Recycling of Palladium

Subjects: Others

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Platinum group metals (PGMs), including palladium, play a pivotal role in various industries due to their unique properties. Palladium is frequently employed in technologies aimed at environmental preservation, such as catalytic converters that reduce harmful emissions from vehicles, and in the production of clean energy, notably in the hydrogen evolution process. Regrettably, the production of this vital metal for our environment is predominantly centered in two countries—Russia and South Africa. This centralization has led to palladium being classified as a critical raw material, emphasizing the importance of establishing a secure and sustainable supply chain, as well as employing the most efficient methods for processing materials containing palladium.

palladium recycling hydrometallurgical pyrometallurgical automotive catalysts

1. Introduction

Platinum group metals (PGMs), a family of rare and valuable elements, play a pivotal role in a multitude of industries due to their exceptional properties. The collective demand for these metals is steadily escalating, driven by their indispensable contribution to modern technologies and emerging sustainable solutions. Among the PGMs, palladium stands as a prominent member, revered for its diverse range of applications that span across electronics [1], pharmaceuticals [2], and jewelry [3]. However, its most notable applications lie in its role in environmental preservation, such as catalytic converters that mitigate harmful emissions in the automotive sector [4] and as a catalyst for renewable energy production [5]. The extensive release of greenhouse gases leads to global warming, posing a significant challenge for environmental sustainability, a major concern for mankind today [6]. The imperative for a transition to green energy highlights the growing interest in clean, renewable energy from both industrial and academic standpoints [7]. Palladium and its alloys are recognized for their excellence in hydrogen production membranes, owing to their superior selectivity and permeation rate in comparison to other inorganic metallic membranes [8]. The role of palladium in preserving the environment is not limited to hydrogen production, as the researchers have succeeded in developing a Pd-catalyzed reaction for the efficient synthesis of fine chemicals under environmentally friendly conditions [9]. As industries continue to harness the unique attributes of palladium, the imperative to ensure its sustainable supply and utilization becomes increasingly pressing. However, securing a steady supply is not a simple task, as worldwide palladium production is nearly monopolized by Russia and South Africa [10]. Other countries that have a major contribution to the worldwide palladium production are Canada, Zimbabwe, and the United States.

The recovery of PGMs from primary ores faces challenges, such as low PGMs content, high energy consumption, and limited concentration recovery. Conversely, secondary resources boast significantly higher PGM concentrations, which makes them highly preferable for exploitation, while simultaneously curbing the need for extensive ore mining. Secondary sources demand significantly less energy consumption, attain superior recovery yields, and bear a diminished environmental footprint [11]. For years, the pyro/hydrometallurgical process has been dominating PGMs' recycling [12], although purely hydrometallurgical methods are constantly researched.

2. Pyro/Hydrometallurgical Process

The process of recovering palladium through pyro/hydrometallurgical methods is widely used for treating spent automotive catalysts [13]. The fundamental principle involves smelting the ground material with the addition of flux. However, due to the differing composition compared to ore concentrates, metal collectors are introduced to aid in the extraction of palladium into the metallic phase [14]. This results in the creation of a PGM-enriched alloy [15]. Subsequent refining steps enable the production of metallic palladium.

Volatilization processes present an alternative to traditional smelting, in which PGMs are volatilized by selective chlorination and condensed in a cooler zone [15]. While this process provides high selectivity by exploiting the differences in vapor pressures of metal chlorides, it also leads to severe furnace corrosion. Another downside of this process is the presence of CO and Cl_2 gases, which pose environmental risks.

Another notable example of pyrometallurgical operation used to recover palladium from spent catalysts is plasma sintering. It is a process that involves the use of a plasma furnace and plasma-torch assembly to sinter material, leading to in situ reduction of its oxidized PGM components [16]. This method is great for reforming spent catalysts but is not suitable for industrial-scale production of palladium.

3. Hydrometallurgical Process

The hydrometallurgical recycling of spent automotive catalysts is presently a vigorously researched topic, as indicated by the SciVal tool (https://www.scival.com/trends/summary?uri=Topic/14964) provided by Elsevier. During the period from 2018 to 2022, Topic T.14964 (Catalyst; Hydrochloric Acid; Catalytic Converters), which falls under Topic Cluster TC.656 (Solvent Extraction; Leaching; Liquid Membranes), achieved a Scholarly Output of 341 publications and a Prominence Percentile of 94.313 [17]. The reasons for the substantial interest in catalyst recycling through the hydrometallurgical route are twofold: the achievement of high recovery rates of PGMs [18] and the potential for producing Pt/Pd-rich solutions that can serve as valuable end products [19]. These solutions find application as precursors in the synthesis of various materials, primarily other catalysts, thereby eliminating the need to reduce these elements into metals during recycling.

Following the initial preparations, primarily milling, the first step in recycling spent catalysts involves leaching. Considering that platinum and palladium fall under the category of noble metals, their leaching in HCl poses difficulties. This process hinges on the modification of the oxidation potential, commonly by prior roasting [20], or by leaching in the presence of H_2O_2, which enables the creation of stable aqua chloro-complexes, thus facilitating their dissolution [21]. In the case of palladium, the following reaction, shown in Equation (1), occurs:

$$Pd + H_2O_2 + 4HCl \rightarrow \left[PdCl_4\right]^{2-} + 2H^+ + 2H_2O \tag{1}$$

It is important to note that the dominance of various forms of palladium complexes can vary depending on the concentration of chloride ions. In some cases, these complexes may replace H_2O as ligands instead of chloride ions [22].

The leaching process of palladium from spent automotive catalysts is a non-catalytic, heterogeneous solid/liquid reaction. The reaction rate, v, can be expressed as the moles reacted or formed per unit surface area over time [23][24], as presented in Equation (2):

$$v = -\frac{1}{bA_{Pd}}\left(\frac{dN_{Pd}}{dt}\right) \tag{2}$$

where b is a stoichiometric coefficient, A_{Pd} is the reacting area of the palladium grain surface, N_{Pd} is the number of moles of the solid palladium phase, and t is the time.

By reformulating Equation (2) using the conversion X, which is a measure of the extent to which a reaction has occurred ($N_{Pd} = N_{Pd0}\,(1 - X)$), we obtain the expression given in Equation (3):

$$v = \frac{N_{Pd0}}{bA_{Pd}}\left(\frac{d\mathrm{X}}{dt}\right) = \frac{\rho_{Pd}V_{Pd0}}{bA_{Pd}}\left(\frac{d\mathrm{X}}{dt}\right) \tag{3}$$

where ρ_{Pd} is the molar density of palladium and V_{Pd0} is the initial volume of the solid palladium particles.

The reaction rate is further influenced by the concentrations, C, of the reactants. This relationship is governed by the rate constant (k), in accordance with the law of mass action [25], as expressed in Equation (4):

$$v = kC_{Pd}^{n}C_{A1}^{a1}C_{A2}^{a2} \tag{4}$$

where $A1$ and $A2$ are the leaching reagents (e.g., HCl and H_2O_2), and parameters n, $a1$, and $a2$ are the reaction orders specific to each reagent. As palladium is present in a solid state, C_{Pd} does not refer to concentration in a solution but rather to the moles of palladium per unit volume in a solid.

If a safe excess of leaching reagents is present in a system, and we assume that their concentrations remain constant throughout the reaction, then only solid palladium particles will be expressed as a function of the conversion ($C_{Pd} = C_{Pd0}$ (1 − X)). With this assumption, resulting in Equation (5):

$$\left(\frac{dX}{dt}\right) = \frac{bA_{Pd}C_{Pd0}^{n}C_{A1}^{a1}C_{A2}^{a2}}{\rho_{Pd}V_{Pd0}}k(1-X)^{n} = k_{R}(1-X)^{n} \tag{5}$$

where k_R is an apparent rate constant that encompasses all parameters remaining constant over time.

The final step involves integrating Equation (5), resulting in a conclusive model that can be employed to describe experimental data obtained during palladium leaching, as expressed in Equation (6):

$$\frac{1}{n-1}\left[\left(1-X\right)^{1-n}-1\right] = k_{R}t, \quad n \neq 1 \tag{6}$$

It is important to note that other, more general models may also be applicable to the process of leaching palladium, such as the Shrinking Core Model [26][27] or the Shrinking Particle Model [28]. However, both of these models assume that solid particles have a predetermined, uniform geometry, which is not always the case.

Several noteworthy novel methods for leaching palladium from spent catalysts have emerged, including ultrasonic-enhanced ozonation in HCl [26], leaching using ionic liquids [29], and microwave-assisted leaching [30], all of which resulted in remarkably high palladium leaching rates. Bioleaching enables recovery of PGMs as well; however, due to poor efficiency, it is not applicable to wide-scale industrial operations [29].

The next step after the leaching process typically involves solvent extraction, which allows for the separation of palladium from other metals using ionic liquids [30]. A solvent extraction setup typically comprises two phases that do not mix: an organic phase, which holds the extractant, diluent, and potentially a modifier, and an aqueous phase, which contains the metals targeted for separation. Considerable research effort is being directed toward enhancing metal separation in a range of strategies, such as the formulation of novel extractants, the utilization of extractant blends, modification of diluents, incorporation of modifiers, and more [31]. Metal ions contained within organic phase can then be extracted back to aqueous phase by stripping [32].

Finally, the last step is producing metallic palladium, which is a relatively easy task. It can be achieved by variety of methods, such as precipitation [20], cementation [33], adsorption [13], and others.

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