Journal of Colloid and Interface Science 364 (2011) 482–489

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Selective adsorption of Pt ions from chloride solutions obtained by leaching chlorinated spent automotive catalysts on ion exchange resin Diaion WA21J

Shaobo Shen [a,b,*], Liang Guishen [b], Tonglin Pan [b], JunZhang He [b], Zhanchen Guo [a]

[a] Key Laboratory of Ecological and Recycling Metallurgy, Ministry of Education of China, Beijing 100083, China
[b] Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:
Received 5 June 2011
Accepted 19 August 2011
Available online 26 August 2011

Keywords:
Spent automobile catalyst
Chloride solution
Pt ions
Ion exchange resin
Diaion WA21J
Adsorption

ABSTRACT

Thermodynamic and kinetics studies for adsorption of Pt ions complexes from the chloride solutions obtained by leaching chlorinated spent automotive catalysts on anionic exchange resin Diaion WA21J were carried out. It was found that only Si, Pt, Rh and Pd from the solution were selectively adsorbed on the resin Diaion WA21J more strongly. The adsorption equilibrium time for Pt ions was about 20 h. The isothermal adsorption of Pt ions was found to fit Langmuir, Freundlich and DKR models. The maximum monolayer adsorption capacities Q_{max} and X_m of Pt ions on the resin based on Langmuir and DKR model were 4.85, 5.36 and 5.69 mg/g as well as 5.01, 5.63 and 5.98 mg/g for temperatures 18 °C, 28 °C and 40 °C, respectively. The apparent adsorption energy E_{ad} based on DKR model were −11.79, −11.04 and −11.04 kJ/mol for the temperatures 18 °C, 28 °C and 40 °C, respectively. Ion exchange was the mechanism involved in the adsorption process. The adsorption of Pt ions on the resin underwent pseudo-first-order kinetic process, and the apparent adsorption activation energy $E_{a,1}$ was 12.6 kJ/mol. The intraparticle diffusion of Pt ions was a main rate-controlling step in most of time of adsorption process.

1. Introduction

The monolithic automotive catalysts are typically cordierite type honeycombs with platinum, palladium and rhodium. These catalysts are called 'three-way' catalysts, since they not only oxidize carbon monoxide and hydrocarbons but also reduce various nitrous oxides. The average loading of platinum group metals (PGMs) per catalytic converter has been 0.05 troy ounces of platinum, 0.02 troy ounces of palladium and 0.005 troy ounces of rhodium [1]. About 34% of total platinum, 55% of total palladium and 95% of total rhodium demand are now used for the production of automotive catalysts [2]. Each year, approximately 10 million automobiles are scrapped in the United States. Based on an equivalent number of converters, it is estimated that 500,000 troy ounces of platinum and 200,000 troy ounces of palladium and 50,000 troy ounces of rhodium will be wasted annually just in the United States. The annual world consumption of these metals for autocatalyst use could double or triple the above numbers [1]. Since these metals are in limited supply, a successful process for their recovery from catalytic converters will play an important part in their future availability and prices. For such PGM recovery processes to be cost-effective, well over 90% of these precious metals must be recovered [2].

In the 20 year than since 1975, although more than 568,000 kg of PGMs have been used in automotive catalysts in the USA alone, only 10% of them have been recovered [3]. Dissolution of palladium, platinum and rhodium presents special problems owing to their generally high ionization potential (the first ionization potential of Pd = 8.3 eV, Pt = 9.0 eV and Rh = 7.5 eV). This coupled with the complex variety of elements in the used catalytic converter makes it difficult to leach these metals from the catalyst and to isolate them from the pregnant solution. Less than 45% and 60% of Rh and Pt, respectively, from spent autocatalysts were recovered by dissolving the autocatalysts in aqua regia at 95 °C [2].

There are a range of hydrometallurgical or pyrometallurgical processes used in PGM recovery. The pyrometallurgical processes usually involved the melting of crushed autocatalyst and flux materials in a crucible containing a molten collector metal such as iron or copper at high temperatures, using a plasma torch [3]. The resulting molten slag is allowed to settle for a period of time while the PGM is recovered into the collector metal at the base of the crucible. After that, aqua regia is usually used to dissolve PGMs in the metal collector phase. The main problem for this method is that the settling time required for the separation of slag and metal collector is long. Moreover, operating temperatures for this method are in the range of 1800–2000 °C in order to molt cordierite support. The main problems related to pyrometallurgical method are that many steps are involved and the consumptions

* Corresponding author at: Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China. Fax: +86 10 82375042.
E-mail address: shaoboshen@metall.ustb.edu.cn (S. Shen).

0021-9797/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2011.08.043

are high in energy and materials and the dissolution of Si–Fe alloys containing PGMs is very difficult.

Dry chlorination methods for extracting PGMs from autocatalysts were developed in recent years [2,4–6]. In the methods, the powder of crushed spent autocatalyst containing PGMs was usually first pretreated with calcination and then chlorinated at 500–800 °C with chlorine in the presence of reducing agent such as carbon monoxide [2]. After that, a diluted hydrochloric acid was used to leach PGMs from the chlorinated powder of spent autocatalyst. Finally, a chloride solution containing Rh, Pd and Pt was obtained as filtrate by separating the leaching mixture by filtration. The extraction efficiencies of Pd, Pt and Rh of dry chlorination methods are usually higher than other methods, especially for Rh [4]. The cordierite materials used as the support of autocatalyst were usually almost not attacked by chlorine under the experimental conditions, which resulted in less consumption in chlorine.

Solvent extraction has been widely used for separation of PGMs from aqueous solutions [7,8]. The prerequisite for this process is that the concentration of each PGM in aqueous solution must be over several hundreds of ppm. However, the concentrations of Pt ions in the chloride solution obtained by leaching chlorinated spent automotive catalysts are usually less than 100 ppm. Therefore, a pre-concentration of Pd in the chloride solution was required. It was found by us that weakly basic anionic exchange resin Diaion WA21J (Mitsubishi Chemical Company) could selectively adsorb low concentrations of Pd, Pt and Rh simultaneously from the chloride solutions, and this phenomenon is first reported in this work. The adsorptions of Pd and Rh from the chloride solutions on this resin have been reported [9,10]. The adsorption of Pt ions on the resin is presented in this work. Besides Pd, Pt and Rh, the chloride solutions also contained Al, Mn, Fe, Mg, Si, Ni, Zn and Pb. The presence of these coexistent ions probably interfered in the adsorption of Pt ions on the resin Diaion WA21J. The HCl concentration in the chloride solution used in this work was about 10% (w/w).

2. Materials and methods

2.1. Chloride solution

The chloride solutions were obtained by leaching chlorinated PGMs containing in the powder of crushed spent autocatalyst according to the literatures [2,4]. The powder of crushed ceramic autocatalyst was first burnt in air at 800 °C and then chlorinated with Cl_2 + CO at 650 °C. The chlorinated powder was then leached with 10% (w/w) HCl. Finally, a chloride solution containing Pd, Rh and Pt was obtained as filtrate by separating the solid residue by filtration. Normally, Pt, Pd and Rh mainly existed in the chloride solutions in the forms of more stable Pt(II), Pd(II) and Rh(III) ions. However, the chloride solutions obtained from leaching chlorinated autocatalysts had higher oxidation–reduction potentials than usual chloride solutions; thus, lower concentrations of Pt(IV) and Pd(IV) than corresponding concentrations of Pt(II) and Pd(II), respectively, were also likely to be present in the chloride solutions. The molar concentration of 10% (w/w) HCl was 3.3 M. At this HCl concentration, Pt(II) existed in the form of Pt(II) complexes such as $PtCl_4^{2-}$ and $PtCl_3^-$, and Pt(IV) existed in the form of Pt(IV) complexes such as $PtCl_6^{2-}$ and $PtCl_5^-$. These Pt anions were suitable to be adsorbed by the anionic exchange resin Diaion WA21J used in the present study. So the chloride solutions thus obtained were used in the adsorption experiments of this work without any adjustment in solution pH before use. The concentrations of Pt from the chloride solution were analyzed by ICP-MS (Thermofisher XII, USA), and the concentrations of the other elements from the chloride solution were analyzed by ICP-AES (J.Y. ULTIMA, France). The concentrations of all main elements from the filtrate, which are denoted as initial concentrations of chloride solution, are listed in Table 1.

2.2. Ion exchange resin Diaion WA21J

The commercial ion exchange resin Diaion WA21J from Mitsubishi Chemical Company was used in this work. It is a weakly basic anionic exchanger with the functional group ($-CH_2N(CH_2CH_2NH)_nH$) and a polystyrene skeleton. Its properties are listed in the literature [9].

2.3. Methods used

The extracted chloride solution containing 10% HCl was used directly in the adsorption experiments without any adjustment in solution pH. Batch technique was selected to obtain equilibrium and kinetic data.

The amount of platinum (II) complexes adsorbed onto anion exchangers, Q_t, was calculated by following equation:

$$Q_t = \frac{(C_0V_0 - C_tV_t)}{W} \times 0.001 \quad (1)$$

where C_0 and C_t are the concentrations of Pt ions at initial and after time t in the aqueous phase (mg/L), respectively; V_0 is the initial volume of the chloride solution containing Pt ions (mL); V_t is the filtrate volume (mL); W is the weight of the original ion exchange resin (g).

The distribution coefficient of Pt ions, K_d (L solution/kg resin), is defined as the ratio of the Pt ions concentration in the solid resin (C_1) to that in the solution (C_2) and calculated by following equation:

$$K_d = \frac{C_1}{C_2} \times 10^3 \quad (2)$$

where C_1 is the Pt ions mass (in mg) adsorbed in 1 g of solid resin (mg/g) and C_2 is the Pt ions mass (mg) left in one liter of chloride solution after adsorption (mg/L).

2.3.1. Adsorption kinetics

Sixty milliliter of chloride solution of the same Pt ions concentration and 0.5000 g of resin Diaion WA21J was placed in each of 11 glass bottles of 200 mL with tight screw plastic lid. Then, the bottles were put in an incubator (BS-1E, China) agitated at

Table 1
Element concentrations (in ppm) in the chloride solution before and after adsorption (chloride solution = 300 mL; resin = 10.0000 g; 21 °C, 150 rpm; 40 h).

Ions	Pt	Al	Mn	Fe	Mg	Si	Ni
Initial conc.	29.5	999.8	736.3	560.0	391.9	312.9	377.0
Conc. after adsorption	2.5	992.9	743.5	556.5	400.3	281.7	385.0
Adsorption efficiency	91.61%	0.69%	−0.98%	0.63%	−2.14%	9.98%	−2.12%
	Ca	Zn	Cr	Pb	Cu	La	Ba
Initial conc.	221.3	242.0	53.9	42.8	20.4	13.1	2.3
Conc. after adsorption	227.4	199.5	55.2	19.2	20.5	13.3	2.3
Adsorption efficiency	−2.76%	17.58%	−2.41%	55.14%	−0.30%	−1.37%	0.00%