Recovery of Platinum from Spent Removing Catalyst of Pt/Al₂O₃ by Ultrasonic-Assisted Acid Leaching

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Abstract. We report the role of ultrasonic procedure on the recovery of Platinum (Pt) from spent removing catalyst of Pt/Al₂O₃. In this study, the Pt was extracted by combining acid leaching of aqua regia and ultrasonic cleaning procedure. The frequency-dependent ultrasonic (low and high-frequency modes) showed a significant change in the Pt content on the Al₂O₃ ball. The morphological analysis showed that the higher frequency of the ultrasonic led the larger number of Pt recovery due to the higher agitation from the ultrasonic wave. This study gives a detail characteristic and modification of the Pt during the recovery, which is the key role on optimization of recovery of the Pt from spent removing the catalyst of Pt/Al₂O₃.

Keywords: Pt/Al₂O₃ catalyst, Pt recovery, ultrasonic-assisted acid leaching, aqua regia

1. Introduction
Platinum Group Metal (PGM), such as Platinum (Pt), is one of the types of Precious Metals (PM) [1]. Platinum has a high economic value and interesting type for various applications such as gold [2]. In contrast to gold, platinum is widely used in industrial fields [3]. One of the exciting applications in industrial fields is catalyst due to its characteristics such as high electrical conductivity, high corrosion, and oxidation resistance, high catalytic activity, and high melting point [4].

The energy requirement plays a role in supporting national development. One of the main energy sources is fuel oil. Every processing of crude oils into fuel oil and other products always uses the catalyst. One of the catalysts often used is Platinum-Alumina [5]. In the process of crude oil refining, the catalyst that has been used for a certain period of time must be recycled. Unfortunately, the remaining production catalyst tends to become one of the wastes of petroleum production. The residual catalyst production will be one of the petroleum production wastes [6]. The previous result study showed that Platinum-Alumina catalyst contains 10% Platinum and 75% Alumina [7]. This result becomes a great potential to separate platinum from the waste of the catalyst. There are several methods that can be used in the separation and purification of Platinum such as leaching, solvent extraction, and the others [5,8].
Considering the demand for precious metals in the world, nowadays platinum has increased because it is widely used in industrial and other fields. However, the amount of platinum in the earth’s crust is very limited [9]. Thus, the separation and purification of PGM from catalyst waste are essential to be studied. In this study, the separation of Pt /Al₂O₃ catalyst from petroleum production waste has been carried out using a combination method of aqua regia leaching with the assistance of ultrasonic waves using an ultrasonic cleaner. In this case, the wave frequency and the ultrasonic time when the leaching is varied to obtain the quantity of Alumina and Pt produced.

2. Methods
The acid leaching is a method used in this work to separate Platinum (Pt) with Pt/Al₂O₃ catalyst. First, the waste sample of Pt/Al₂O₃ catalyst was prepared in a beaker glass, and then aqua-regia solution was prepared using a mixture of HCl and nitric acid (HNO₃) in a ratio of 3: 1. The prepared catalyst waste was mixed in aqua regia solution in the one beaker glass. The leaching is carried out in an ultrasonic cleaner by maintaining the ultrasonic frequency for 10 and 20 min. Here, low and high frequency ultrasonic were used.

Furthermore, the samples were separated from the aqua-regia solution. The samples were dried using a hot plate at a temperature of 50 ºC. The samples were characterized by using X-Ray Fluorescence (XRF) PANalytical MiniPal 4 to determine the elements contained in the samples and Scanning Electron Microscopy (SEM) FEI-INSPECT S50 with 20,000 times magnification to observe the morphological change of the samples.

Figure 1. Schematic illustration of recovery of Pt from Pt /Al₂O₃ catalyst using ultrasonic-assisted acid leaching.
3. Results and Discussion

Table 1 presents the element content of Pt/Al₂O₃ by frequency level of ultrasonic waves and leaching time. The result confirms that the leached Pt/Al₂O₃ for low frequency shows the increase in the percentage of Al by increasing the leaching time. Moreover, the decrease in the percentage of Al is observed in the leached Pt/Al₂O₃ for 20 minutes by increasing the frequency level of the ultrasonic waves. Also, the result confirms that the leached Pt/Al₂O₃ for 20 minutes shows the increase in the percentage of Pt by increasing the frequency level of the ultrasonic waves. Moreover, the decrease of the percentage of Pt is observed in the leached Pt/Al₂O₃ for the low frequency with the longer leaching time. This result shows the same trend with a previous report [10], where the increase of leaching time promotes the reduction of Pt concentration from Al₂O₃ balls.

Table 1. The element contents of the sample with variation of ultrasonic frequency.

| Element | Parameter | Initial | Low frequency | 20 min |
|---------|-----------|---------|---------------|--------|
|         |           |         | 10 min | 15 min | Low frequency | High frequency |
| Al      |           | 59      | 81.1   | 82.6   | 84.2          | 83.4          |
| P       |           | 17      | 5.1    | 4.7    | 4.5           | 4.5           |
| Ca      |           | 11.1    | 3.10   | 2.89   | 2.45          | 2.66          |
| Cr      |           | 0.91    | 0.31   | 0.32   | 0.31          | 0.30          |
| Mn      |           | 0       | 0.10   | 0.11   | 0.11          | 0.12          |
| Fe      |           | 3.05    | 2.61   | 2.60   | 2.39          | 2.47          |
| Ni      |           | 0.95    | 0.45   | 0.38   | 0.38          | 0.46          |
| Cu      |           | 0.36    | 0.16   | 0.17   | 0.17          | 0.17          |
| Zn      |           | 0       | 0.06   | -      | -             | 0.05          |
| Yb      |           | 0.2     | 0.2    | 0.2    | 0.2           | 0.1           |
| Re      |           | 0       | 0.09   | -      | -             | 0.1           |
| Pt      |           | 5.8     | 6.76   | 5.90   | 5.02          | 5.40          |
| Th      |           | 0       | -      | 0.1    | 0.2           | 0.3           |
| Pr      |           | 1.5     | -      | -      | -             | -             |
| V       |           | 0.2     | -      | -      | -             | -             |

To provide further information of material reduction from Al₂O₃ surface, the morphology of Pt/Al₂O₃ samples were investigated by SEM. The morphologies of Pt/Al₂O₃ samples with the different frequency treatment which is low frequency and high frequency shown in Figure 2. The result shows that the higher frequency of the ultrasonic led the larger number of Pt recovery. In addition, the reduction of Pt from Al₂O₃ surface increase by the longer leaching time, which has a good agreement with XRF results. This is presumably due to the higher agitation from the ultrasonic wave. The higher agitation from the ultrasonic wave introduces a higher force, which dissociates Pt clusters from Al₂O₃ surface. The role of agitation in Pt extraction has been reported in a previous study [11], where agitation speed promoted the reduction of particle size but has no effect on the recovery of Pt. Here, our method has been successfully enhanced recovery of Pt by maintaining frequency mode and leaching time. We revealed that the combination of frequency mode and leaching time could enhance recovery of Pt from Pt/Al₂O₃ catalyst.
Figure 2. SEM images of initial Pt/Al₂O₃ (a) and leached Pt/Al₂O₃ for 10 min with low (b) and leached Pt/Al₂O₃ for 15 min with low (c) and leached Pt/Al₂O₃ for 20 min with low (d) and high frequency (e).

4. Conclusion
Recovery of Pt from Pt/Al₂O₃ catalyst has been successfully performed by ultrasonic-assisted acid leaching. We found that the frequency-dependent ultrasonic (low and high-frequency modes) played an important role in the reduction of Pt content on the Al₂O₃ balls. The content of Pt decreased with the increase of leaching time and the decrease of the frequency ultrasonic. The morphological analysis showed that the higher frequency of the ultrasonic led the higher number of Pt reduction from Al₂O₃ balls due to the higher agitation from the ultrasonic wave. Further study of recovery of Pt by applying wide range ultrasonic frequency with small frequency change is needed to investigate the optimum condition. Our study can be used as an optimization technique for recovery of Pt and further developed as a strategy to fulfill Pt demand.

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