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STUDIES ON PLATINUM RECOVERY FROM SOLUTIONS AFTER LEACHING OF SPENT CATALYSTS BY SOLVENT EXTRACTION

Beata POSPIECH

Department of Chemistry, Czestochowa University of Technology, 42-200 Czestochowa, Armii Krajowej 19, Poland, bak@wip.pcz.pl

Abstract. The results of studies on the separation of platinum(IV) ions by solvent extraction from aqueous solutions after leaching of spent catalysts have been reviewed. The following processes have been discussed: acid leaching of spent catalysts and solvent extraction of platinum(IV) ions by using organophosphorous acids, amines and oximes as the extractants. In hydrometallurgical leaching of spent automobile catalysts many reagents such as *aqua regia* solutions, aluminum chloride solutions with low concentrations of nitric acid as an oxidant, and sodium cyanide solutions were tested. After leaching, the metal ions in leach solutions have to be separated and purified by solvent extraction. Typical leach liquor contains economically valuable metal ions such as platinum(IV), palladium(II), rhodium(III) nickel(II) and manganese(II). The influence of several factors on the efficiency and selectivity of platinum(IV) ions extraction from leach solutions was shown. The optimum conditions of these processes were also reported on the ground of literature survey.

keywords: platinum, spent catalyst, leaching, solvent extraction

1. Introduction

Spent catalysts from automobile industry contain a number of important nonferrous metals such as platinum (Pt), palladium (Pd), nickel (Ni), iron (Fe) and manganese (Mn). Platinum exhibits excellent catalytic activity, therefore platinum is also used in petrochemical industry for the catalytic reforming process. Actually, an increasing demand for platinum is observed. Natural resources of platinum group metals (PGMs) are limited. On the other hand, the demand for these metals increases throughout due to their use as conductors in the electronic industries, automobile and industrial catalysts, jewellery, biomedical devices, dental and medical prosthesis, etc. (Swain et al. 2010; Lee et al. 2010; Angelidis et al. 1996). Spent catalysts are the potential source of important metals and it is also a source of hazardous, toxic chemical element such as Pb, Hg, Cd, V and their association. Therefore, the spent catalysts are hazardous industrial waste. Environmental laws concerning spent catalyst disposal have become increasingly more severe in recent years (Singh 2009; Marafi and Stanislaus 2003).

This paper reports leaching of spent catalysts and the solvent extraction separation of platinum ions from leach liquors. The aim of this paper is to show the possibility of selective platinum recovery by hydrometallurgical processes. In this paper, the platinum supply, demand, and recycling were shown.

2. Platinum production and demand

Initially, catalysts containing mainly nickel, cobalt, copper and iron had been assessed as autocatalysts. They were susceptible to poisons derived from the fuel. The eventually chosen catalysts were based on the highly active platinum group metals (Tweeg 1999). The PGM recovery from spent catalysts has been increased during the last 10 years. The increase of PGMs in industry is connected mainly with the still growing number of cars. Catalysts allow to reduce considerably three major impurities in the atmosphere, that is carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxide (NO) (Saternus and Fornalczyk 2009).

Table 1. Platinum supply, demand and recycling (2005 to 2010) (Matthey 2011)

Mega grams	2005	2006	2007	2008	2009	2010
Supply						
South Africa	159.1	164.7	157.7	140.4	144.2	144.2
Russia	27.7	28.6	28.5	25.1	24.4	25.7
North America	11.3	10.7	10.1	10.1	8.1	6.5
Zimbabwe	4.8	5.1	5.3	5.6	7.2	8.7
Others	3.6	3.3	3.7	3.6	3.6	3.4
Total Supply	206.5	212.4	205.3	184.8	187.4	188.5
Demand by Application						
Autocatalyst	118.1	121.5	128.9	113.7	68.0	97.2
Chemical	10.1	12.3	13.1	12.4	9.0	13.8
Electrical	11.2	11.2	7.9	7.1	5.9	6.8
Glass	11.2	12.6	14.6	9.8	0.3	10.7
Investment	0.5	-1.2	5.3	17.3	20.5	20.2
Jewellery	76.6	68.02	65.6	64.1	87.4	75.1
Medical & Biomedical	7.7	7.8	7.2	7.6	7.8	7.9
Petroleum	5.4	5.6	6.5	7.5	6.5	5.3
Other	7.0	7.4	8.2	9.0	5.9	7.9
Total Demand	247.8	245.4	257.3	248.5	211.3	245.1
Recycling						
Autocatalyst	-24.0	-26.8	-29.1	-35.1	-25.8	-33.7
Electrical	0.0	0.0	0.0	-0.2	-0.3	-0.3
Jewellery	-15,5	-17.2	-20.4	-21.6	-17.6	-23.2
Total Recycling	-39.5	-44.0	-49.5	-56.9	-43.7	-57.2

South Africa is the largest producer of platinum. About 80% of the world’s PGM come from the Bushveld complex in South Africa. Russia is the second largest supplier of platinum, accounting for roughly 10%. Platinum production capacity is estimated to grow to approximately 0.281 gigagram (Gg) in 2010 from about 0.192 Gg in 2002. Before 1999, supply and demand were largely balanced and prices were stable. The platinum demand has outgrown supply almost every year since 1999. As a consequence, the balance between supply and demand has become increasingly unsettled. Table 1 gives platinum supply, demand by application, and recycling since 2005 to 2010 (Matthey 2011).

Growing demand in spite of rapid price rise indicates very low demand elasticity. Actually, platinum remains heavily used for jewelry. Demand from that sector dropped from 40% to 32% in 2010, due to higher platinum prices (Yang 2009). Figure 1 shows the price of platinum since 2007 to 2011 (Matthey 2011).

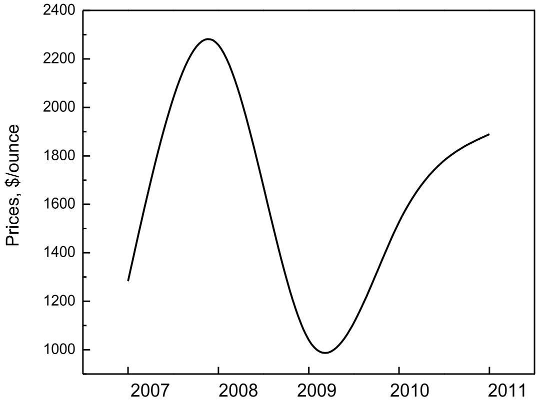

Fig.1. Platinum price in years 2007–2011 (Matthey 2011)

3. Main available processes of PGMs from spent catalysts

Nowadays the spent auto catalysts are reworked with the use of hydrometallurgical methods and high temperature treatment of the material. The aim of these technologies is the extraction of pure metal (Brumby et al. 2005; Fornalczyk and Saternus 2007, 2010). Recovery of valuable metals from spent catalyst requires application of the modern, technically advanced, economically valuable and environmentally friendly hydrometallurgical technology. The solvent extraction process enables recovery of valuable metals such as platinum from secondary or spent materials and protects the environment from hazardous and toxic compounds (Charewicz et al. 2001, Chmielewski et al. 2005). Hydrometallurgical processes may be classified in two major groups (Angelidis et al. 1996): a) feed digestion (leaching), b) solution purification with metals separation using solvent extraction (the noble metals are extracted from the substrate by oxidant acidic solution, leaving the bulk of the substrate unaffected). The conventional methods such as precipitation, cementation, ion-exchange and reductive exchange have been used to separation of platinum from liquid wastes. Solvent extraction (SX) is one of the most important processes in hydrometallurgy and is applied for the recovery of many valuable metals.

4. Acid leaching of spent catalysts

Many authors have investigated the recovery of valuable metals such as Pt from a spent catalyst by HNO_3/HCl mixture leaching. They studied also the kinetics of platinum extraction from spent reforming catalysts in *aqua regia* solutions under atmospheric pressure and at temperature up to 100ºC (Baghalha et al. 2009). HNO_3 and HCl in *aqua regia* undergo reactions (1) and (2):

$$HNO_3 + 3\,HCl \leftrightarrow NOCl + Cl_2 + 2H_2O \tag{1}$$

$$NOCl + H_2O \leftrightarrow HNO_2 + HCl\,. \tag{2}$$

The role of HNO_3 (NO_3^-) is to be the oxidant. The role of HCl is to provide the complexing agent (Cl^-). Dissolution of Pt from the catalyst is a redox and complexing reaction:

$$8H^+ + 8Cl^- + 2NO_3^- + Pt \rightarrow PtCl_6^{2-} + 4H_2O + 2NOCl\,. \tag{3}$$

By kinetic modeling using a power-law rate equation for Pt extraction, the reaction order was calculated to be 1.5 for Pt concentration in solid and 1.3 for the hydrogen ion molarity in the solution. The effect of temperature on Pt extraction kinetics was modeled using the Arrhenius equation. The activation energy for the Pt extraction equal to 72.1 kJ/mol. This value indicates that Pt extraction in *aqua regia* is controlled by the surface chemical reaction of Pt dissolution.

Jafarifar et al. (2005) studied also the leaching of the catalyst in freshly prepared *aqua regia*. The sample of the catalyst contained 0.20% Pt, 0.43% Re and other impurities such as iron oxide and large amount of aluminosilicate supporting carrier. This work has investigated two alternative methods for leaching. In the first method spent catalyst was refluxed with *aqua regia* at the liquid/solid ratio of 5 for 2.5 h. In the solution after leaching the concentration of Pt was approximately 30 g/dm^3. In the second method, microwave radiation was used at a power of 150 W with *aqua regia* at liquid/solid ratio of 2 for 5 min. The reactions were:

$$18\,HCl + 4\,HNO_3 + 3\,Pt \rightarrow 3H_2[PtCl_6] + 4\,NO + 8\,H_2O \tag{4}$$

$$7\,HNO_3 + 3\,Re \rightarrow 3\,HReO_4 + 7\,NO + 2\,H_2O\,. \tag{5}$$

After leaching the platinum was separated from rhenium and recovered as diammonium hexachloroplatinate with efficiency of 96.5% and 98.3%, respectively by these methods. The platinum precipitate was converted to platinum powder at 400ºC according to reaction:

$$(NH_4)_2PtCl_6 \rightarrow Pt + 2NH_4Cl + 2\,Cl_2\,. \tag{6}$$

Studies on platinum dissolution from a spent Pt-NiO/Al_2O_3 industrial catalyst were carried on by Angelidis and Skouraki (1996). Aluminium chloride solution with low concentrations of nitric acid as an oxidant instead of *aqua regia* was used to leach the spent catalyst. The Pt recovery increases as nitric acid concentration increases. It was confirmed that it does not affect platinum dissolution yield, but minimizes excess reagents consumption.

Pt recovery from a spent dehydrogenation catalyst using cyanide leaching was studied by Shams et al. (2004). The best Pt recovery results were obtained for pH values in range of 8-9 at 140-180ºC. Decoking of the coked catalysts is not necessary during high temperature cyanide leaching from catalysts. The level of platinum recovery obtained by cyanide leaching compared with others hydrometallurgical methods using, for example, *aqua regia* or hydrochloric acid, which has a recovery of more than 95%, looks too low for a cost effective platinum recovery procedure.

Aqua regia leaching was used to recovery of platinum from the dust of spent catalyst arising from nitric acid production plant (Barakad and Mahmoud 2004). *Aqua regia* was prepared by mixing concentrated hydrochloric acid (36%) and concentrated nitric acid (65%) by the volume ratio of 3 HCl to 1 HNO_3. The maximum recovery of 98% was attained with a liquid/solid ratio of 10 at 109ºC after 1.5 h. Solvent extraction with 10% trioctylamine (TOA) in kerosene was proposed for separation of iron(III) from Pt(IV) ions from solution containing 0.1 g/dm^3 Pt(IV) and Fe(III). Pt(IV) ions were extracted with TOA by an ion exchange mechanism. The effect of HCl concentration in aqueous solution was investigated. Solutions containing Pt(IV) and Fe(III) ions were prepared in the presence of different hydrochloric acid concentration (0.01 M – 7 M). Excellent separation of Pt(IV) from Fe(III) was obtained utilizing 0.01 M HCl. The separation factor (*D*) for platinum over iron reached a value of > 4000 in 0.01 M HCl. Platinum was separated from the leach liquor as diammonium hexachloroplatinate $(NH_4)_2PtCl_6$ by precipitation using ammonium chloride.

5. Solvent extraction of platinum

Many researcher have studied the extraction of metals from spent catalysts. The physical and chemical properties of PGMs are very similar, and thus, is difficult to separate these metals from aqueous solutions. Literature reports that Pt(II) forms mainly chloride complexes $PtCl_4^{2-}$ in aqueous chloride solutions. Pt(IV) forms in chloride solutions stable anionic complexes $PtCl_6^{2-}$. Table 2 shows the values of stability constants of chloride complexes for Pt(IV) at different ionic strengths (Stability, 1982). The platinum(IV) chloride complexes $PtCl_6^{2-}$ are stable at pH values below 1 to prevent hydrolysis and in the presence of excess chloride ions to prevent adsorption on the undissolved substrate (Angelidis et al., 1996). The values of stability constants of $PtCl_6^{2-}$ complexes at constant ionic strength (I =3.0 M) is equal to 2.76.

The separation of Pt and Pd from aqueous solutions is very difficult. The commercial organophosphorus compounds, amines, oximes, thio-phosphoric acids, phosphonic acids, thiophosphinic acid, thiourea have been proposed for the extraction in order to separate of Pt(IV) from other metal ions. Several publications have dealt with the application of organophosphorus acids and the derivatives of organophosphorus compounds in extraction of platinum from aqueous chloride solutions. The studies on application of tributyl phosphate (TBP) and Aliquat 336 in selective extraction of Pt(IV) from solution after leaching automobile catalyst containing Pd(II), Fe(III), Ni(II), Mn(II) and Cr(VI) by solvent extraction were reported by Lee et al. (2010). The extraction behaviour of Pt and other metal ions from aqueous phase (pH 3.2) as a function of Aliquat 336 concentration in kerosene was investigated. The efficiency of platinum(IV) ions extraction increased with the increase of extractant concentration. The best separation factor was obtained with 0.011 M Aliquat 336. This extractant can be used to separations of Pt(IV) and Pd(II) ions with efficiency 99.9 % and 99.8 %, respectively.

The separation of Pt(IV) and Pd(II) from associated metals like Fe(III), Cu(II), Ni(II), Zn(II), Al(III) from synthetic solutions containing 1 g/dm^3 of Pt(IV) and 1 g/dm^3 Pd(II) were investigated by solvent extraction with 0.5 vol.% LIX 841 (2-hydroxy-5-nonylacetophenone oxime in mixture with a high flash point hydrocarbon dilent) in kerosene. A 5 vol.% solution of Alamine 336 (tertiary amine of mixed tri-octy/decyl amine) in kerosene was used for co-extraction of Pt(IV) and Fe(III). The 0.5 M thiourea and dilute 0.1 M HCl solution were used for stripping of these metals. Purity of the Pd(II) and Pt(IV) strip solutions were 99.7% (Reddy et al. 2010).

Table 2. Values of stability constants of chloride complexes for Pt(IV) (Stability, 1982)

Medium and ions strength, M	β_1	β_2	β_3	β_4	β_5	β_6
0.1 $NaNO_3$	-	-	3.08	2.46	-	-
1.0 $NaNO_3$	-	-	3.15	2.55	-	-
3.0 $NaClO_4$	- 0.25	-	-	-	-	-
3.0 H_2SO_4	-	-	-	-	-	2.76

Separation of Pt(IV) and Pd(II) from chloride solution using Alamine 300 at concentrations from 0.001 to 0.01 M in the presence of 0.5 M HCl in aqueous phase was also studied (Swain et al. 2010). The extraction reaction can be explained with equations:

$$PtCl_6^{2-}{}_{aq.} + 2R_3NH^+Cl^-_{org.} \Leftrightarrow (R_3NH)_2(PtCl_6)_{org} + 2Cl^-{}_{aq} \quad (7)$$

$$PdCl_4^{2-} + 2R_3NH^+Cl^-_{org.} \Leftrightarrow (R_3NH)_2(PdCl_4)_{org} + 2Cl^-{}_{aq} \quad (8)$$

The loaded organic phase was stripped by NaSCN as $H_2Pt(Cl)_4(SCN)_2$. NaSCN was the best stripping agent for platinum and $(NH_2)_2Cs$ with HCl was the best stripping agent for palladium. Platinum of about 99.99% purity and 98% pure palladium can be separated from a mixed solution of Pt and Pd chloride by this process.

Liquid-liquid extraction of platinum, palladium, and rhodium with Cyanex 921 (tri-octyl phosphine oxide) from aqueous hydrochloric acid media has been studied by Mhaske and Dhadke (2001). A synthetic solution was similar in composition to that expected from the leaching of spent catalysts in 6.0 M HCl. The separation of these metal ions from their mixtures was carried out by taking advantage of their different extraction and stripping conditions with Cyanex 921. The effect of HCl concentration was investigated. It was observed that extraction of Pt(IV), Pd(II) and Rh(III) decreases at higher concentration of HCl due to the mass action effect of the chloride ions. Platinum metals were extracted also with different concentrations of Cyanex 921 from 1 to 100 mmol/dm^3 in toluene. The Cyanex 921 concentration for Pt(IV) was optimised at 6.0 M HCl and in the presence of 250 mmol/dm^3 tin(II) chloride. The stripping of Pt(IV) was observed at 4.0 to 6.0 M HNO_3. The proposed method is rapid for the separation of Pt, Pd and Rh with recovery efficiency about 99.8 %.

6. Conclusion

The recycling of catalysts is required for economic and environmental reasons. Platinum, along with some other platinum group metals (PGMs), is the main active component of industrial and automobile catalysts. Leaching and separation conditions for the recovery of platinum from spent catalyst have been evaluated. Leaching with *aqua regia* at temperatures above 70ºC is difficult in industrial practice because of the highly aggressive nature of this solution and decomposition of gaseous products. The study showed that the substitution of hydrochloric acid by aluminum chloride and the use of low nitric acid concentrations instead of *aqua regia* do not affect considerably platinum recovery from powdered industrial platinum based catalysts. Literature survey indicated that solvent extraction of platinum(IV) ions is simple, rapid and suitable for metal ions separation from solution after leaching of spent catalysts. The results of investigations indicate that the hydrometallurgical techniques for recovery of platinum are cost effective and environmentally friendly.

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