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Recovery of Platinum From Spent Reforming Catalyst by Acid Leaching and Coprecipitation

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Abstract

Platinum content in a spent reforming catalyst were extracted by oxalic acid at temperatureup to 80°C.Pt extraction was increased by increasing the reaction time . The presence of coke covering did not effect on the spent catalyst. According to previous study, after the dissolution with oxalic acid, platinum in the leachate exist as ionic form such as $[PtCl_6]^{4-}$ and $[PtCl_4]^{2}$.Fe(II) solution were added to the leachate containing Pt to be a molar ratio of 1/10 [Pt(Ⅳ)/Fe(II)] .The solution was adjusted to the pH 6 with NaOH solution to precipitate iron hydroxide.Only about 20% of platinum was coprecipitated with Fe(II) hydroxide after 30min.These are different from the result of model experiment, and we discussed the problem and the solution toward practical recovery of Pt from the spent catalyst.

Keywords:

1. Introduction

Platinum is very important in various industries, such as automobile, chemical, jewelry. Johnson Matthey (2011) reported industrial demand for platinum is predicted to climb to 1.96 million ounces in 2011, a record high. Due to the sharp increase in its consumption, high cost and low material resource, the recovery of platinum from spend catalyst is needed. Thus, many researchershave studied the recovery of platinum from spend catalysts through pyrometallurgical and hydrometallugical processes (Pinheiro et al., 2004; Zanjani,et al., 2009).The latter process generally consumes less energy and are based on selective dissolution of base material or precious metals. Therefore, this study focuses onhydrometallugical process.

Platinum/alumina catalyst is widely used in petroleum refining industry. Reforming catalysts are typically made by impregnation of a porous γ-alumina with an aqueous solution of chloroplatinicacid.It is reported that a specific adsorption of platinum complex onto alumina surfaces is an electrostatic adsorption with outer-sphere interaction (Shelimov et al., 2000). Therefore the dissolution of some part of alumina surface can be an effectively way to separate platinum from the catalytic support.

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Several processes have been described in the literature for extraction platinum from spent reforming catalyst.

The selective dissolution of alumina, cobalt and platinum from Fischer-Tropsch catalysts, was investigated by using different lixiviants such as sodium hydroxide, nitric acid, hydrochloric acid, sulfuric acid and aqua regia. Almost all platinum were recovered by aqua regia leaching as chloroplatinic acid (Matjie et al., 2005). Another group studied the recovery of platinum from spent reforming catalysts by dissolution in the binary and ternary mixtures of the fluoride-containing media with hydrogen peroxide and nitric acid and hydrochloric acid. The result showed that hydrofluoric acid + hydrogen peroxide binary mixture dissolved 99.9% of alumina and 5-10% of platinum, while most platinum remained as solid residues and was finally recovered by aqua regia leaching (Pinheiro et al., 2004). Most research groups focused their works on strong and toxic reagents such as cyanide, hydrofluoric acid and aqua regia. Moreover, their processes consist of complicated multi-step processes. The objective of this study is to establish a practical, effective and environmental friendly platinum recovery process.

Aluminum dissolution by aqua regia is an acid-attack reaction, while the dissolution by oxalic acid is controlled by the surface complex formation of oxalic ligand (Parinayok., 2011).Oxalic acidis weakly acid solution.Oxalic acid is more environmentally friendly compared to strong acid such asaquaregia.Thus, this study is focusing on oxalic acid. The dissolution alumina from reforming catalyst was investigated by oxalic acid. The effect of temperature, coking and the solution pH on the Pt extraction rate and recovery was investigated. After the dissolution, platinum in the leachate exit$[PtCl_6]^{4-}$and$[PtCl_4]^{2-}$. In order to recover platinum,$[PtCl_6]^{4-}$and$[PtCl_4]^{2-}$have to be concentrated.

There are the method of coprecipitation of platinum(IV) complex ions with iron(II) hydroxide and their simultaneous reduction at pH6 and at the initial Pt(IV)/Fe(II) molar ratio of 1/200 (Parinatok et al., 2011).This method is simple, effective and environmental friendly. In order to investigated whether this method can be applied to recover platinum from spend reforming catalyst, Fe(II) is added to the solution dissolving spent catalyst by oxalic acid.

The objective of the study is to establish a practical, effective and environment friendly platinum recovery process.

2. Experiment

2.1. Reagants

The regents used in this study were of analytical reagent grade (Wako Pure Chemical).All the solution were prepared with ultra-pure water. The spent catalysts were supplied from a petroleum refinery. The spent catalysts areusuallycoked. In this study the coked catalyst and decoked burnt at 600℃ are used as sample. According to the previous study, the chemical composition of the catalyst was determined by XRF as shown inTable 1 (Parinayok., 2011).

Table 1.Chemical composition of spent reforming catalysts (Parinayok,2011)

Elements	Al_2O_3	Cl	Fe_2O_3	SO_3	SnO_2	Pt(ppm)
Weight (%)	95.05	0.935	1.47	0.092	0.496	2700

In this study, Pt concentration inspentcatalystisdetermined as2700ppm.The extracted Pt % is calculated using this value. Al concentration in spent catalyst is calculated as 50.34%. The extraction % of Al is estimated using this value.

2.2. Platinum Separation by dissolution of alumina by oxalic acid

Dissolution experiment of alumina in spent catalyst by oxalic acid (0.3 or 0.5M) were carried out at room temperature, 60℃and 80℃ with solid/liquid ratio of 1:100(1 gram of spent reforming catalyst and 100ml oxalic acid).Oxalic acid solutions were magnetically stirred were monitored constantly by pH meter (Horiba D-52) during the all experiments. The beginning of the dissolution (t=0) was defined as the time catalyst was added. After1,2,5,8,11and24hr, aliquot of the sample solution was collected and filtered with a 0.45μm membrane filter. The concentration of platinum was determined by flame AAS (Jarell Ash-835)and Al in the solution ICP-