



Recovery of palladium, platinum, rhodium and ruthenium from catalyst materials using microwave-assisted leaching and cloud point extraction



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ABSTRACT

The recovery of Pd, Pt, Rh and Ru from an automotive catalyst and from an alumina-supported Ru catalyst was studied. Microwave-assisted leaching of Pd, Pt, Rh and Ru was combined with cloud point extraction to obtain an environmentally friendly recycling method. A series of leaching experiments with HCl, HNO₃ and *aqua regia* at five different temperatures (90–210 °C) was performed in a microwave oven. *Aqua regia* and HCl were able to leach >90% of Pd, Pt, Rh and Ru at temperatures above 150 °C. At 120 °C slightly lower recoveries were observed, but also the leaching of the matrix elements was decreased. A cloud point extraction (CPE) method was applied to the samples obtained after HCl leaching at 120 °C. The method was first optimized to a suitable concentration level of Pd, Pt, Rh and Ru (>1 mg L⁻¹) by using a factorial design. Then, the appropriately diluted leach solutions (1 M HCl) were extracted and the recoveries of 91 ± 6% for Pd, 91 ± 5% for Pt, 85 ± 6% for Rh and 66 ± 11% for Ru were achieved. Simultaneously, the concentrations of the matrix elements (Al, Ce, Zr) were reduced by over 95%.

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1. Introduction

Palladium, platinum, rhodium and ruthenium, together with iridium and osmium, are called platinum group elements (PGEs). These elements have a wide variety of applications in automobile, chemical, electrical, and medical industries (Cowley, 2013). For example, Pd, Pt and Rh are most commonly used in catalytic converters of automobiles. PGEs, especially Pt, are also used in jewelry. The abundance of PGEs in the earth's crust is low and their primary sources are geographically concentrated in certain locations (e.g., South Africa, Russia, North America and Zimbabwe) (Mudd, 2012). For example, in year 2012 South Africa was the biggest supplier of Pt and Rh, whereas Russia was the biggest supplier of Pd (Cowley, 2013). High demand of PGEs during the last decades, together with environmental, social, economic and political aspects related to their production, have led to discussion on the availability of PGEs in the future (Glaister and Mudd, 2010; Gordon et al., 2006; Mudd, 2012; Yang, 2009).

Due to their various applications, PGEs are available in many secondary sources (e.g., in spent catalyst materials). High economic value of the PGEs, together with their high concentration levels in the secondary sources, when compared to the primary sources, makes the recovery of PGEs in spent materials feasible (Hagelüken, 2007, 2012; Jha et al., 2013). PGEs can be recovered from spent catalyst materials using pyrometallurgical and hydrometallurgical methods. In pyrometallurgical

processing, the catalyst materials are smelted in a high temperature (usually above 1500 °C) in the presence of suitable fluxes to form a liquid slag, from which the PGEs are collected to a collector metal (e.g., Cu or Fe) (Benson et al., 2000; Willner et al., 2014). In hydrometallurgical methods, the PGEs are leached from the catalyst materials using suitable reagents, for example acid or cyanide solutions (Jha et al., 2013). Hydrometallurgical methods can be applied for the PGE recovery either directly, after pyrometallurgical processing or after other pretreatment methods (e.g., thermal pretreatment or dissolution of base metals in sulfuric acid) (Jha et al., 2013). After initial leaching/dissolution of the PGEs, further refining can be used to separate the PGEs from base metals or from each other. For example, precipitation, extraction methods or ion-exchange can be applied for these purposes (Barakat and Mahmoud, 2004; Gupta and Singh, 2013; Jafarifar et al., 2005; Lee et al., 2010; Marinho et al., 2010; Mhaske and Dhadke, 2001; Nikoloski and Ang, 2014; Shams et al., 2004).

In industrial scale, pyrometallurgical methods are commonly used (Crundwell et al., 2011). These methods are effective, but slow and highly energy consuming. Hydrometallurgical methods, on the other hand, consume less energy, but often result to lower recovery efficiencies and tend to produce large amounts of waste solutions (Hagelüken, 2007; Rumpold and Antrekowitsch, 2012). Recently, many studies have targeted to develop environmentally friendly recovery methods for the PGEs. A lot of effort has been put to improve the leaching efficiency of these valuable metals in hydrometallurgical treatment of spent catalysts (Jimenez de Aberasturi et al., 2011; Kizilaslan et al., 2009; Nogueira et al., 2014; Rumpold and Antrekowitsch, 2012;

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Upadhyay et al., 2013). For example, *aqua regia* is known to leach platinum with good efficiency (Baghalha et al., 2009; Barakat and Mahmoud, 2004; Matjie et al., 2005). However, gaseous compounds are formed during the leaching process and some of these compounds (e.g., NO) are considered to be harmful to the environment (Jha et al., 2013; Kizilaslan et al., 2009). Since the formation of chloro complexes enhances the leaching of PGEs, there have been several attempts to increase the oxidizing power of HCl by other reagents than HNO₃ to obtain more environmentally friendly leaching solutions. For example, the addition of H₂O₂ (Kizilaslan et al., 2009; Rumpold and Antrekowitsch, 2012), H₂O₂ and H₂SO₄ (Jimenez de Aberasturi et al., 2011), cupric ions (Cu²⁺) (Nogueira et al., 2014) or electro-generated chlorine (Upadhyay et al., 2013) to HCl solutions have been studied.

According to the literature, the leaching time could be significantly reduced by using microwave-assisted heating, even though the mechanism of interaction of microwaves with hydrometallurgical systems is not well-known (Al-Harashshah and Kingman, 2004; Jafarifar et al., 2005). A fundamental study has been performed for sulfide minerals (Al-Harashshah et al., 2006). The outcome of the study was that the dissolution of metals is probably increased due to thermal effects, for example due to formation of a superheated layer close to the periphery of the reaction vessel and/or selective heating of the mineral with microwaves. When the PGEs are concerned, Jafarifar et al. (2005) achieved a substantially faster leaching of Pt from a spent catalyst with *aqua regia* using microwave heating (150 W, 5 min) when compared to conventional heating (2.5 h).

The aim of this work was to develop environmentally friendly methods for the recovery of Pd, Pt, Rh and Ru from catalyst materials. The two most important targets in this study were (1) good recoveries for Pd, Pt, Rh and Ru and (2) efficient separation of Pd, Pt, Rh and Ru from matrix elements. Consequently, microwave-assisted leaching was combined with cloud point extraction for the recovery of Pd, Pt, Rh and Ru. Al, Ce and Zr, commonly used in catalyst support materials, were used as model matrix elements when the separation of Pd, Pt, Rh and Ru was investigated.

Cloud point extraction (CPE) methods were found to be attractive separation methods for the leached PGEs, because they consume low amounts of relatively environmentally friendly reagents. The principles of CPE have been comprehensively reviewed e.g., by Bezerra et al. (2005). Shortly, in CPE neutral complexes of metal ions are formed with a complexing agent. These hydrophobic compounds are extracted from an aqueous solution to micelles formed by an added surfactant, and the small volume surfactant-rich phase is separated from the aqueous phase by heating the system above its cloud point temperature. CPE methods have previously been used in analytics with the aim to pre-concentrate very low amounts of PGEs for instrumental determinations (Meeravali and Jiang, 2008; Mesquita da Silva et al., 2001; Niemelä et al., 2009; Simitchiev et al., 2008). Thus, CPE could have potential in recovering PGEs from leach solutions and/or dilute waste solutions containing PGEs to ensure their complete recovery. According to our knowledge, the applicability of a CPE method for recycling of Pd, Pt, Rh and Ru was evaluated for the first time in this study.

2. Experimental

2.1. Materials

Two different catalyst materials were used in studying the recovery of Pd, Pt, Rh and Ru. The first material was a pulverized ($\varnothing < 74 \mu\text{m}$) recycled monolith automotive catalyst (NIST SRM 2557) with the certified values of $1131 \pm 11 \text{ mg kg}^{-1}$ for Pt, $233.2 \pm 1.9 \text{ mg kg}^{-1}$ for Pd and $135.1 \pm 1.9 \text{ mg kg}^{-1}$ for Rh ($\pm 99\%$ confidence interval). Indicative values for Al (20 wt.%), Ce (1.3 wt.%) and Zr (300 mg kg^{-1}), among other matrix elements, were also given in the certificate of this material (NIST Certificate of Analysis, 1993). The second material used was a virgin alumina-supported Ru catalyst (0.5% Ru on 3 mm alumina tablets,

Alfa Aesar). A sub-sample of this catalyst material was taken and ground to a homogeneous powder ($\varnothing < 300 \mu\text{m}$) prior to the experiments.

2.2. Procedure

2.2.1. Reagents

Ultrapure water, purified with a Millipore Gradient (Millipore Corp.) water purification system, was used throughout this study. Concentrated HCl (37–38%, J.T. Baker, Baker Analyzed) and HNO₃ (65%, J.T. Baker, Baker Analyzed) were used in the leaching experiments. Triton X-100 (C₁₄H₂₂O(C₂H₄O)_n ($n = 9–10$), Sigma-Aldrich, laboratory grade), 2-mercaptobenzothiazole (2-MBT, C₇H₅NS₂, Merck, p.a.), NH₄OH (25%, J.T. Baker, Baker Analyzed) and SnCl₂·2H₂O (VWR BDH Prolabo, AnalaR NORMAPUR) were used in the cloud point extraction experiments. Appropriate dilutions of a mixed standard solution, containing 50 mg L^{-1} of Pd, Pt, Rh and Ru in 1 M HCl, were used in the optimization of the CPE method and in the quantification of the PGEs. The standard solution was prepared using the following commercial stock solutions (1000 mg L^{-1}): Pd in 0.5 M HNO₃ (Merck), Pt in 2 M HCl (Merck), Rh in 5% HCl (Fluka Analytical) and Ru in 10% HCl (VWR BDH Prolabo). Appropriate dilutions of the following 1000 mg L^{-1} commercial stock solutions were used in the quantification of the matrix elements (Al, Ce and Zr): Al in H₂O (Titrisol, Merck), Ce in 5% HNO₃ (TraceCERT, Fluka) and Zr in 10% H₂SO₄ (in-house standard solution, ZrOCl₂·8H₂O (Merck, p.a.)).

2.2.2. Microwave-assisted leaching

Catalyst samples (0.1–1.6 g) were weighed into 100-mL microwave digestion vessels (XP-1500 plus high pressure Teflon® TFM vessels, CEM Corp.) and 8 mL of either HCl, HNO₃ or *aqua regia* (6 mL HCl + 2 mL HNO₃) was added. The vessels were closed and the catalyst materials were leached in a microwave oven (CEM MARS 5X, CEM Corp.) with a two-stage program. In the first stage, the solutions were heated to the target temperature (90, 120, 150, 180 or 210 °C) at 15 min, and in the second stage, the temperature was held at the target value for 10 min. The solutions were allowed to cool down close to the room temperature prior to opening of the vessels. Temperature profiles for microwave-assisted leaching at 120 and 210 °C are presented in Fig. 1(A).

2.2.3. High pressure asher leaching

For comparison, catalyst samples (0.1 g) were carefully weighed into high pressure asher's 90-mL quartz vessels and 8 mL of HCl was added. The vessels were closed, set in the heating block and inserted into the pressure vessel of the high pressure asher (HPA-S, Anton Paar GmbH). The system was pressurized with nitrogen to 100 bar and a two-stage digestion program was run. In the first stage, the solutions were heated to 120 °C at 15 min, and in the second stage, the temperature was held at 120 °C for 10 min. Before depressurizing and opening steps the system was allowed to cool down close to the room temperature. Temperature profile for the high pressure asher leaching at 120 °C is presented in Fig. 1(B).

2.2.4. Cloud point extraction

The cloud point extraction method applied in this study had previously been used in analytical determinations of Pd, Pt and Rh (Niemelä et al., 2009; Simitchiev et al., 2008). The solutions obtained after microwave-assisted leaching of the samples with HCl were diluted to 50 mL with water and the undissolved residue was allowed to settle down. To perform the CPE, 10 mL aliquots of these solutions were taken into 50-mL centrifuge tubes and diluted to 20 mL with water to obtain solutions with approx. 1 M HCl concentration. Two mL of Triton X-100 (10%, m/v, in UP-H₂O) and 1 mL of 2-MBT (1%, m/v, in 0.5 M NH₄OH) were added and the samples were left to stand for 15 min before the addition of 1.5 mL of SnCl₂ (10%, m/v, in 6 M HCl). The centrifuge tubes were placed in a water bath (Julabo TW8, Julabo GmbH) and the

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