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Adsorption of Pd(II) complexes from chloride solutions obtained by leaching chlorinated spent automotive catalysts on ion exchange resin Diaion WA21J

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ABSTRACT

It was found that Rh, Pd and Pt contained in the spent ceramic automotive catalysts could be effectively extracted by dry chlorination with chlorine. In order to concentrate Pd(II) contained in the chloride solution obtained from the dry chlorination process, thermodynamic and kinetics studies for adsorption of Pd(II) complexes from the chloride solutions on anionic exchange resin Diaion WA21J were carried out. It was found that Pd, Pt, Rh, Al, Fe, Si, Zn and Pb from the chloride solution could be adsorbed on the resin. The isothermal adsorption of Pd(II) was found to fit Freundlich, Langmuir and Dubinin–Kaganer–Radushkevich models under the adsorption conditions. The adsorption of Pd(II) on the resin was favorable according to the values of $1/n$ and R_L from Freundlich and Langmuir adsorption isotherms, respectively. The maximum monolayer adsorption capacities Q_{max} based on Langmuir adsorption isotherms were 5.70, 4.84 and 4.05 mg/g and the corresponding value X_m based on Dubinin–Kaganer–Radushkevich were 5.55, 4.69 and 4.01 mg/g at temperatures 18 °C, 28 °C and 40 °C, respectively. The apparent adsorption energies (E_{ad}) based on Dubinin–Kaganer–Radushkevich isotherm were −15.43, −16.22 and −23.57 kJ/mol for the temperatures 18 °C, 28 °C and 40 °C, respectively. Chemical adsorption was a main mechanism involved in the adsorption process. Pd(II) adsorption on the resin could be accelerated by increasing the adsorption temperature. The adsorption of Pd(II) from the chloride solution on the resin underwent pseudo-first order kinetic process and the apparent adsorption activation energy E_a was 15.0 kJ/mol. The intra-particle diffusion was a main rate controlling step in the Pd(II) adsorption process under the adsorption conditions.

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 is 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 [1]. The annual world consumption of these metals for auto-catalyst 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 past 20 years 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 auto-catalysts were recovered by dissolving the auto-catalysts by using aqua-regia at 95 °C [2].

There is a range of hydrometallurgical or pyrometallurgical processes used in PGM recovery. The pyrometallurgical processes usually involved the melting of crushed auto-catalyst and flux materials in a crucible containing a molten collector metal such

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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 were in the range 1500–1650 °C in order to melt cordierite support. The main problems related to pyrometallurgical method are that many steps are involved and the consumptions are high in energy and materials.

Dry chlorination methods for extracting PGMs from auto-catalysts were developed in recent years [2,4–6]. In the methods, the powder of crushed spent auto-catalyst containing PGMs were usually first calcined 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 auto-catalyst. Finally, a chloride solution containing Rh, Pd and Pt was obtained as filtrate by separating solids residue by filtration. The extraction efficiencies of Pd, Pt and Rh of dry chlorination methods were usually higher than other methods, especially for Rh [4]. The cordierite material, which was the support of auto-catalyst, was almost not attacked by chlorine under the experimental conditions. This resulted in a 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 Pd in the chloride solution obtained by leaching chlorinated spent automotive catalysts were usually less than 100 ppm. Therefore, a pre-concentration of PGM in the chloride solution was required. Adsorbing PGM in the chloride solution with ionic exchange resins is a possible way to concentrate PGM in the chloride solution. If PGM in the chloride solution could be adsorbed efficiently, PGM would be enriched by eluting them from the adsorbed resin or transforming the adsorbed resin into ash by ashing. It was found by us in this work that weakly basic anionic exchange resin Diaion WA21J (Mitsubishi Chemical Company) could adsorb low concentrations of Pd, Pt and Rh simultaneously from the chloride solutions. Therefore, adsorption of Pd(II) complexes from the chloride solutions with resin Diaion WA21J was studied in this work. Besides Pd, Pt and Rh, the chloride solutions also contained Al, Mn, Fe, Mg, Si, Ni, Zn and Pb etc. The presence of these co-existent ions probably interfered in the adsorption of Pd(II) ions on the resin Diaion WA21J. The HCl concentration in the chloride solution used in this work was about 10% (w/w). So far nothing has been mentioned in the literature concerning adsorbing Pd(II) ions with ion exchange resins from such kind of chloride solutions. Thus thermodynamic and kinetics studies for adsorption of Pd(II) complexes from the chloride solutions on anionic exchange resin Diaion WA21J was performed in this work.

2. Materials and methods

2.1. Chloride solution

The chloride solutions were obtained by leaching the chlorinated powder of crushed spent auto-catalyst containing PGMs according to the literatures [2,4]. The powder of crushed ceramic auto-catalyst 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% HCl. Finally, a chloride solution containing Pd, Rh and Pt was obtained as filtrate by separating the solid residue by filtration. 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 Pd 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, 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 Table 2.

2.3. Methods used

The extracted chloride solution containing 10% HCl was used directly in the adsorption experiments without any adjustment in

Table 2
Properties of ion exchange resin Diaion WA21J.

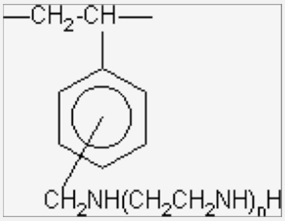
Properties	Quantitative value
Chemical structure	
Ion-exchange capacity (mEq/mL)	>2.0
Water content (%)	40–52
Particle size distribution	
>1180 μm	<5%
<300 μm	<1%
Effective size (mm)	>0.40
Maximum temperature (°C)	<100

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	Pd	Pt	Rh	Al	Mn	Fe	Mg	Si
Initial conc.	43.9	29.5	8.9	999.8	736.3	560.0	391.9	312.9
Conc. after adsorption	4.3	2.5	0.9	992.9	743.5	556.5	400.3	281.7
Adsorption efficiency	90.21%	91.53%	89.89%	0.69%	−0.98%	0.63%	−2.14%	9.98%
	Ca	Zn	Cr	Pb	Cu	La	Ba	Ni
Initial conc.	221.3	242.0	53.9	42.8	20.4	13.1	2.3	377.0
Conc. after adsorption	227.4	199.5	55.2	19.2	20.5	13.3	2.3	385.0
Adsorption efficiency	−2.76%	17.58%	−2.41%	55.14%	−0.49%	−1.53%	0.00%	−2.12%