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Improved and selective platinum recovery from spent α-alumina supported catalysts using pretreated anionic ion exchange resin

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Abstract

Improved and selective recovery of platinum from a spent dehydrogenation platinum α-alumina supported catalyst using a strong basic ion exchange resin is reported. Platinum and other precious metal group (PMG) complexes are leached using concentrated hydrochloric acid along with about 0.20 vol.% nitric acid as an oxidizing agent from de-coked and crushed spent catalyst. Effects of hydrochloric acid concentration, time, and temperature in leaching stage are investigated. The strong basic anionic resin is treated by sodium hydroxide solution to replace chloride anion by hydroxyl group ion. The supernatant of the leaching process is passed through a fixed column of hydroxylated strong base anionic resin. The treated resin on which the platinum complex is adsorbed is dried and burned in an oxidizing atmosphere at 750–800 °C. The recovered gray metallic powder is mainly platinum. Results compared with those obtained from untreated anionic resin show that adsorption of platinum complexes onto the treated anionic resin is more selective and the yield of separation is considerably improved. The breakthrough curves of the pretreated anion exchanger and that of untreated exchange resin reveals that the capacity of the hyroxilated resin is decreased by about 14%. These breakthrough curves can be used for calculation of height of a practical exchange plate (HPEP) for design purposes.

Keywords: Platinum recovery; Ion exchange; Spent catalyst; Precious metals; Dehydrogenation catalyst; Strong basic resin (SBR); Breakthrough curve

1. Introduction

The environmental catalysis and its pertinent technologies have attracted much attention in the past decade. Strong demand for diesel vehicles, more stringent emissions legislation, and the rapid shift from palladium- to platinum-rich catalytic converter systems in gasoline powered vehicles has increased the demand for platinum consumption worldwide. Automotive CO and NO_x emission control catalysts used in catalytic converters are usually guaranteed for 40,000–80,000 km depending upon the quality of the product. During the course of use, the catalyst content of the converter is thermally shocked and disturbed by going through repeated low and high temperature cycles. This leads to gradual loss of activity of the catalyst because active surface area of the catalyst in the converter is diminished, and there would be a need for replacement of the used catalytic converter. Several million spent catalytic converters are disposed annually worldwide, each containing about 0.5–1 g of platinum and 1–2 g of all platinum group metals (PGMs) [1].

Demand for improved and/or new polymer, petrochemical, chemical, and refining catalysts is also increasing. In the fluid catalytic cracking (FCC), hydrodesulfurization (HDS), residue fluid catalytic cracking (RFCC), dehydrogenation, reforming, hydrogenation, and other catalytic processes in petroleum, petrochemical, pharmaceutical and chemical industries vast variety and voluminous amounts of catalysts are used.

In 1991 the catalyst demand in the USA was 190,000 metric tons and the produced catalyst waste was 12,000 metric tons/year. In the same year in Europe alone, 60,000 metric tons of spent FCC/RFCC catalyst, and 105,000 metric tons of the same catalyst waste were produced in Japan. The catalyst demand of FCC and RFCC catalyst has been in the order of 570,000 metric tons in 1998 [2]. In 1990s more than 130 new catalysts or improved catalysts were introduced within the USA for catalytic chemical, petroleum, biochemical, and environmental processes [3]. These statistics show that catalytic technology will con-

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tinue to be a key player in process industries for many years to come.

Heterogeneous catalysts contain appreciable amounts of precious metals. In petroleum and chemical industries the deactivated catalysts are replaced periodically by fresh catalysts. The cycle time of replacement is usually short because of catalyst decay induced by fouling, poisoning and/or thermal degradation/sintering. Deposition of coke, which is various forms of carbonaceous materials that vary widely from a graphitic well-ordered molecular structure to insoluble high molecular weight aromatic and/or polymeric compounds, is the most common catalyst fouling process. Poisoning occurs because of strong chemical bounds between a feed component, such as sulfur, or catalytic reaction products with active sites on the heterogeneous catalyst surface. Thermal degradation is provoked by high temperatures and/or thermal shocks due to heating and cooling in presence of a suitable physicochemical environment. Numerous workers have reviewed causes and methods of prevention or alleviation of different deactivation processes and we do not intend to overview them in this communication (e.g., see [4–9] among others).

The lifetime of all catalysts is limited and it could be in order of 1 min to several years, and even if the in situ regeneration of the catalyst is possible, eventually it must be replaced by fresh catalyst. Although regeneration and reuse of the spent catalysts are always preferred, however, if economics of the precious metals recovery from spent catalysts is not justifiable, then spent catalyst must be disposed. Trimm [10] has treated the criteria for disposal of spent catalysts. Platinum along with some other platinum group metals are the main active ingredients of these catalysts, and these precious metals will remain imbedded in the matrix of the support of the spent catalysts, which is usually some type of ceramic, such as alumina and the like. In addition to auto-catalysts, the petroleum, petrochemical, and chemical industries produce considerable amounts of the spent catalysts containing platinum and other precious and rare metals annually.

The spent catalyst is considered an environmentally hazardous waste because it commonly contains contaminants such as coke, vanadium, nickel to name but a few. Therefore, there exist serious environmental concerns with regard to spent catalysts.

The world's reserve of precious group metals was estimated to be about 78,000 metric tons in the year 2000 [11]. The platinum supply and demand statistics from 1997 to 2002 is listed in Table 1 [12]. Comparison of the total supply and demand figures in a time span of five consecutive years shows that with the exception of 1998 that there has been a week surplus/balance in supply and demand, the platinum demand always has exceeded the platinum supply. Also, from 1997 to 2002 the platinum demand has increased about 24%, and there has been a gradual growth in the share of the amount of the platinum recovery in auto-catalyst sector (from 7.2% in 1997 up to 9% in 2002). The most recent market analyses also show that demand for platinum in 2003 and 2004 increased by about 1% to 202,791 kg and 0.75% to 204,657 kg, respectively. Supply in 2003 and 2004 was less than the demand for about 4.5 and 1.2%, respectively [13,14].

Natural resources of platinum and platinum group metals are limited and because of their extensive use in catalysis, electronic devices, and space materials, biomedical devices, etc., their demand is increasing. Therefore, low rate of production of these metals due to their low concentration in related ores, and their high costs of production from naturally occurring supplies has made precious metals recovery from spent catalysts a viable and cost effective alternative of their preparation. Regarding the outlook of increasing demand versus limited global reserves of platinum group metals in general, and platinum in particular, mandates a revision of the consumption and utilization of these strategic metals. Furthermore, the potential environmental haz-

Table 1
Platinum supply and demand, 1997–2002 [12]

	Year					
	1997	1998	1999	2000	2001	2002
Supplier	Supply (kg)					
South Africa	115100	114500	121300	118200	127500	138100
Russia	2800	40400	16800	34200	40500	29600
North America	7500	8900	8400	8900	10900	1100
Others	3700	4200	5000	3300	3400	4200
Total	154300	16800	151500	164600	182300	182900
Application	Demand (kg)					
Autocatalyst:gross	56900	56000	50000	58800	78400	78400
Recovery	−11500	−12600	−13100	−14600	−16200	−17800
Chemical	7300	8700	10000	9200	9000	9300
Electrical	9500	9300	11500	14200	12000	12000
Glass	8200	6800	6200	7900	8900	8100
Bars and bullion coins for investment	7500	9800	5700	−1900	2500	2800
Jewelry	67200	75600	89600	88000	79300	86500
Petroleum	5300	3900	3600	3400	3900	4200
Other	9200	9500	10400	11700	13500	14600
Total	159600	167000	173900	176700	191300	198100