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

Min-seuk Kim, Eun-young Kim, Jinki Jeong, Jae-chun Lee* and Wonbaek Kim

Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources,
Gwahang-no 92, Yuseong-gu, Daejeon 305-350, Korea

In this study, the recovery of platinum and palladium from petroleum catalysts has been elaborated using a method consisting mainly of dissolving alumina substrate in sulfuric acid thereby concentrating the precious metals in the residue. The effect of dissolution temperature and time, concentration of sulfuric acid, and pulp density on the dissolution of alumina substrate was investigated systematically. The optimum dissolution conditions for the platinum catalysts AR-405 and R-134 were: sulfuric acid 6.0 mol/L, dissolution temperature 100 °C, dissolution time 2–4 h, pulp density 220 g/L. The dissolution of R-134 catalyst the substrate consisting only of γ-Al₂O₃ phase was higher than that of AR-405 which contained the mixture of γ-Al₂O₃ or α-Al₂O₃. The optimum conditions for LD-265 are: sulfuric acid concentration 8.0 mol/L, dissolution temperature 100 °C, pulp density 220 g/L and time 18 h. It was found that platinum and palladium which was impregnated to alumina substrate as fine particles, also dissolved to some extent during sulfuric acid treatment. They could be recovered by a cementation process using aluminum powder. The complete recovery of Pt from AR-405 and R-134 catalysts was possible by the proposed method. Nevertheless, the method may not be applicable to LD-265 catalyst due to the time-consuming substrate dissolution process.

[Received June 23, 2010; Accepted July 15, 2010; Published August 25, 2010]

Keywords: platinum, palladium, catalysts, recovery, sulfuric acid

1. Introduction

Platinum and palladium have long been used as the reforming and hydrogenation catalysts in petroleum industries, respectively.1–4) The demand of the petroleum catalysts is expected to remain strong as many refineries and petrochemicals plants are under construction and more to be constructed in the near future. The petroleum catalysts containing platinum or palladium are discarded when its catalytic function deteriorates.2,5) In the catalysts, small amounts of platinum or palladium are contained in large volume of support materials, typically alumina.5)

Platinum and palladium in spent petroleum catalysts can be recovered through various hydrometallurgical6–13) or pyrometallurgical routes.10,14,15) The hydrometallurgical treatment is believed to be pertinent to smaller scale plants while the pyrometallurgical treatment is more suitable for larger plants. Basically two process options are mostly available for the recovery of platinum and palladium using the hydrometallurgical methods. In the first method, platinum or palladium is extracted directly from catalyst substrate using leachants. In this method, the catalyst is leached in aqua regia or in hydrochloric acid with oxidants such as nitric acid, sodium chlorate, sodium hypochlorite and chlorine gas.16) Meng and Han17) modified the conventional leaching method using halogen salts as an oxidant in autoclave. Nevertheless, in this method also the problem such as the loss of platinum and palladium due to the leachate entrapped in the micro pores of the catalyst substrate could not be avoided. The second method is based on total dissolution of alumina substrate thereby concentrating insoluble or sparingly soluble platinum and palladium into the residue. This method has the advantages such as recovery of aluminum sulfate as a byproduct and lesser consumption of the toxic leachant than in the first method.10)

In this study, recovery of platinum and palladium from the spent petroleum catalysts has been examined by dissolving the catalyst substrates in sulfuric acid thereby concentrating platinum and palladium in the leach residue. The effect of temperature and time, concentration of sulfuric acid, and pulp density on the dissolution of the substrate has also been investigated. Platinum and palladium dissolved in sulfuric acid to some extent could also be recovered in a cementation process using aluminum powder as a reducing agent.

2. Experimental

2.1 Materials

The samples of the spent catalysts used in this study were three commercial petroleum catalysts generated in refinery and petrochemical industries of Korea. They were the reforming catalysts (AR-405, Axens and R-134, UOP) and the hydrogenation catalyst (LD-265, Axens). The catalysts were spherical in shape with the diameter of 2 mm, 1.6 mm, and 2–4 mm for AR-405, R-134, and LD-265, respectively. The substrates of catalysts were identified as mostly alumina by X-ray diffractometer (XRD, D-max-2500PC, Rigaku Co.). All the catalyst samples were ground to pass through a sieve of 500 μm size and representative samples were made by coning and quartering method. The amounts of platinum and palladium were analyzed to be 0.45 mass% Pt, 0.24 mass% Pd, and 0.25 mass% Pt, and 0.25 mass% Pd in AR-405, R-134, and LD-265, respectively. Aluminum powder of 53–104 μm was used to reduce platinum contained in the solution after the sulfuric acid dissolution of substrates. All other reagents were of analytical grades.

*Corresponding author, E-mail: jlee@kigam.re.kr
2.2 Removal of oil from the spent catalysts
To begin with, the spent catalysts were calcined in order to remove the oil containing carbon and sulfur. Thermogravimetric analysis was carried out using the thermogravimetric analyzer (Du Pont Instruments 951) to arrive at the optimum calcination temperature. The spent catalysts calcined at the optimum temperature were examined for the phase analysis by X-ray diffractometer using Cu-Kα radiation.

2.3 Dissolution of catalyst substrate
The dissolution of catalyst substrates was carried out in a 2 L glass vessel with three necks, which was housed in a constant temperature bath. The temperature of the bath was controlled within ±5°C. The ground sample of the spent catalyst was calcined for 30 min at 600°C in an electrically heated muffle furnace. The catalyst after calcination was ground to less than 500 μm size and a known weight of the sample was dissolved in 0.5 L sulfuric acid solution of desired concentration which was preheated to a set temperature. The solution was agitated by a polytetrafluoroethylene coated stainless steel stirrer at 300 rpm to achieve effective leaching of alumina. About 10 mL slurry sample was taken out at regular intervals for chemical analysis during the experiment. After the termination of dissolution, the vessel was withdrawn from the bath, and distilled water was added to the reacted slurry to suppress the crystallization of aluminum sulfate. The slurry was then filtered and the solution was analyzed. The residue was dried fully in an electrical oven and analyzed to determine the amount of platinum and palladium.

2.4 Cementation of platinum and palladium
Platinum and palladium dissolved in the sulfuric acid solution were 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. After the dissolution of the catalyst substrate, 250 mL filtrate solution was transferred to the glass vessel and heated to a predetermined temperature. Aluminum powder was then added to the solution and was stirred at a low speed. During the experiment about 5 mL solution sample was taken out at a regular interval for chemical analysis. After completion of the cementation reaction, the solution was discharged and filtered to collect platinum and palladium particles. The filtrate was then analyzed to estimate the content of platinum and palladium and was also characterized with a scanning electron microscope (SEM, JSM-6400, Jeol Ltd.) and X-ray diffractometer. The amount of platinum, palladium, and aluminum in the solution was analyzed by an inductively coupled plasmaatomic emission spectrometry (ICP-AES, JY-38 plus, Jobin Yvon Ltd.). Platinum and palladium in the spent catalysts and in the dissolution residues were analyzed by a fire-assay method(18) followed by an ICP-AES.

3. Results and Discussion
3.1 Removal of oil from the spent catalysts
The spent catalysts generated in petroleum industries are contaminated by oil. The oil on the surface of spent catalysts may retard the dissolution of alumina substrate in sulfuric acid and contaminate the solution. Therefore, it should be removed prior to dissolution. To determine the optimum calcination temperature for effective oil removal, a thermogravimetric analysis was carried out. Figure 1 shows the TGA curves for the three spent catalysts. The weight loss was found to be higher for AR-405 and R-134 than that of LD-265 at all temperatures. The rapid weight loss of both catalysts between 400°C and 500°C appears to reflect the combustion of oil. Afterwards, the weight loss at temperatures between 500°C and 800°C became insignificant. The weight loss of LD-265 was comparatively small and was only about 1.8 mass% at 800°C. This suggests that LD-265 was less contaminated by oil than AR-405 and R-134.

Based on the results of TGA study, the effectiveness of calcination process was examined for the removal of oil by actually measuring the carbon and sulfur contents after calcination. Figure 2 shows the effect of temperature on the residual amount of carbon and sulfur in the spent petroleum catalyst (AR-405). (Calcination time; 30 min.)
change occurred in alumina phases during roasting at 600 °C.

The effect of particle size on the dissolution of spent catalysts was not obvious. When the particles were larger than 300 μm, AR-405 dissolved less because of the larger size of the particles. This can easily be explained by the reduction of surface area (130.3 m²/g for 300–420 μm size) or by the increase of insoluble α-Al₂O₃ phase in larger particles or a combination of both. However, when the particles were smaller than 210 μm, AR-405 dissolved less. In case of finer particles (size of 210 to less than 45 μm), the increased density of solution with substrate dissolution may cause undissolved particles with high surface area (140.1–150.1 m²/g) to remain suspended. The agitation of solution makes the suspended fine particles circulate along with the solution maintaining the diffusion layer.  

Table 1 Dissolution of AR-405, R-134, and LD-265 catalysts by 6.0 mol/L sulfuric acid solution at 100 °C for 4 h. (Pulp density: 220 g/L)

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>AR-405</th>
<th>R-134</th>
<th>LD-265</th>
</tr>
</thead>
<tbody>
<tr>
<td>-45</td>
<td>86.3</td>
<td>151.1</td>
<td>95.2</td>
</tr>
<tr>
<td>+45–106</td>
<td>89.2</td>
<td>148.3</td>
<td>95.5</td>
</tr>
<tr>
<td>+106–210</td>
<td>89.2</td>
<td>140.3</td>
<td>97.5</td>
</tr>
<tr>
<td>+210–300</td>
<td>92.3</td>
<td>137.4</td>
<td>98.3</td>
</tr>
<tr>
<td>+300–420</td>
<td>89.9</td>
<td>130.3</td>
<td>98.2</td>
</tr>
<tr>
<td>+420–500</td>
<td>83.5</td>
<td>120.7</td>
<td>98.1</td>
</tr>
</tbody>
</table>

completed after calcination at temperatures above 400 °C. However, in case of carbon, about 2.3 mass% still remained after calcination at 400 °C. It was removed completely only after the sample was calcined at temperatures over 600 °C. Therefore, the optimum calcination conditions for the removal of both carbon and sulfur were chosen to be 600 °C temperature and 30 min time. The spent catalysts after calcination at the optimum conditions were analyzed by XRD. Figure 3(a)–(c) shows the diffraction patterns of the as-received samples of AR-405(a), R-134(b), and LD-265(c) spent catalysts. As indexed on the patterns, the major phases in AR-405 and R-134 were identified as the mixture of γ-Al₂O₃ and α-Al₂O₃, and γ-Al₂O₃ respectively, whereas δ-Al₂O₃ was the main phase in LD-265 catalyst. No phase change occurred in alumina phases during roasting at 600 °C.

3.2 Dissolution of catalysts substrate

It is expected that platinum and palladium could be recovered as insoluble particles by dissolving alumina substrate of the spent catalysts in sulfuric acid. To start with, the catalysts were sieved to get six particle size fractions before dissolution. Each fraction of the catalyst was dissolved in 6.0 mol/L sulfuric acid for 4 h at 100 °C temperature and the pulp density of 220 g/L. Table 1 summarizes the results of dissolution experiment. It is seen that R-134 dissolves more than AR-405 for all particle sizes. The lower dissolution of AR-405 as compared to R-134 may be attributed to the presence of less soluble α-Al₂O₃ phase (Fig. 3(a)) in the former.

The effect of particle size on the dissolution of spent catalysts was not obvious. When the particles were larger than 300 μm, AR-405 dissolved less because of the larger size of the particles. This can easily be explained by the reduction of surface area (130.3 m²/g for 300–420 μm size) or by the increase of insoluble α-Al₂O₃ phase in larger particles or a combination of both. However, when the particles were smaller than 210 μm, AR-405 dissolved less. In case of finer particles (size of 210 to less than 45 μm), the increased density of solution with substrate dissolution may cause undissolved particles with high surface area (140.1–150.1 m²/g) to remain suspended. The agitation of solution makes the suspended fine particles circulate along with the solution maintaining the diffusion layer. The diffusion layer hinders the contact between the particles and the sulfuric acid thereby reducing the dissolution of the substrate (Table 1). The dissolution of LD-265 catalyst was however, found to be much less (37.5% max.) than that of R-134 and AR-405 for all particle sizes. In an effort to further understand the difference in the dissolution behavior of the three catalysts, their leach residues were examined by XRD to analyze the phases.

Figure 4 shows the X-ray diffraction patterns of the dissolution residues of AR-405 (a), R-134 (b), and LD-265 (c) catalysts. Before dissolution, AR-405 catalysts mainly contained a mixture of γ-Al₂O₃ and α-Al₂O₃ phases (Fig. 3(a)) whereas after dissolution only the peaks of α-Al₂O₃ remained along with platinum. This implies that γ-Al₂O₃ was completely dissolved out in sulfuric acid solution while leaving some amount of α-Al₂O₃ undissolved (Fig. 4(a)). It is interesting to find strong α-Al₂O₃ peaks from dissolution residue of R-134 which was not observed before dissolution on comparing Fig. 3(b) and Fig. 4(b). It is believed that the major phase viz. γ-Al₂O₃ of the catalyst (R-134) was dissolved completely leaving insoluble α-Al₂O₃ as the major phase of the residue which could have been present in insignificant amount in the untreated material or formed by transformation to α-Al₂O₃ in the reforming process of refinery. Similarly, the apparent platinum peaks in the dissolution residues of AR-405 (Fig. 4(a)) and R-134 (Fig. 4(b)) suggest that platinum was enriched in the
residues. In a similar manner, it is reasonable to assume that the low solubility of LD-265 catalysts is directly related to the insoluble nature of $\delta$-$\text{Al}_2\text{O}_3$ phase (Fig. 4(c)).

Figure 5 shows the effect of sulfuric acid concentration on the dissolution of alumina substrate of catalysts AR-405, R-134, and LD-265 after calcination. The calcine was leached for 4 h at 100°C temperature and the pulp density of 220 g/L. The dissolution behavior of the catalysts AR-405 and R-134 was very similar. With increase in acid concentration up to 6.0 mol/L, the dissolution of alumina increased sharply and there after no further dissolution was observed with increase in acid to 8.0 mol/L. At 6.0 mol/L sulfuric acid, the percent alumina dissolution was found to be 92% and 98% for AR-405 and R-134, respectively. At low acid concentrations of 2.0 and 3.0 mol/L, the dissolution of alumina was as low as 40%. As stated previously, higher solubility of alumina from R-134 than that of AR-405 may be correlated with the presence of the mixed phases viz. $\gamma$-$\text{Al}_2\text{O}_3$ and $\alpha$-$\text{Al}_2\text{O}_3$ in the sample and the lower dissolution of $\alpha$-$\text{Al}_2\text{O}_3$ in the process. Considering this, to dissolve alumina from AR-405 completely it may be inevitable to treat the calcine once more with concentrated sulfuric acid. The percent dissolution of LD-265 palladium catalyst was very low, being only 40 mass% in 8.0 mol/L sulfuric acid. As is evident from Fig. 5, the optimum sulfuric acid concentration for substrate dissolution of AR-405 and R-134 catalysts turned out to be 6.0 mol/L.

The optimum dissolution time was then determined using the conditions such as 6.0 mol/L sulfuric acid, 100°C temperature and 220 g/L pulp density and results are shown in Fig. 6. The dissolution of alumina substrate of AR-405 and R-134 catalysts increased with dissolution time up to 3 h after which it becomes insignificant. The percent dissolution of alumina was about 92% and 98% for AR-405 and R-134 catalysts, respectively after 4 h.

Results given in Fig. 7 show the effect of time on the dissolution of alumina substrate of calcined LD-265. The experiment was conducted in 8.0 mol/L sulfuric acid at 100°C temperature and a pulp density of 220 g/L. The dissolution of alumina increased with time. It may also be seen that the dissolution of LD 265 was much slower than that of AR-405 and R-134. About 90% alumina dissolution was achieved after 18 h under this condition. When the dissolution time was longer than 18 h the evaporation of solution made the viscosity of the slurry too high to continue further experiment. Even though the increase in the sulfuric acid concentration beyond 8.0 mol/L may enhance the dissolution, the possible precipitation of $\text{Al}_2(\text{SO}_4)_3$ poses another problem. Therefore, it can be concluded that the method is not practical in case of LD-265 catalyst due to the sluggish dissolution reaction and high acid requirements.

In order to further optimize the parameters for acid leaching of the spent catalysts (AR-405 and R-134), the effect of pulp density on the dissolution of substrate was evaluated at 100°C and a dissolution time of 4 h. It is seen from Fig. 8 that the dissolution of alumina at the pulp density of 180–220 g/L is almost constant (92%). When the pulp density was higher than 220 g/L, the dissolution decreased. At higher pulp density the formation of $\text{Al}_2(\text{SO}_4)_3$ with 6.0 mol/L sulfuric acid reaches saturation thereby reducing the dissolution rate.20
The optimum conditions for the leaching of alumina substrate of AR-405 and R-134 spent catalysts are: sulfuric acid-6.0 mol/L, dissolution temperature-100°C, time-2-4 h and pulp density-220 g/L. However, the optimum conditions for LD-265 are: sulfuric acid concentration-8.0 mol/L, dissolution temperature-100°C, pulp density-220 g/L and time-18 h.

3.3 Dissolution of platinum and palladium

It was found that platinum which was impregnated to alumina substrate as fine particles, also dissolved to some extent during sulfuric acid treatment. This was not expected because platinum is known as insoluble in sulfuric acid solution. Therefore, the reason for platinum solubilization was not very obvious. It is likely that either a certain chemical modification of platinum in the catalyst has occurred during the operation in petroleum refinery or chloro-platinic acid has remained unreduced partially during the calcination process of the catalyst manufacturing. The detection of chloride (1.17 mass%) from platinum catalyst appears to support this assumption at least partially and in this case the dissolution of platinum may take place by forming chloro complexes (PtCl\(_6^{2-}\)).

Figure 9 shows the effect of time on the dissolution of platinum from the calcined spent catalysts: AR-405 and R-134. Here, the dissolution of the calcined spent catalysts was carried out in 6.0 mol/L sulfuric acid at 100°C and 220 g/L pulp density. It is seen that a substantial amount of platinum is dissolved in 1 h time and the dissolution behavior is similar to that of alumina substrate as shown in Fig. 6. The amounts of platinum dissolution varied in the range 360 to 520 mg/L (37 to 52%) and 400 to 450 mg/L (75 to 86%) for AR-405 and R-134, respectively. At the optimum conditions previously chosen for the alumina substrate dissolution, the solubility of platinum from AR-405 and R-134 was found to be 520 mg/L and 440 mg/L, respectively. Above results show that the dissolution of platinum from R-134 is much higher than that from AR-405.

Figure 10 shows the dissolution behavior of palladium from the calcined LD-265 sample in 8.0 mol/L sulfuric acid at 100°C and pulp density of 220 g/L. The dissolution of palladium increased with time up to 12 h after which it no longer increased. The amount of palladium after dissolution of 18 h was about 250 mg/L. This corresponds to about 45 mass% of Pd in the LD-265 spent catalyst. The percent dissolution of alumina substrate of AR-405 and R-134 spent catalysts under the optimum dissolution conditions (sulfuric acid 6.0 mol/L, temperature 100°C, time 2-4 h, pulp density 220 g/L) was 92 and 98%, respectively while that of platinum was 52 and 83%, respectively. Platinum content in the residue of AR-405 and R-134 after substrate dissolution was measured to be 1.8 mass% and 0.81 mass%, respectively. Pd content in the residue of LD-265 spent catalysts dissolved at the optimum conditions was 2.71 mass%. The dissolution of platinum and palladium from the spent catalysts is expected to vary depending on the actual operation conditions of catalysts in the industries and on the pretreatment history. Platinum and palladium enriched in the dissolution residues can be completely recovered by treating the Pt/Pd-enriched resides with aqua regia.9)
3.4 Recovery of platinum and palladium

Platinum and palladium dissolved during the dissolution of alumina substrate by sulfuric acid can be recovered by a cementation method using aluminum as a reductant. In this study, Al powder was used as reductant to prevent the contamination of impurities in aluminum sulfate (Al\(_2\)(SO\(_4\))\(_3\)) solution obtained by sulfuric acid dissolution of alumina substrate.

The reductive precipitation reaction of platinum and palladium can be written as:

\[
3\text{PtCl}_6^{2-} + 4\text{Al} \rightarrow 3\text{Pt} + 4\text{Al}^{3+} + 18\text{Cl}^{-} \\
E^o = -0.932 \text{ V} 
\]

\[
3\text{Pd}^{2+} + 2\text{Al} \rightarrow 3\text{Pd} + 2\text{Al}^{3+} \\
E^o = -2.59 \text{ V} 
\]

Figure 11 shows the results of cementation experiment to recovery of platinum and palladium from the solution obtained by dissolving Pt spent catalyst (AR-405) and Pd spent catalyst (Ld-265) at pre-determined optimum conditions. The cementation was conducted for 10 min at 60°C. The amount of dissolved platinum and palladium for AR-405 and LD-265 was 514 and 250 mg/L, respectively. To prevent precipitation of aluminum sulfate in the saturated solution, distilled water was added. As a result, the final concentration of Pt and Pd for cementation experiment for AR-405 and LD-265 becomes 230 and 120 mg/L, respectively. It is seen that the amount Pt and Pd obtained by the reductive precipitation increased with Al addition. When 0.5 g/L Al was added, about 85% of Pt and 92% of Pd were reduced. The minimum amount of aluminum for the complete reduction of platinum and palladium was 3 g/L (71 equivalent of aluminum) and 2 g/L (71 equivalent of aluminum) for AR-405 and LD-265, respectively.

The surface morphology of the cemented platinum and palladium particles obtained by this process may be seen from the SEM images presented in Fig. 12. The platinum particles were mostly spherical in shape with almost uniform size in the range 0.2–0.3 μm. The picture also shows that a few platinum particles after cementation got agglomerated to 0.5 μm size. On the other hand, the SEM image of the cemented palladium particles shows mostly the well developed dendritic morphology of generally 2 × 4 μm size with a few particles of even smaller size (2 × 3 μm) while exhibiting good crystallinity. The XRD patterns of the cemented products produced from the spent catalysts are presented in Fig. 13. This clearly shows the well resolved peaks corresponding to the platinum and palladium phases in these metal powders which corroborated the SEM study. The grade of the cemented platinum and palladium powders was found to be 95.4 mass% and 98.2 mass%, respectively.
4. Conclusions

The recovery of platinum and palladium from spent catalysts of petroleum refineries was endeavored through total dissolution of catalyst substrate in sulfuric acid. The optimum dissolution conditions for the platinum catalysts AR-405 and R-134 were: sulfuric acid 6.0 mol/L, dissolution temperature 100°C, dissolution time 2~4 h, pulp density 220 g/L. The dissolution of R-134 catalyst the substrate consisting only of γ-Al<sub>2</sub>O<sub>3</sub> phase was higher than that of AR-405 which contained the mixture of γ-Al<sub>2</sub>O<sub>3</sub> or α-Al<sub>2</sub>O<sub>3</sub>. Resultantly, the percent dissolution of alumina substrate was about 92% in case of AR-405 and was 98% in case of R-134 at the optimum dissolution conditions. The optimum dissolution conditions for the palladium catalyst LD-265 were: sulfuric acid 8.0 mol/L, dissolution temperature 100°C, dissolution time 18 h, pulp density 220 g/L. The percent dissolution of alumina substrate was about 90% in this case.

During the sulfuric acid dissolution of spent catalyst, platinum and palladium was found to dissolve to some extent. The percent dissolution of Pt was 52% (520 mg/L) and 83% (440 mg/L) in case of AR-405 and R-134, respectively. It was 230 mg/L (45%) in case of LD-265 spent catalyst. Rapid recovery of platinum and palladium was possible by the cementation using aluminum powder at 60°C. For the complete recovery of platinum and palladium, 71 and 66 equivalents of aluminum were required for AR-405 and R-134, respectively. In conclusion, the complete recovery of Pt from AR-405 and R-134 catalysts was possible by the proposed method. Nevertheless, the method may not be applicable to LD-265 catalyst due to the time-consuming substrate dissolution process.

Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea. The authors are very grateful to Dr. B. D. Pandey for his valuable comments for the improvement of manuscript.

REFERENCES