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Recovery of Platinum from Spent Petroleum Catalysts by Substrate Dissolution in Sulfuric Acid

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Abstract

Spent catalysts containing platinum were generated in petroleum refinery and other chemical industries. The reclamation of precious metals from such wastes has long been attempted in view of their rare, expensive and indispensable nature. In this study, the recovery of platinum from petroleum catalysts was attempted by a method consisting mainly of dissolving alumina substrate with sulfuric acid thereby concentrating insoluble platinum. Also, platinum dissolved partially in sulfuric acid was recovered by a cementation method using aluminum metal as a reductive agent. The effect of temperature, time, concentration of sulfuric acid, and pulp density on the dissolution of substrate was investigated. When the substrate of platinum catalyst was $\gamma-Al_2O_3$ about 95% alumina was dissolved in 6.0M sulfuric acid at 100°C for 2 hours. When the substrate was the mixture of $\gamma-Al_2O_3$ and $\alpha-Al_2O_3$ about 92% was dissolved after 4 hours. As a result, more than 99% of platinum could be recovered by this method and aluminum sulfate was obtained as byproduct.

Keywords: Platinum, Catalysts, Recovery, Sulfuric acid

Introduction

Platinum has been employed as a reforming catalyst in the petroleum refining industry. Their demand is expected to remain strong as the platinum catalyst is adopted in the new refining processes as the dearomatisation of diesel fuel[1]. The reforming catalyst containing platinum is discarded when its catalytic function deteriorates. In catalysts, small quantities of platinum is associated with large volumes of support materials consisting generally of alumina[2]. Platinum from spent catalysts can be recovered through the hydro or pyrometallurgical routes[3-7]. The hydrometallurgical treatment is known to be applicable to the smaller scale plant meanwhile the pyrometallurgical treatment is suitable for the larger scale plant. There are several process options for recovering platinum from spent catalysts by the hydrometallurgical process. Platinum can be extracted directly from catalyst substrate using the leachants or extracted from the dissolution residue remained after total dissolution of the substrate. In the first method, the catalyst is leached in hydrochloric acid with oxidants such as nitric acid, sodium chlorate, sodium hypochlorite, and chlorine gas. Han etc.[8] has developed a new technology using halogen salts with oxidant in autoclave. Nevertheless, the process can not avoid the problems such as the loss of platinum due to the leachate trapped in the micropores of the catalyst substrate. The second method involves the total dissolution of alumina substrate concentrating insoluble platinum into the residue. This process has the advantages such that aluminum sulfate (alum) can be recovered as a byproduct and the leachant is consumed much less than in the first method.

In this study, the recovery of platinum from spent petroleum catalysts was investigated by dissolving catalyst substrate with sulfuric acid and concentrating insoluble platinum. Platinum dissolved partially in sulfuric acid solution could be recovered by cementation using aluminum powder as a reductive agent. The effect of dissolution temperature and time, concentration of sulfuric acid, and pulp density on the dissolution of substrate were examined. The dissolution behavior of platinum during dissolution of substrate was investigated. Also, experiments to recover platinum from the dissolution solution was conducted.

Experimental

Materials

The spent catalysts used in this study were two kinds of commercial platinum catalysts spent in petroleum refineries in Korea. They were AR-405 and R-134 and had spherical shapes with diameters of about 2 and 1.64 mm, respectively. The substrates of catalysts were identified mainly as alumina by X-ray difffractometry. The contents of platinum in both catalysts were 0.45% and 0.24%, respectively. Aluminum powders of 150~270 mesh were used to precipitate platinum reductively from the solution generated in the dissolution step of catalyst substrates. Other reagents used were of analytical grades.

Calcination of catalyst

The spent catalysts were calcined to remove the oil containing carbon and sulfur. A muffle furnace was used for the calcination. About 100 g of the catalysts was charged to the muffle furnace preheated to a predetermined temperature and heated for a desired time. During calcination 5g of the catalysts was discharged at regular intervals for the analysis of carbon and sulfur.

Dissolution of catalyst substrate

The dissolution experiments were carried out in a 2,000 ml glass vessel of three necks which was kept in a constant temperature bath. The temperature was controlled within ± 5°C. The stirring speed was adjusted by a motorized controller. The catalysts were ground and calcined at 600°C for 30 min. The ground catalysts were weighed and dissolved in 500 ml sulfuric acid solution which was preheated to a desired temperature. Several slurry samples of about 10 ml were taken at regular intervals for chemical analysis. After the termination of dissolution experiments, the vessel was withdrawn from the bath, and distilled water was supplied to the reacted slurry to suppress the precipitation of aluminum sulfate crystals. The slurry was filtered and the liquid was collected for chemical analysis. The residue was then dried and analyzed for platinum.

Cementation of platinum

Platinum dissolved in the sulfuric acid solution was recovered by cementation using aluminum powder as a reductant. The cementation was carried out in a 500 ml glass vessel with three necks which was kept in a constant temperature bath. A 250 ml solution obtained in the dissolution of the catalyst substrate was fed to the glass vessel and heated to a predetermined temperature. Aluminum powders were added to the solution and solutions of about 10 ml were taken at regular intervals for analysis. When the cementation reaction was completed, the solution was discharged and filtered to collect platinum particles. The filtrate was analyzed for the contents of platinum.

X-ray diffraction was used for the identification of the catalysts and the residue using Cu Kα radiation. The thermogravimetric analysis of the catalysts was carried out by a Du Pont Instruments 951 Thermogravimetric Analyzer. The platinum concentration was analyzed by a fire-assay method[9] followed by Inductively Coupled Plasma Spectrophotometer(ICPS). Platinum and aluminum in solution was analyzed by ICPS.

Results and Discussion

Removal of carbon and sulfur

The spent catalysts generated in the petroleum refinery were heavily contaminated by oil. As the oil on the surface of the catalysts may retard the dissolution reaction and contaminate the solution, it should be removed prior to the dissolution experiment.

The thermogravimetric analysis was carried out to determine the optimum calcination temperature for the spent catalysts. The result is shown in Figure 1. It can be seen that there is a rather continuous weight loss for both catalysts from room temperature to about 400°C. A rapid weight loss is seen at temperatures between 400°C and 500°C. Above 500°C weight change is insignificant up to 800°C.

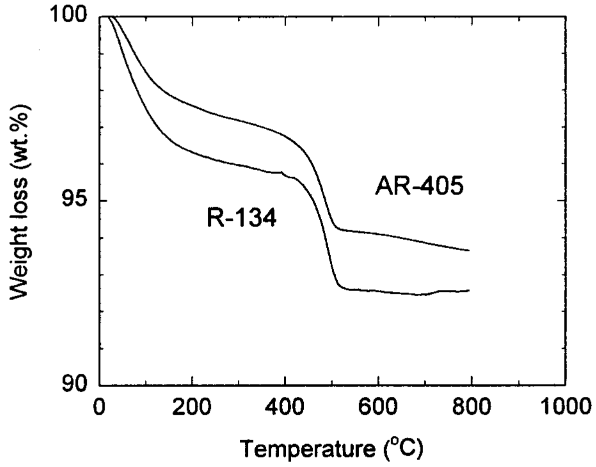

Figure 1. TGA curves of the spent platinum catalysts(R-134 and AR-405) generated in Korean petroleum refinery.(Heating rate: 20°/min)

Figure 2 shows the amount of carbon and sulfur in the catalyst(AR-405) after calcination at various temperatures for 30 minutes. It can be seen that sulfur was almost completely removed after calcination at temperatures over 400°C. However, carbon remained about 2.3% after calcination at 400°C and was removed completely at 600°C. Based on these results, the optimum calcination conditions for carbon and sulfur removal were chosen as 600°C and 30 minutes.

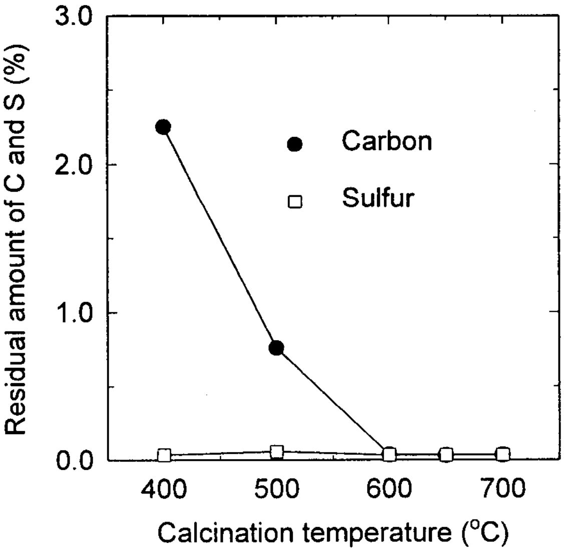

Figure 2. Effect of calcination temperature on the residual amount of carbon and sulfur in the spent petroleum catalyst. The Catalyst was AR-405 and calcination was done for 30 minutes.

Dissolution of catalysts substrate

When the alumina substrates of platinum catalysts were dissolved by sulfuric acid platinum are recovered as insoluble particles. Table 1 summarizes the dissolution experiment. The dissolution of R-134 are seen to be higher than that of AR-405 at all particle sizes. The effect of particle size on the dissolution rate was not very pronounced. However, when the particles are smaller than 210μm the dissolution decreased slightly as the size decreases As the substrate dissolves into the solution the density of solution increases and the fine particles are suspended in the solution. The agitation of solution makes suspended fine particles circulate along with the solution thus maintaining the diffusion layer. This diffusion layer makes the particles difficult to contact the sulfuric acid for the dissolution to occur thus reducing the dissolution rate as observed. For particles larger than 300μm the dissolution of R-134 was not effected by particle size. However, in case of AR-405, it decreases with particle size slightly. This can be attributed to the reduction of surface area as particle size becomes larger as shown in Table 1.

Table 1. Dissolution of the catalysts by 6.0 M sulfuric acid solution at 100°C for 4 hrs. (pulp density; 220g/L)

Particle size (μm)	R-134	AR-405	
	Dissolution (%)	Dissolution (%)	Surface area (m^2/g)
- 45	95.2	86.3	151.1
45 ~ 106	95.5	89.2	148.3
106 ~ 210	97.5	89.2	140.3
210 ~ 300	98.3	92.3	137.4
300~ 420	98.2	89.9	130.3
420~ 500	98.1	83.5	120.7

As can be seen in Table 1, the dissolution of AR-405 was lower than that of R-134 at all particle sizes. To further look at this difference the residue of AR-405 catalysts after dissolution experiments was examined by X-ray diffractomerty. Figure 3 shows the diffraction patterns of AR-405 catalysts. (A) and (B) represent the patterns from fine and coarse size residues after dissolution. (C) is the pattern of raw spent catalysts. The diffraction pattern of raw catalysts shows that they are the mixtures of γ-Al_2O_3 and α-Al_2O_3 phases. After dissolution only α-Al_2O_3 peaks are observed suggesting that γ-Al_2O_3 dissolves completely while α-Al_2O_3 does not.

One thing to be noted here is that platinum peak is seen clearly in the pattern for fine residue samples. This may indicate that platinum is not dissolved and concentrated in the residue. R-134 catalyst consisting only of γ-Al_2O_3 dissolves completely and as a result their dissolution is higher than that of AR-405.

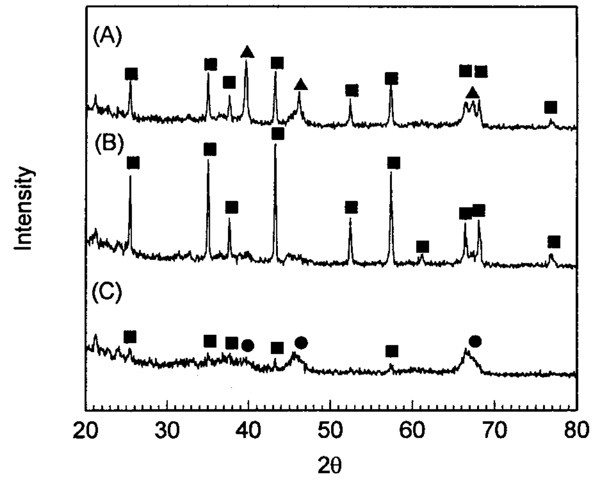

Figure 3. XRD patterns of (A) fine and (B) coarse residues generated in the dissolution of spent catalyst with sulfuric acid solution and (C) raw spent catalyst(AR-405) (●; γ-Al_2O_3, ■; α-Al_2O_3, ▲; Pt)

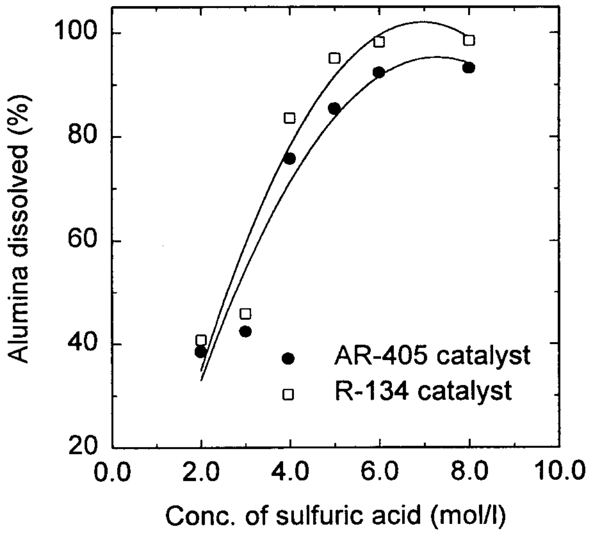

Figure 4. Effect of acid concentration on the dissolution of alumina substrate in sulfuric acid solution at 100°C for 4hrs. (Pulp density; 220g/l, particle size; 210 ~ 300μm)

Figure 4 shows the effect of sulfuric acid concentration on the dissolution of alumina substrate of R-134 and AR-405 catalysts. The effect of acid concentration on the dissolution behavior of both catalysts was similar. The dissolution increased sharply with acid concentration upto 6.0 M. At 6.0M, it was 92% and 98% for AR-405 and R-134, respectively. Further increase in the concentration did not increase the dissolution further. At low concentrations of 2.0M and 3.0M, the dissolution is low as 40%. As stated previously, the dissolution of R-134 is higher that that of AR-405 which is the mixture of both alumina phases since α-Al_2O_3 does not dissolve well. Due to this fact it may be inevitable that the residue should be treated once more with conc. sulfuric acid to dissolve AR-405 completely.

As can be seen in Figure 4, the optimum concentrations of sulfuric acid for substrate dissolution turned out to be between 6.0M to 8.0M. Based on this condition, experiments were conducted to determine the optimum dissolution time and the results are given in Figures 5 and 6.

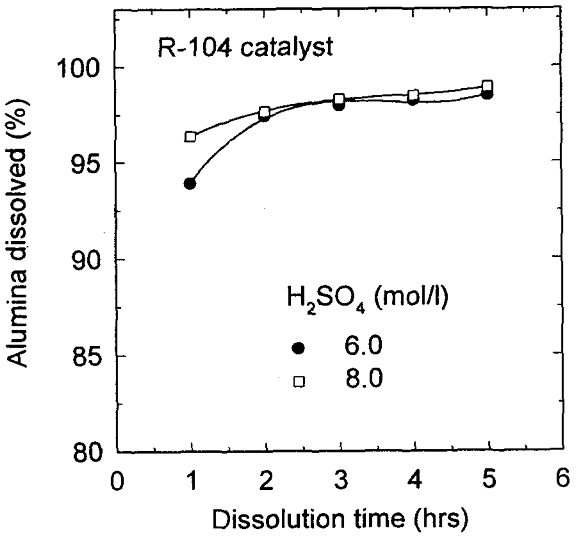

Figure 5. Effect of time on the dissolution of alumina substrate in sulfuric acid at 100°C. (Pulp density; 220g/l, particle size; 210 ~ 300μm)

Figure 5 shows the dissolution of alumina from R-104 with time. The dissolution increases with time upto 3 hours after which the increase becomes insignificant. At the early stage of dissolution as 1 hr, the dissolution in 8.0M acid is higher than in 6.0M. However, as dissolution time becomes longer the difference became insignificant. After 3 hours the dissolution percent of alumina substrate was about 98% in 6M and 8M solutions.

The dissolution curve for R-405 catalyst was similar to that of R-104 as shown in Figure 6. The dissolution increases rapidly to 3 hours and becomes constant. The dissolution at 8.0M acid was higher and the difference becomes small when the time was longer than 3 hours.

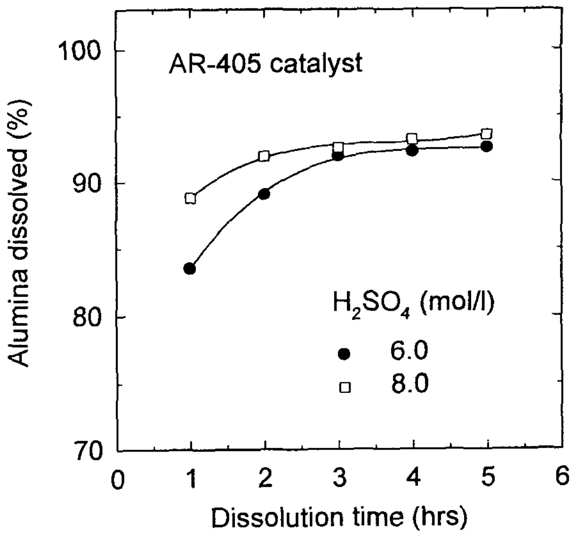

Figure 6. Effect of time on the dissolution of alumina substrate in sulfuric acid at 100°C. (Pulp density; 220g/l, particle size; 210 ~ 300μm)

Dissolution of platinum

During the sulfuric acid treatment platinum impregnated to alumina substrate as fine particles was found to dissolve. This is not expected since platinum should be insoluble to sulfuric acid solution. The reason for this is not obvious. It may be that either some chemical change occurs during the operation of the catalyst in petroleum refinery or that the chloroplatium acid may be remained unreduced during the calcination for the manufacturing of catalyst. This assumption appears to be evidenced by the fact that about 1.17% chloride was identified by the chemical analysis of platinum catalysts.

Figure 7 shows the dissolution of platinum in sulfuric acid. The dissolution of platinum increases sharply with acid concentration. The dissolution of platinum is closely related to that of alumina substrate. The amounts of platinum dissolved were 320~520mg and 320~440mg for AR-405 and R-134, respectively. Meanwhile the platinum content in the catalyst was found to be 0.45% for AR-405 and 0.24% for R-134. Therefore, the dissolution of platinum in R-134 is much higher. No further platinum dissolution occurred at acid concentrations higher than 6.0M as was observed previously in the case of alumina substrate dissolution.

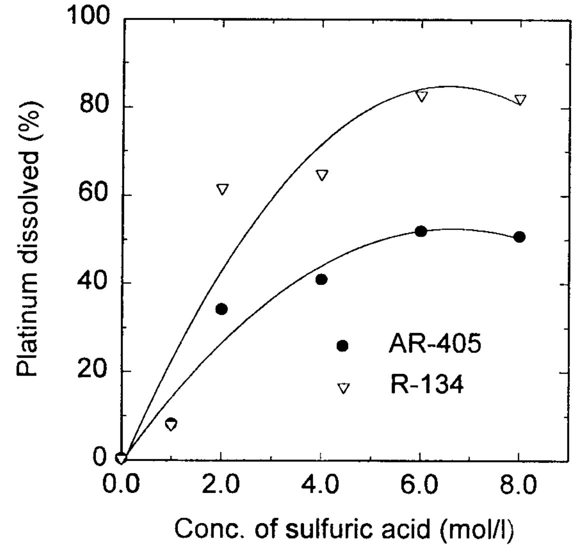

Figure 7. Effect of acid concentration on the dissolution of platinum from spent catalysts in sulfuric acid solution at 100°C for 4hrs. (Pulp density; 220g/l, particle size; 210 ~ 300μm)

Figure 8 shows the platinum dissolution with time. Significant amounts of dissolution occurred during 1 hour of dissolution. The dissolution curve was similar to that of alumina substrate. However, the dissolution behavior of platinum is expected to vary depending on the operation condition of catalyst or on the pretreatment history.

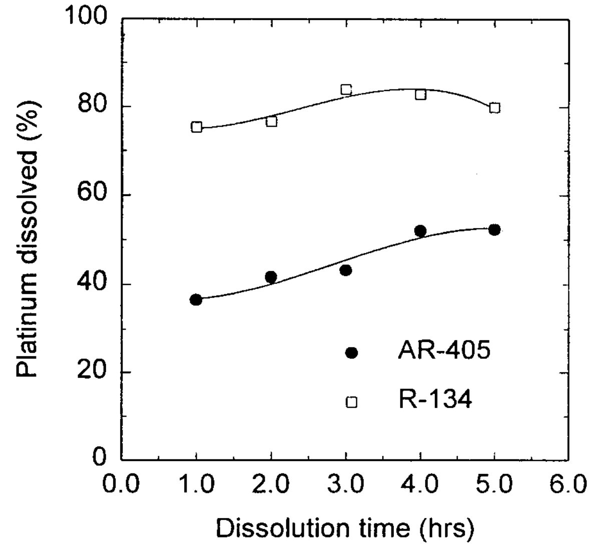

Figure 8. Effect of dissolution time on the dissolution of platinum from spent catalysts in 6.0M sulfuric acid solution at 100°C. (Pulp density; 220g/l, particle size; 210 ~ 300μm)

At the optimum dissolution conditions for substrate the dissolution of platinum from AR-405 and R-134 was 520 mg and 440 mg, respectively. The conditions were sulfuric acid concentration of 6.0M, temperature of 100℃, dissolution time of 2 – 4 hrs, pulp density 220g/l.

Cementation of platinum

Platinum dissolved during the dissolution of alumina substrate by sulfuric acid can be recovered by a cementation method using aluminum as a reductant. The reductive precipitation reaction of platinum can be written as follows:

$$H_2PtCl_6 + 2\,Al \Rightarrow 2\,AlCl_3 + H_2\uparrow + Pt\downarrow \qquad (1)$$

The cementation experiment was conducted by making a 1.0M sulfuric acid solution and adding 0.2 g/l of platinum. Figure 9 shows the effect of reaction temperature on the reductive precipitation of platinum. As can be seen in the Figure, the cementation reaction was rather tedious at 25℃. The reductive precipitation can be observed visually only after 5 minutes and the reduction at this point was about 8%. After 8 minutes the reaction was completed and virtually all of the platinum was reduced. Raising the temperature was found to enhance the reaction continuously. At temperatures over 40℃ the reaction finishes in 1-2 minutes. At temperatures over 60℃ the reductive precipitation of platinum terminates in 1 minute.

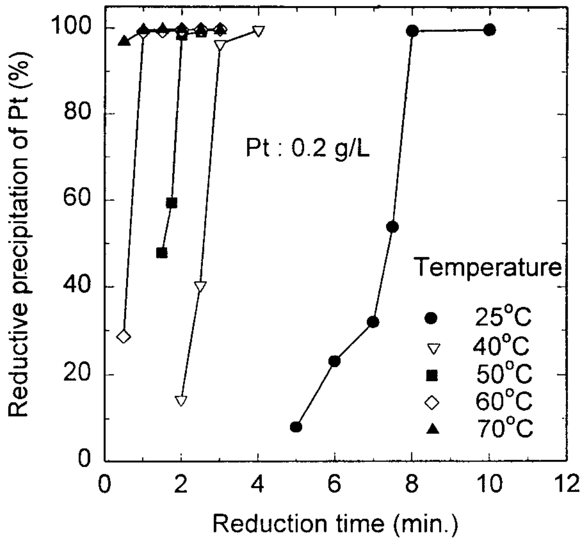

Figure 9. Effect of temperature and time on the reductive precipitation of platinum from 1.0M sulfuric acid solution. (Pt; 0.2g/l, Addition of Al powder; 5.0g/l)

The amount of platinum dissolved at the above listed optimization conditions are 514 mg which corresponds to concentration of 230 mg/l after adding water to prevent the precipitation of aluminum sulfate as described in experimental part. The stoichiometric amount of aluminum powder (W_{Al}) necessary for platinum reduction as in Equation 1 can be calculated as follows;

W_{Al} = (molecular weight of Al x weight of Pt in solution/ molecular weight of Pt) x 2

This gives the aluminum necessary for the reduction precipitation of 230mg/l platinum as 63.6 mg/l.

Figure 10 shows the results of platinum cementation based on the above calculations. The solution temperature was 60℃ and time was 10 minutes. About 92% of platinum was reduced with 0.5 g/l of aluminum. With the addition of 1.0g/l 95% was reduced. For a complete reduction, 17.5g/l of aluminum which corresponds to 27 equivalent is required.

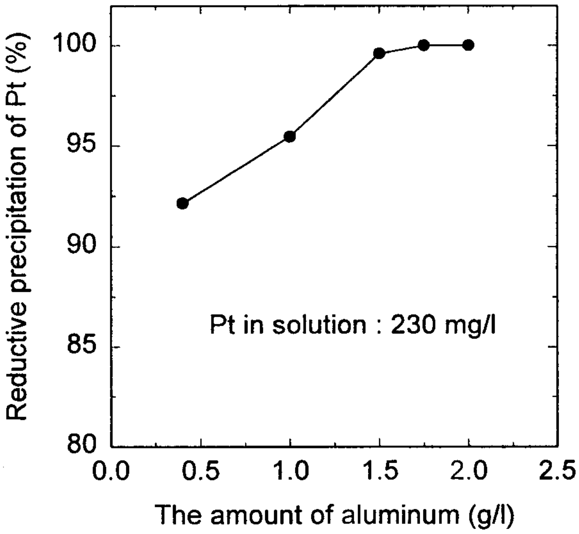

Figure 10. Effect of the amount of aluminum on reducing platinum from aluminum sulfate solution by cementation using aluminum powder as a reductant at 60℃ for 10 min

Conclusions

The recovery of platinum from spent catalysts in petroleum refineries was attempted by a total dissolution of catalyst substrate using sulfuric acid. The optimum dissolution conditions for the catalyst AR-405 and R-134 are 6.0M sulfuric acid, 100℃, dissolution time of 2 to 4 hours, pulp density of 220g/l.

At the optimum dissolution conditions for platinum catalysts the dissolution of platinum for AR-405 and R-134 was 520mg(52%) and 440mg(83%), respectively. Platinum was recovered from the solution after the sulfuric acid dissolution of the substrate using a cementation method. The cementation at temperatures over 40℃ provided successful recovery of platinum in short period. For a complete recovery of Pt 27 equivalent of aluminum was necessary.

Acknowledgment

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