The surface area of used catalysts was enhanced from 92.5 m<sup>2</sup>.g<sup>-1</sup> to 160 m<sup>2</sup>.g<sup>-1</sup> in the regenerated alumina. So it very useful to mix certain proportion of regenerated alumina and new one to produced any required surface area alumina and properties that can be used in reforming catalysts preparation and also in other low surface area requirements catalysts preparations. It is well known that activated alumina as a support constitute the major part of industrial catalysts and it is produced in multiple processes from kaolin or bauxite so by regeneration of it two benefits will be achieved the first one is economizing alumina production and the second one is reducing or eliminating the problems of disposal of waste catalysts which is one of the principles of green chemistry. On the other hand platinum as precious metal is very expensive and the content of it in earth crust is limited so in recycling of it we are saving and investing money and reducing the environmental problems associated with disposal.

**TABLE 1:** Show the physical properties of spent and recovered alumina

Properties	Spent catalyst	New alumina	Impregnated alumina	Regenerated alumina
Shape	extrudates	extrudates	extrudates	extrudates
Size /mm	1.6 x 3	1.6 x 3	1.6 x 3	1.6 x 3
Surface area / m <sup>2</sup> .g <sup>-1</sup>	92.5	180	170	160
Pore volume / cm <sup>3</sup> .g <sup>-1</sup>	0.40	0.55	0.50	0.47
Bulk density / g.cm <sup>-3</sup>	0.75	0.70	0.71	0.70
Loss on attrition / wt%	3	1	1.5	1.5
Hardness / N	110	120	120	115
Acidity , Cl %	0.5	0.0	0.0	1

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