

Review

A Review of Recovery of Palladium from the Spent Automobile Catalysts

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Abstract: The spent automobile catalysts (SAC) is the major secondary source of palladium and the production of SAC is increasing rapidly over years. The price of palladium keeps rising over the years, which demonstrates its preciousness and urgent industrial demand. Recovering palladium from the spent automobile catalysts benefits a lot from economic and environmental protection aspects. This review aims to provide some new considerations of recovering palladium from the spent automotive catalysts by summarizing and discussing both hydrometallurgical and pyrometallurgical methods. The processes of pretreatment, leaching/extraction, and separation/recovery of palladium from the spent catalysts are introduced, and related reaction mechanisms and process flows are given, especially detailed for hydrometallurgical methods. Hydrometallurgical methods such as chloride leaching with oxidants possess a high selectivity of palladium and low consumption of energy, and are cost-effective and flexible for different volume feeds compared with pyrometallurgical methods. The recovery ratios of palladium and other platinum-group metals should be the focus of competition since their prices have been rapidly increased over the years, and hence more efficient extractants with high selectivity of palladium even in the complexed leachate should be proposed in the future.

Keywords: spent automobile catalysts; palladium recovery; hydrometallurgy; platinum group metals; palladium leaching



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1. Introduction

Platinum group metals (PGMs) such as platinum (Pt), palladium (Pd), and rhodium (Rh) are widely used in automobile, chemical engineering, petroleum, electrical, and electronic industries due to their distinct physical and chemical properties: catalytic activity, electric conductivity, and corrosion resistance [1–5]. The increasing demand for PGMs causes a high consumption rate of high-grade PGMs ore. The increasing depletion of high-grade PGMs ore forces people to turn to the exploitation of low-grade ore. However, the cost of exploring PGMs from low-grade ore is much expensive and brings critical environmental issues [6,7]. Although researchers have studied fungible materials to partially replace the use of PGMs in products such as automobile catalysts, the net consumption of PGMs is still high due to the increasing demand for engines in automobiles. About 65% of palladium, 45% of platinum, and 84% of rhodium are used every year for catalytic converters to decrease harmful emissions from engines [3,5,8,9]. With the enforcement of stricter emission regulations, the rapid development of the new-energy automobile industry will lead to a larger drain on PGMs supply. Meanwhile, PGMs in spent catalysts from numbers of outdated vehicles need to be properly recycled.

The raw ore of PGMs is limited in the Earth's crust and is mainly distributed in South Africa and Russia. Table 1 shows the total production of palladium and platinum from

mines worldwide, which decreased in 2020 compared to 2019 [10]. Production of PGMs in South Africa, the world's leading supplier of PGMs ore, decreased by 11% compared with that of 2019 owing to temporary lockdowns related to the COVID-19 pandemic as well as increased labor costs, increased costs of electricity, an unreliable supply of electricity, and challenges related to deep-level mining [11].

Table 1. World mine production and reserve of PGMs in the year 2019 and 2020 (Kgs).

Country	Production of Palladium		Production of Platinum		PGM Reserve (2020)
	2019	2020	2019	2020	
South Africa	80,700	70,000	133,000	120,000	63,000,000
Russia	98,000	91,000	24,000	21,000	3,900,000
Zimbabwe	11,400	12,000	13,500	14,000	1,200,000
United States	14,300	14,000	4150	4000	900,000
Canada	20,000	20,000	7800	7800	310,000
Other Countries	2420	2600	3730	3800	NA
World total	227,000	210,000	186,000	170,000	69,000,000

Compared with natural raw ore, the spent automobile catalysts indeed own several advantages. Palladium, like gold, is an international precious metal spot and trading species. Palladium surpassed the price of platinum for the first time in the year 2018, and then exceeded the price of gold in the year 2019 [12]. Spot palladium hit a record high at 481.7 RMB/g or 2397.2 USD/oz in 2021 in the past ten years, while platinum was only 219.6 RMB/g or 1092.7 USD/oz and gold hovered at 361.4 RMB/g or 1798.6 USD/oz. As for rhodium, its price reached as high as 3631.8 RMB/g or 18074.0 USD/oz, which was ten times of that of gold. [12]. The price of palladium keeps increasing at a fast speed at present as shown in Figure 1. Palladium could partially substitute platinum in catalytic converters for most gasoline-fueled vehicles, and industries favored using palladium over platinum in catalytic converters because the price of palladium was lower than platinum decades ago, which resulted in amounts of palladium remaining in the automobile exhaust catalysts [13–16].

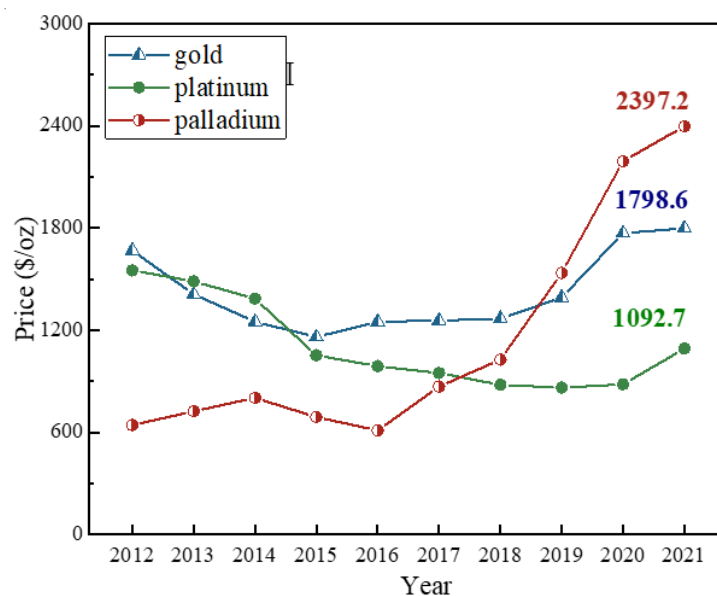


Figure 1. The price tendency of gold, platinum, and palladium from the year 2012 to 2021.

The great consumption of palladium products leads to a great amount of waste and scrap containing palladium. Recovery of palladium from the spent automobile catalysts

has become an important source of palladium supply [17]. Compared with natural raw ore, the spent automobile catalysts indeed possess several advantages for palladium recovery. For one thing, the concentration of palladium in raw ore is pretty low, in the range of 2~10 ppm (g/t), and is generally associated with base metal sulfide minerals. While the spent catalysts are up to $1\sim9 \times 10^3$ ppm, that is, thousands of times higher than that of raw ore. The recovery ratios of palladium from the spent automobile catalysts with hydrometallurgical technologies, e.g., traditional cyanide leaching or chloride leaching, could reach over 95%, and through pyrometallurgy, such as iron capture, the recovery efficiency of palladium is as high as 99% [2]. For another, the next is the carrier of spent catalysts commonly is Al_2O_3 , activated carbon, and cordierite, which indicates no need to deal with ferromagnetic silicate gangue like raw material. Besides, the spent catalysts are easy to collect due to their concentrated usage, and some industries have formed completed recovery processes [5,18]. The advantages listed above make the spent catalysts relatively easy to process, together with low capital investment, low environmental pollution, and high economic benefits. Recovery of palladium from the spent catalysts is beneficial from the perspectives of economic efficiency and environmental protection.

Over the last few years, the recovery of PGMs from waste materials has raised great interest. Several researchers indeed have reviewed the development of recovery of PGMs from the secondary materials [3,4,19–21], while these works are not detailed in palladium recovery from the spent automobile catalysts. The objective of this paper is to summarize and review the development of recovering palladium from the spent automobile catalysts. The processing flow, related mechanism, economic benefits, and environmental impacts of those proposed methods are compared and discussed. Besides, physical–chemical properties of palladium and a brief introduction of deactivation reasons for the spent automobile catalysts are given to help get a better understanding of palladium recovery.

2. Palladium and Its Spent Catalysts

2.1. Palladium and Its Components

Palladium is in group VIII of the fifth cycle in the periodic table, with a density of 12.02 g/cm^3 and a high melting point (1550°C), and is a good conductor of heat and electricity. Besides, the catalytic performance also plays an important role in the wide application of palladium. The detailed physical properties of palladium are shown in Table 2 [22].

Table 2. The detailed physical properties of palladium.

Physical Properties	Palladium	Physical Properties	Palladium
Atomic number	46	Melting point/ $^\circ\text{C}$	1550
The electron configuration	$4d^{10}$	Heat of fusion/(kJ/mol)	16.9
Atomic weight	106.4	Boiling point/ $^\circ\text{C}$	2900
Atomic volume/ 10^{-6} m^3	8.859	Sublimation heat kJ/mol	372
Atomic radius/nm	0.137	Density (20°C)/(g/ cm^3)	12.02
Electronegativity	2.1	Specific heat (25°C)/(kJ/mol)	26.0
The crystal structure	Face-centered cubic	Thermal conductivity ($10\sim100^\circ\text{C}$)	0.18
Lattice constant/ $\text{\AA}$	0.38895	Resistivity (0°C)/(mu $\Omega \text{ cm}$)	9.93
The first ionization potential/mV	8.33	Temperature coefficient of Resistance ($0\sim100^\circ\text{C}$)	0.0038

Palladium generally presents plus divalent, trivalent, and tetravalent in compounds. A purple oxide film is formed on the surface of palladium when heated in the air. Palladium compounds such as palladium dichloride can be used for refining, electroplating, and production of pure palladium sponges through thermal decomposition. Palladium monoxide and palladium hydroxide are major raw materials for palladium catalysts. The schematic diagram for the connections between palladium and its compounds is shown in Figure 2 [22].

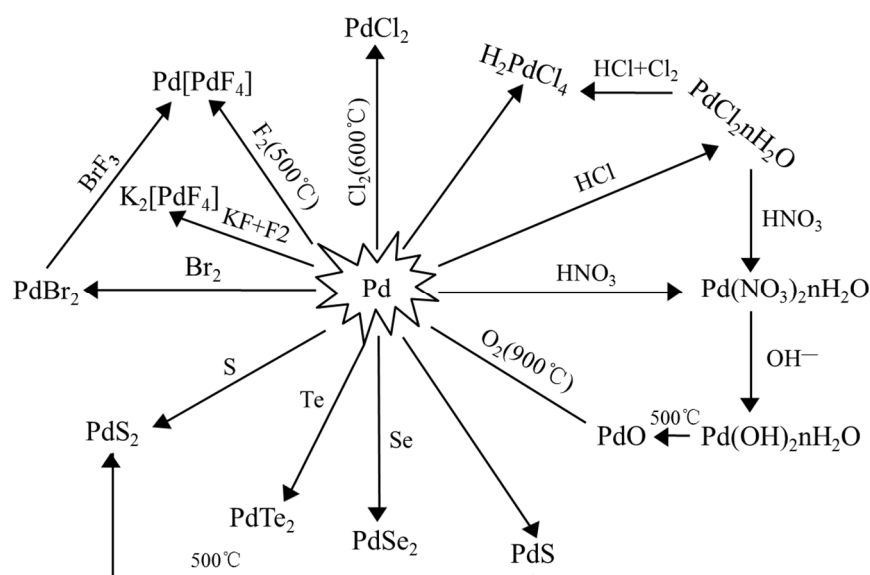


Figure 2. The schematic diagram for the connections between palladium and its compounds.

Palladium, located behind hydrogen in the order table of the redox potential of chemical elements, has the most active chemical properties among PGMs. Palladium is hard to oxidize due to its superior chemical stability. Once converted into cationic, palladium turns into a strong oxidizer with a high oxidation potential. Palladium is easily soluble in concentrated nitric acid, hydrogen iodide, aqua regia, and hot potassium cyanide. In addition, hot sulfuric acid, calcium chloride, and molten sodium sulfate also can erode palladium. The corrosion performances of palladium in different corrosive mediums are listed in Table 3 [22].

Table 3. The corrosion performance of palladium.

Corrosive Medium	Temperature/°C	Erosion Resistance	Corrosive Medium	Temperature/°C	Erosion Resistance
Concentrated H ₂ SO ₄	25	A	NaOH(aq)	25	A
	100	B	KOH(aq)	25	A
	250	C	NH ₄ OH	25	A
HNO ₃ (0.1 mol/L)	25	A	HgCl ₂ (aq)	100	A
	25	B	KCN(aq)	25	C
	25	C		100	D
(1 mol/L)	25	C	CaCl ₂ (aq)	100	C
(2 mol/L)	25	D	FeCl ₃ (aq)	25	C
(70%)	25	A		100	D
HCl (36%)	25	B	NaClO ₃ (aq)	25	C
(36%)	100	D	Molten caustic soda	-	B
HBr (density 1.7)	25	D	Molten potash	-	B
HI (density 1.6)	25	A	Molten sodium peroxide	-	D
HClO ₄ (density 1.6)	100	A	Molten sodium sulfate	-	C
H ₃ PO ₄	25	D	Molten sodium carbonate	-	B
Aqua regia	25	A	Molten sodium nitrate	-	C
CH ₃ COOH	100				

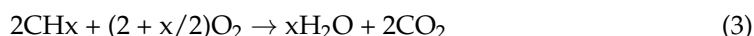
A—no corrosion; B—slight corrosion; C—corrosion; D—serious corrosion.

2.2. The Spent Automobile Catalysts and Their Deactivation Reasons

The catalytic converter in automobile primarily aims to convert CO, unburned CH_x, and NO_x in the off-gas to non-toxic CO₂, H₂O, and N₂ [23,24]. Automobile exhaust catalysts in catalytic converters have to deal with CO, CH_x, and NO_x simultaneously, so they are also called three-way catalysts (TWC) [25]. TWC here possesses good thermal stability, high catalytic sensitivity, and mechanical strength. Redox reactions of vehicle exhaust should be

finished in the catalytic converter within a very short time. Reactions (1)–(8) show the main reactions happening during catalytic transformation, and palladium-containing catalysts mainly convert CO and NO_x into harmless gases.

Oxidation reactions for CO and unburned CH_x:



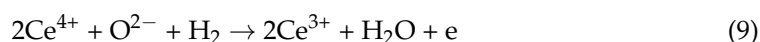
Reduction reactions for NO:



Other reactions:



The automobile catalysts consist of four parts: carrier, active alumina coating, auxiliary, and PGMs' active component. The carrier has a strong thermal stability to withstand the exhaust temperature of the automobile engine at 200~1000 °C, a high mechanical strength to endure the long-term friction of highly corrosive airflow, and a small heat capacity to reach relatively high work temperature (400~500 °C) quickly. Besides, materials of carriers should be convenient to obtain and do no harm to the catalyst [26,27]. The honeycomb ceramic carrier, composed of cordierite (2MgO·2Al₂O₃·5SiO₂), a kind of silicate mineral, is generally coated with a high specific surface for PGMs' active component to load onto to improve the comprehensive catalytic performance. Coating of γ-Al₂O₃ possesses a high specific surface area, together with good thermal stability and mechanical strength, is the most widely applied coating for TWCs. Auxiliary of TWCs, composed of oxides of rare earth, alkaline earth, and transition metals, can be categorized into two types: one is the electronic reagent, via changing the electronic structure, surface property, and adsorption capacity of reactants to reduce the activation energy of catalytic reaction and improve the reaction speed; the other is structural auxiliary, which is used to reinforce the structural stability of catalysts to improve their service life. Take CeO₂-based composite as an example; transformation of Ce³⁺/Ce⁴⁺ (Reaction (9)) plays a vital role in the purification process by adjusting the concentration of oxygen [28]. Additives of metallic oxides such as Zr, Ba, Co, Mn, Cu, Fe, etc. can also improve the catalytic performance.



The key metals in TWCs are PGMs such as platinum (Pt), palladium (Pd), or rhodium (Rh) as the active components. Noble metals can not only enhance the redox performance but also improve the oxygen storage capacity of support (including carrier, coating, and auxiliary). The support can improve the catalytic performance and endurance ability through dispersing PGMs and inhibiting PGMs sintering under high temperatures.

Interaction of platinum, palladium, and rhodium with CeO₂-based composite oxides (CeO₂, CeZrO_x, CeZrM, M = rare earth) can help to restrain the sintering of PGMs and improve TWCs catalytic performance [29–31]. The mechanism of metal–support interaction could be described as follows: the formation of PM–O and PM–O–M (M = rare earth) bonds decrease the total energy of the whole catalyst system and stabilize PGMs on the surface of support [32,33].

Automobile exhaust catalysts are deactivated due to fouling, poisoning, and thermal degeneration [34–37]. The deposition of coke (C) is the most common reason for catalyst fouling. Poisoning occurs because of strong chemical bonds between the exhaust and

catalytic reaction by-products onto the surface of catalysts. Under strict conditions such as high temperature, the sintering of platinum, palladium, and rhodium happens, causing both palladium particle growth and loss of active area for PGMs diffusion into the bulk of the support. Palladium is gradually oxidized into PdO, resulting in the loss of catalytic activity. All the deactivation reasons above make the spent catalysts heterogeneous and complicated. Besides, the support of soluble alkali γ -Al₂O₃ converts into insoluble alkali α -Al₂O₃, also causing great difficulty in the recovery of PGMs from the spent automobile catalysts.

3. The Development of Recovering Palladium from the Spent Automobile Catalysts

With the rapid development of the automobile industry, palladium has been widely used in automobile catalysts due to its unique and excellent catalytic performance [38]. Around half of the global palladium is used to produce automobile catalysts. However, the recycled palladium from spent catalysts is less than 25% of its application [39]. The general overflow of recovery of PGMs from the spent catalysts can be broken into several steps: homogenization, preconcentration/pre-treatment, leaching/dissolution, extraction/metal isolation, and purification. Methods of recovering palladium from spent catalysts can be divided into hydrometallurgical and pyrometallurgical methods. Hydrometallurgy includes traditional cyanide leaching, thiosulfate leaching, HCl(aq) + oxidants leaching, bio-recovery, and supercritical fluid extraction; pyrometallurgy includes incineration, chloride volatilization, and metal collection. In particular, the hydrometallurgical methods are reported more frequently because of their flexibility for raw material, lower energy consumption, and mild operation environment. In this section, we introduce and evaluate related studies and technologies of recovering palladium from the spent automobile catalysts.

3.1. Pretreatment

The spent catalysts undergo mechanical processing such as segregation, crush, or milling and then are moved to a pyro/hydrometallurgical process, so as to make the leaching or separation of metals more effective. Thermal pretreatment is employed for spent catalysts to improve the recovery efficiency of metals by eliminating the hydrocarbons and charcoal presented on the surface of spent catalysts. Through thermal pretreatment in a suitable atmosphere (hydrogen, oxygen, nitrogen, or air), the undesired organic constituent of spent catalysts is removed, while desired metals are retained and moved to the next process [5,40].

Differing from the thermal treatment above, the electromagnetic microwave can assist dipolar molecules and metal ions to chemically bind together. Microwave irradiation is widely applied in laboratories to improve extraction ratio and save time, and is especially fit for those alkali-insoluble or acidic-insoluble materials. Researchers have obtained the increased leaching efficiency of palladium from the spent catalysts with microwave assistance [41–45]. The microwave technology has been applied to enhanced leaching, microwave drying, microwave carbothermal reduction, and microwave sintering, and it has broad prospects in metallurgical industry due to its unique conductive heating. In hydrometallurgical pretreatment, the spent catalysts are leached by using a suitable acidic or alkaline solution in the presence of iodine, bromine, chlorine, or hydrogen peroxide to deal with their carriers [46–48]. In this way, the encapsulation of PGMs by the carrier could be unpacked, and the contact area between leachate and precious metals is expanded. As a result, the recovery yield of palladium improved.

3.2. Hydrometallurgy

3.2.1. Leaching or Extraction

The key to leaching is to effectively separate palladium from its carrier and gain leachate with a relatively high concentration of desired metals and minimize the presence of any contaminants. Technological factors such as temperature, reagents, reaction time, etc., could have a significant impact on the efficiency of metal leaching [49,50]. Hydrometal-

lurgical methods are widely accepted for recovering PGMs from the spent catalysts due to their low reagent cost, high efficiency of metal recovery with a mild operational condition, no exhaust emission, and less investment of equipment. However, potential environmental risks still exist with the generation of waste liquid, requiring a wastewater treatment system in the following process. Furthermore, the content of PGMs in leachate is relatively low; thus, a suitable process for palladium recovery from leachate is needed.

Traditional Cyanide Leaching

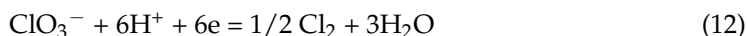
Traditional cyanide leaching has been studied due to its high recovery efficiency of precious metals from the spent catalysts [51,52]. The cyanide medium (CN^-) is as coordination ions adsorbed on the surface of palladium metal. Palladium can form ligand bonds with the lone pair electrons provided by carbon or nitrogen atoms. Thus, the complex of $\text{Pd}(\text{CN})_4^{4-}$ is formed and keeps stable in the solution. The reaction formula of palladium in cyanide medium (Reaction (10)) illustrates that oxygen functions as an oxidant during the leaching.



In the early 1990s, the national mining authority of the United States proposed the cyanide method to recover PGMs from spent automobile catalysts. Researchers in China improved the process by pretreating the automobile catalysts with pressurized alkali leaching with an oxygen pressure of 1.5 MPa, NaCN 6.25 g/L, solid:liquid = 1:4, and 160 °C [51]. In this way, the leaching ratio of palladium could rise to 98%, which was more efficient than the former. The cyanide leaching is mainly controlled by a surface chemical reaction, and the leaching efficiency depends upon the concentrations of both cyanide and oxygen [53]. However, cyanide is a kind of hypertoxic agent, which restricts its wide use in industry from the environmental protection and human health aspects.

HCl(aq) + Oxidant Leaching

Chloride leaching is widely used for PGMs recovery with HCl as the chloride source, together with oxidants to speed the dissolution of metals. Oxidants such as H_2O_2 , HNO_3 , NaOCl, Cu(II), and NaClO_3 have been proposed [54,55]. The typical oxidant of NaClO_3 , whose redox reactions can be described as Reaction (12), is the cathodic reaction in which ClO_3^- gains electrons and is reduced to Cl_2 ; Reaction (13) is the anodic reaction in which palladium loses electrons and is oxidized into Pd(II) ion [56].



Oxidants such as H_2O_2 , NaClO_3 , HNO_3 , Cu(II) play a vital role in achieving an amazing leaching ratio of palladium and improving the leaching efficiency of palladium. More than 95% of Pd was dissolved at 80 °C for 2 h in HCl + H_2O_2 solution when the ratio of liquid/solid was 20 [57]. Chloride salts such as MgCl_2 or NH_4Cl aim to enhance the selectivity of palladium over other metals in spent catalysts [56]. Chloride leaching possesses the advantage of a high recovery ratio and it has already been applied to the hydrometallurgical industry. However, recovery of palladium from the leachate is difficult, especially when the concentration of palladium in leachate is pretty low because various kinds of chloride ions are generated and presented in leachate. The typical process flow of HCl(aq) + oxidant leaching is shown in Figure 3.

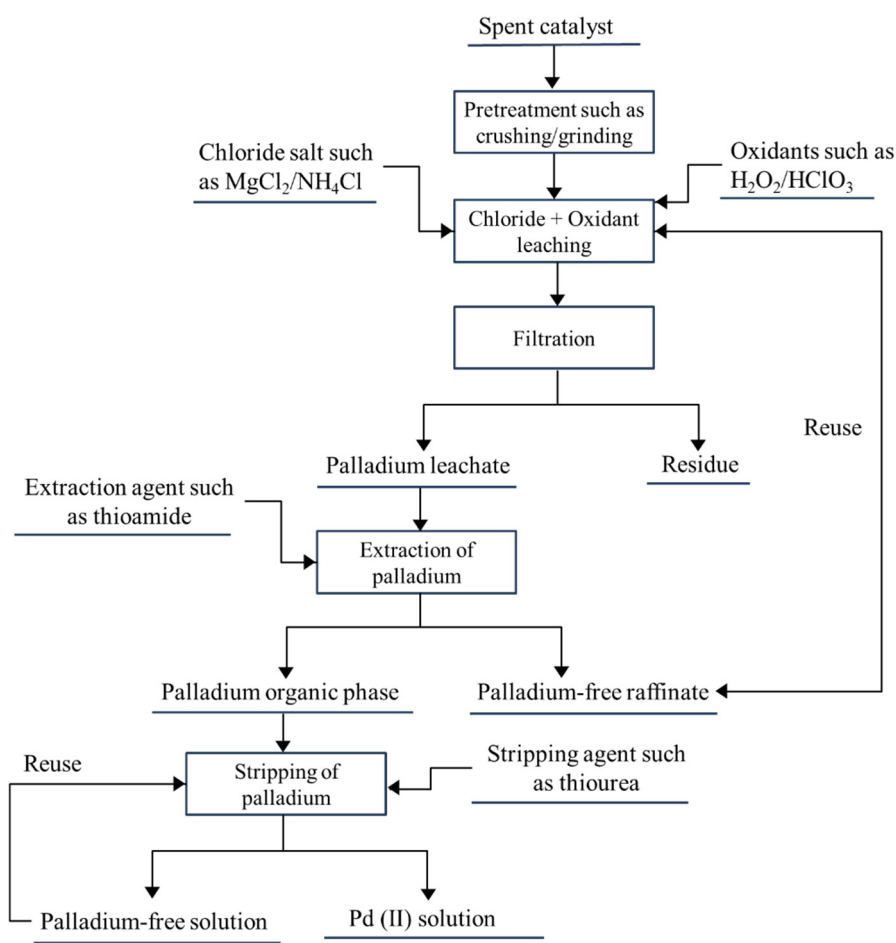


Figure 3. The flowchart of chloride leaching combined with solvent extraction.

Bio-Leaching

Bio-leaching makes use of microorganism or microorganism metabolite to directly or indirectly react with metals in the spent catalysts. Reactions such as reduction, oxidation, decomposition, and adsorption play an important role in dissolving metals from the spent catalysts [58].

Bioleaching of metals from spent catalysts consists of two stages. The first stage involves the transformation of elemental sulfur particles to sulfuric acid through an oxidation process by bacteria. In the second stage, desired metals within the spent catalysts are leached from the solid materials to solution by the action of sulfuric acid that is produced by the leaching bacteria [59]. As for the subsequent recovery of desired metals from the leachate, several studies based on the use of bacterial strains and communities for PGM recovery have shown the potential of pure bacterial culture for biological reduction of Pd(II) to Pd(0), such as *Desulfovibrio desulfuricans* and *Shewanella oneidensis* [60,61]. Though the bio-leaching method is eco-friendly and economical, it is time-consuming because the kinetics process of bio-reactions in the system is pretty slow. Bio-recovery is suitable for metal recovery for its economic benefits, particularly when the content of metal in the solid matrix is pretty low.

Supercritical Fluid Extraction

The supercritical fluid process is a kind of highly efficient and environmentally friendly separation technology and has been widely applied to pharmaceutical, perfume, and food industry use. Under supercritical conditions of solvent, generally high pressure and/or high temperature, supercritical fluid (SCF) is formed. SCF combines physical properties of both liquid and gas (Table 4) [22]: the density of SCF is close to liquid and a relatively

large density of SCF indicates a good solubility for extracted substances. The solubility of SCF changes with the adjustment of temperature or pressure to achieve efficient separation between desired and undesired substances. The viscosity of SCF is close to gas, and the relatively low viscosity and high diffusivity of SCF cause it to penetrate the solid matrix more easily. Besides, SCF extracts and transmits desired substances quickly. Critical data of common solvents have been shown below (Table 5) [62].

Table 4. Physical properties of gas, liquid and supercritical fluid (SCF).

Physical Properties	Density/(g/cm ³)	Viscosity/(g/cm·s)	Diffusion Coefficient/(cm ² /s)
Gas (25 °C, 101.325 Pa)	$(0.6\sim2) \times 10^{-3}$	$(1\sim3) \times 10^{-4}$	0.1~0.4
Liquid (25 °C)	0.6~1.6	$0.2\sim3 \times 10^{-2}$	$(0.2\sim2) \times 10^{-5}$
SCF	0.2~0.9	$(1\sim3) \times 10^{-4}$	$10^{-3}\sim10^{-4}$

Table 5. Critical data of common solvents.

Solvent	Boiling Point/(°C)	Critical Temperature/(°C)	Critical Pressure/(MPa)
Ammonia	−33.4	132.3	11.28
Carbon dioxide	−78.5	31.06	7.39
Chlorotrifluoromethane	23.7	196.6	4.22
Dichlorodifluoromethane	−29.8	111.7	3.99
Diethyl ether	34.6	193.6	3.68
Ethane	−88.0	32.4	4.89
Ethyl alcohol	78.2	243.4	6.38
Ethylene	−103.7	9.5	5.04
Methane	−164.0	−83.0	4.6
Methyl alcohol	64.7	240.5	7.99
Methylbenzene	110.6	318	4.11
Propane	−44.5	97	4.26
Propylene	−47.7	92	4.62
Water	100	374.2	22.00

The process of supercritical fluid extraction indicated in Figure 4 could be described as follows: spent material is added into the extraction reactor at the beginning. The solvent is pumped by a high-pressure pump (5) and heated by a heat exchanger (4) to reach its critical point. The extraction reaction in the extraction reactor is extremely fast, generally occurring within a few minutes. After extraction, SCF carried with different solubility substances enters into segmented desorption reactor (1). With the adjustment of temperature and/or pressure, different materials are left in different tanks of (1). In this way, the extraction and separation are achieved. The waste heat of SCF is collected by the heat exchanger (4) and the solvent is purified and regenerated in the regeneration reactor. Regenerated solvent is thoroughly processed by the heat compressor and stored in storage tank for the duration of the cycle [22].

Supercritical carbon dioxide (scCO₂), for example, is an environmentally friendly, inexpensive, and readily available solvent, which has gained great attraction as an important commercial solvent for PGMs extraction from spent materials [63]. However, scCO₂ is not effective enough to extract desired substances in SCF extraction, thus SCF chelating agents are studied, such as acetyl acetone (AA), tri-n-butyl phosphate/nitric acid complex (TBP/HNO₃/H₂O) and bis(2,2,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) [62,64]. Those chelating agents could chelate with metals in the solid matrix with high speed and form stable metallic chelates, which own a great solubility in SCF to achieve a highly selective and efficient extraction of metals. Functional CO₂-philic polymer in scCO₂ for a greener method of extracting Pd from spent catalysts has been investigated. At pressure (8~20 MPa) and temperature(313~353 K) and a 10 min dynamic extraction time, Pd was successfully recovered from the solid matrix with an extraction efficiency of almost 100% [65]. Fluorinated polymers bearing complexing units were carried out in scCO₂

under mild conditions (40 °C and 25 MPa). Up to 40% of palladium was extracted from the commercially supported catalysts with full recovery of the original alumina support [64].

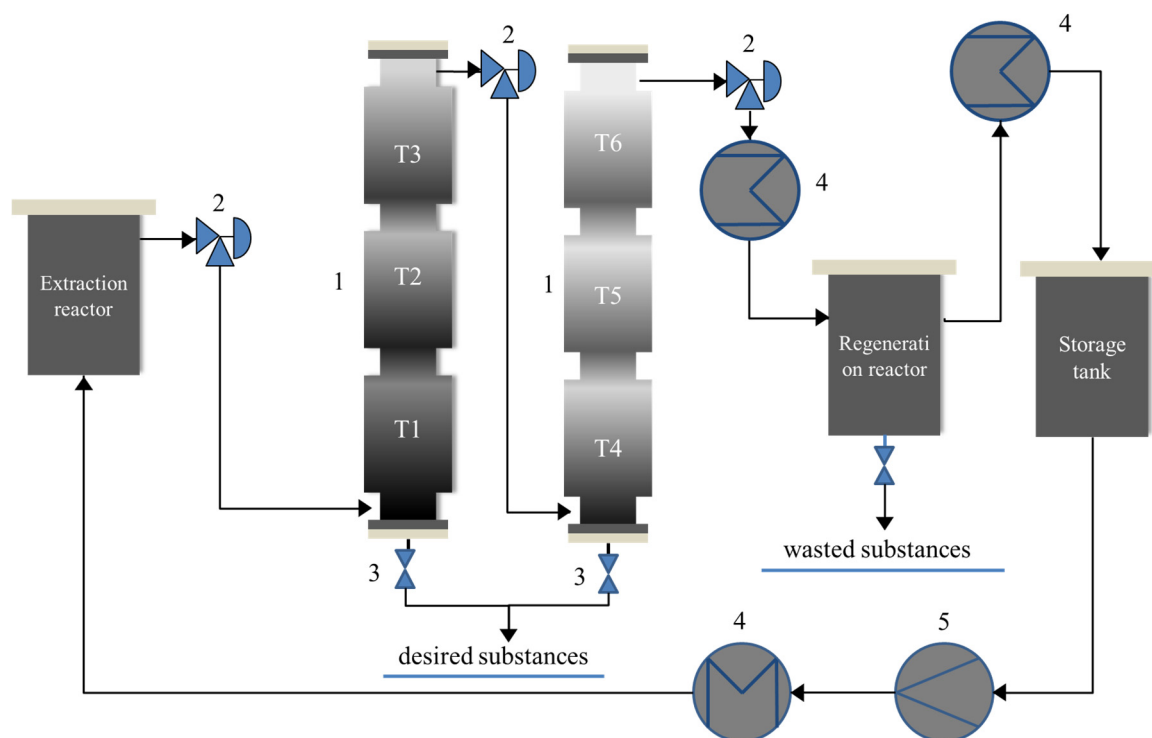


Figure 4. The schematic diagram of supercritical fluid extraction (1—segmented desorption reactor; 2—high-pressure valve; 3—normal valve; 4—heat exchanger; 5—high-pressure pump).

Other Innovative Methods

A few new concepts or methods concerning the recovery of platinum or palladium from the spent catalysts have been proposed recently. Latsuzbaia et al. [66] utilized the concept of platinum transient dissolution, which is triggered by a repetitive change in platinum surface oxidation state, for recycling platinum from spent fuel cells. N. Hodnik et al. [67] improved the electrochemical transient dissolution mechanism by alternatively employing oxidative and reductive conditions without the use of external potential control. That is the so-called transient electrochemical dissolution process triggered by repetitive cycling between two gases, leading to an electrodeless-induced surface potential alteration, without the use of external potential control (potentiostat). Their improvement yielded 100% and over 90% recovery ratios of palladium and platinum, separately, from an end-of-life automotive catalytic converter (0.5 M HCl and 1 M NaCl). The induced surface potential alteration approach provides a whole new technology to leach and to recycle platinum, respectively, from metal ores to end-of-life products in much milder and safer conditions than current state-of-the-art processes.

Deep eutectic solvents (DESs), which are considered to be ionic liquid analogs, have also been reported in the recovery of precious metals due to their low toxicity and volatility as well as their biodegradability and relatively low cost. O. Lanaridi et al. [68] studied the DES choline chloride/p-toluene sulfonic acid (p-TsOH) 1:1.8 to leach Pt and Pd (100%) and partial for Rh (approx. 50%), along with many other elements present in the car catalyst matrix, under the conditions of car catalyst: DES: HNO₃ 65% 1:5:1, mixed for 4 h, at 80 °C, and a liquid–liquid (L-L) extraction with ILs.

Eugeniu Vasile et al. [69] recycled three-way catalyst converters in a two-step method: hydrodynamic cavitation followed by sonoelectrochemical dissolution. The hydrodynamic cavitation separates the Pd and Pt from the cordierite, leading to an apparent increase in Pd and Pt concentrations of 9% and 34%, respectively. The results showed that 40% of the

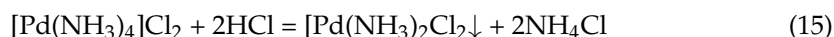
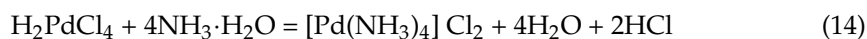
available Pd and Pt can be recycled in just 1 h with the help of a sonotrode operating at 20 kHz and 75 W, while in the absence of hydrodynamic cavitation and using conventional electrochemistry less than 10% of the available Pt and Pd is recovered in 1 h. The technologies mentioned above are innovative and greener compared with the state of art methods. However, these technologies have only been studied in the laboratory and need further research.

3.2.2. Separation or Recovery of Palladium from Leachate

Palladium needs to be further separated from other PGMs or base metals after hydrometallurgical leaching. The enrichment and purification methods of palladium from leachate studied at present include precipitation, solvent extraction (liquid–liquid extraction), and ion exchange. The final product after enrichment and purification could be palladium sponge or palladium chloride.

Precipitation

The precipitation method is a traditional one of separating palladium from leachate, which can be divided into diamminedichloro palladium precipitation and ammonium hexachloropalladate precipitation [70,71]. The former possesses a relatively high selectivity for palladium from other PGMs than the latter. The reactions happening during diamminedichloro palladium precipitation (Reactions (14) and (15)) illustrate that chlorine complex of palladium from chloride medium leaching reacts with ammonium hydroxide and forms soluble complex ($[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$) while other metals turn into hydroxide precipitation; thus, palladium is separated from other metals. Hydrochloric acid is added for maintaining the pH of the leachate between 0.5–1.5 to form the yellow sediment of diamminedichloro palladium, and then palladium is purified after filtration. After the two steps of ammonification and acidification repeat several times, the recovery ratio of palladium is over 90% and the product purity exceeds 99.6% [72].



Researchers made use of diamminedichloro palladium precipitation to recover palladium from the leachate of spent catalysts [73]. The precipitation reactions of this method were indicated as Reactions (16) and (17): Chlorine was added to oxidize metal Pd(0) into Pd(II) completely; Pd(II) in leachate can form crimson sediment ($[\text{Pd}(\text{NH}_4)_2]\text{Cl}_6$) after over-dose ammonium chloride is added into the leachate because of the low solubility of the sediment.



Spent catalysts were processed with aqua regia under the conditions of a temperature 90 °C and reaction time 2.5 h, and then the filter liquor was obtained after filtration. The ammonia and hydrochloric acid were added into filter liquor to obtain the precipitate of palladium. After repeating the process of ammonification and acidification three times, the recovery ratio of palladium was over 98%. The precipitation method is only suitable for relatively simple leachate due to its poor selectivity. Besides, unit operations such as filtration and purification of palladium sediment are intermitted, which causes inconvenience for continuous production.

Solvent Extraction

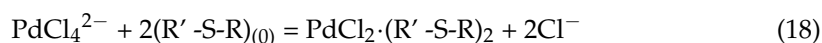
The solvent extraction, also called liquid–liquid extraction, can be described as palladium ion reacting with an extraction agent and then forming and enriching palladium complex in the organic phase. After the separation of organic and inorganic phases, palladium can be stripped from the organic phase with a suitable stripping agent. The geometric

structure of $[\text{PdCl}_4]^{2-}$ is planar square, which makes it the most stable complex among other chlorides PGMs. The extraction agents include sulfide, phosphate, and amine derivatives. Sulfide derivatives such as di-*n*-octylsulfide, thioether, and sulfoxides have been widely used for extracting palladium from leachate of waste materials [48,57,74–76]. Phosphate derivatives such as tri-*n*-butyl phosphate (TBP), tri-*n*-butylphosphate, thio-phosphoric acid, phosphonic acid and trihexyl(tetradecyl) phosphonium chloride (Cyphos IL 101) have also been reported [76–78]. Amine derivatives, including amine and oxime, such as tri-*n*-octylamine and, thiodiglycolamides have recently been employed as the extraction agents for Pd(II) and Pt(IV) from leachate [79–81]. Those extractants which have been investigated widely to recover palladium from the chloride medium solutions of spent catalysts are summarized in Table 6.

Table 6. Extractants for palladium recovery from the leachate of spent catalysts.

Extractants	Industrial Applications	Conditions	Evaluations
LIX84I [55]	YES	leachate at pH = 2, A/O = 3.	Pd recovery ratio >99%; Strong acid corrosion.
Cyanex921 [82]	YES	6 M HCl, A/O = 2.	High selectivity for Pd; Mild reaction conditions.
Dithiodiglycolamide(DTDGA) [83]	NO	3 M HCl, A/O = 1, back extraction of palladium using 0.01 M thiourea in 0.1 M HCl.	High selectivity for Pd; Pd recovery ratio 98.8%.
BSO [48]	NO	>4 M HCl, A/O = 3.	Pd extraction ratio >99%; Solution of high acidity
Cyphos 101IL [78]	NO	6 M HCl, all extractants in toluene, A/O = 1.	Pd extraction ratio 100%; Real SACs solutions were not involved.
Propiconazole and penconazole [84]	NO	3~4 M HCl, A/O = 2, using ammonia solution to extract Pd.	High selectivity for Pd; High acidity solution.

Researchers studied 2-hydroxy-5-nonylaceto-phenone oxime (LIX 841) with kerosene diluter to extract palladium from leachate of spent catalysts, which contained platinum, palladium, iron, manganese, nickel, etc. The palladium could be effectively extracted when the content of LIX 841 in kerosene was >0.2%. Then thiourea and hydrochloric were used as stripping agents, and the total recovery ratio of palladium was >99% [55]. Ramachandra used LIX 841 and Alamine 336 to extract platinum and palladium (A/O = 3), and then platinum and palladium were stripped with 0.5 mol/L thioureas and 0.1 mol/L hydrochloric acids, respectively. The recovery ratios of the two precious metals both were > 99% [85]. Using the regenerated organic phase could still achieve high recovery efficiency for palladium and platinum even after several extracting and stripping cycles. Thioether, a kind of organic sulfide, is easy to bond with palladium and form $\text{PdCl}_2 \cdot (\text{R}'\text{-S-R})_2$ neutral extraction complex, which possesses a high selectivity for palladium. Thioether can extract palladium from a complicated solution containing a large number of base metals and other PGMs. The extraction reaction of palladium is shown as Reaction (18).



Though organic sulfide above owns a high selectivity for palladium, its extraction speed of it is slow. In addition, the synthetic process of thioether accompanies with a smelly raw material of mercaptan, which limits it to be mass-produced. So, researchers studied the performance of synthesized benzylisooctyl sulfoxide (BSO) for palladium extraction. The result showed that between the concentration of $C_{(\text{HCl})} = 0.1\sim 4.0$ mol/L, the extraction ratio of Pd^{2+} using BSO gradually increased with the increase in acidity. At the concentration of $C_{(\text{HCl})} = 4.0$ mol/L, the extraction ratio of Pd was beyond 99%. However, the high acidity of the solution is harmful to equipment.

The solvent extraction method has been widely used in the metallurgy industry due to its excellent selectivity and relatively high efficiency compared with the precipitation method. Besides, regeneration of the organic phase is relatively easy. However, it is hard to recover the desired metal by one-stage extraction and stripping. In addition, segmented

operations require a large investment for the factory area and also decrease the recovery efficiency.

Ion Exchange

The ion exchange method is based on the exchange reaction occurring between ion exchange resin and ions in solution. After the exchange reaction is finished, the resins are eluted with an eluting agent. This method is more economical compared with the two methods above, as the ion-exchange resin is cheap and can be recycled after regeneration. According to the properties of functional groups, ion-exchange resins can be divided into seven categories: strong acidic, weakly acidic, strong alkaline, weak alkaline, oligomeric, acid-base amphoteric, and oxidative reductive resins. The anion exchange resins are widely used for the extraction of PGMs because PGMs tend to form anion complexes.

Synthetic polyvinyl alcohol amidoxime (PVAAO) chelated fiber was used to adsorb palladium in the leachate of spent catalysts, and the adsorption ratio of palladium was >99%. The fiber was eluted with the solution containing 5% thiourea and 0.5 M nitric acid, and the elution ratio of palladium was >99% [86]. The adsorption performance of dt-1016 anion exchange resin for ultra-trace platinum and palladium was studied. The results showed that adsorption ratios of platinum and palladium in 0.025M HCl medium arrived at 99.60% and 97.95%, respectively. However, the resin regeneration was not introduced [86].

Nikoloski performed comparative research among ammonia functional resin (Lewatit Mono Plus (M +) MP 600), polyamine functional resin (Purolite S985), and thiourea functional resin (XUS 43600.00). Thiourea functional resin (XUS 43600.00) showed the best adsorption performance in the experiments. Singh and Ruhela proposed polymeric beads encapsulated by dithiodiglycolamide to separate and recover palladium from the leachate of spent automobile catalysts. The sorption kinetics of palladium were fast, and the kinetics data fit well with the pseudo second-order equation model for the sorption of palladium ions onto the beads. More than 99% of palladium was eluted by using 0.01 M thiourea in 0.1 M HCl medium [87]. The ion exchange methods have become popular in the recovery of precious metals from the leachate in recent years due to their low cost and simple operation. However, the functional resins might easily be poisoned after repeating several times, and hence the adsorption ability of the resins could be degraded. The selectivity and regeneration of resins are of great importance for their further applications.

3.3. Pyrometallurgy

Pyrometallurgical technology has attracted attention for recovering PGMs from spent automobile catalysts for its simple and short-flow process, no pollution of wastewater, and large-scale application potential [13,88,89]. Pyrometallurgy can be divided into incineration, chlorination volatilization, and metal capture methods. Incineration leads to the production of a large amount of gas waste. As a result, this method has hardly been reported on recovering palladium from spent automobile catalysts. The chlorination volatilization process has been used in industry for a long period of time owing to its high efficiency. Meanwhile, the vapor of volatile metals (e.g., calcium, magnesium, cadmium, and zinc) causes a great potential threat to human health. Metal capture is an effective method for PGMs recovery from spent catalysts even with a pretty low content of these metals. However, melting under high-temperature (1200–2000 °C) has high energy consumption and the investment for equipment is high.

3.3.1. Chlorination Volatilization Method

Chlorination volatilization is based on the volatility difference of metal chlorides. Chlorine mixes with carbon monoxide, oxygen, carbon dioxide, phosgene, etc., as a chlorinating agent. Auxiliary agents such as KCl, NaCl, CaCl₂, etc., are added to make palladium chloride volatilize completely, so as to effectively separate palladium from the spent catalysts. Chlorination volatilization could achieve an excellent palladium volatilization ratio of 99% after reacting for 1–3 h at the temperature of 850–900 °C [90]. However, this method

causes a great threat to the environment due to the production of a great amount of smoke dust deriving from volatile metals, and it needs great investment for equipment with high temperature resistance and corrosion resistance.

3.3.2. Metal Capture Method

In the metal capture process, the solubility, melting points, and chemical properties of both capturing agents and palladium have to be considered. Spent catalyst powder containing PGMs is melted in a furnace together with a collector (Lead, Copper, Iron, Nickel, etc.) and fluxing agent (lime, cryolite, borax, soda ash, etc.) to generate a metallic alloy (M-PGMs) and a slag. Palladium is collected by metal and transferred into the metallic alloy, while the carrier of spent catalysts is moved into the slag. Alloy and slag are easy to separate due to the density difference. This method is widely applied, especially for spent catalysts with insoluble carriers and low content of PGMs.

Because copper could be recycled as a high-purity copper with electrolysis, copper capture is more suitable for recovering PGMs. The waste catalyst was melted together with copper metal or copper oxide, flux agent, and reducing agent under a high temperature, and then the copper alloy gathering PGMs and oxidized slag were formed. Under the optimum experiment conditions of CaO/SiO_2 1.05, CuO 35~40%, reduction agent 6%, 1400 °C and 5 h melting time, the recovery ratios of Pt, Pd and Rh were 98.2%, 99.2%, and 97.6%, respectively [45]. The flowchart of copper capture for recovering PGMs from waste catalysts is shown in Figure 5.

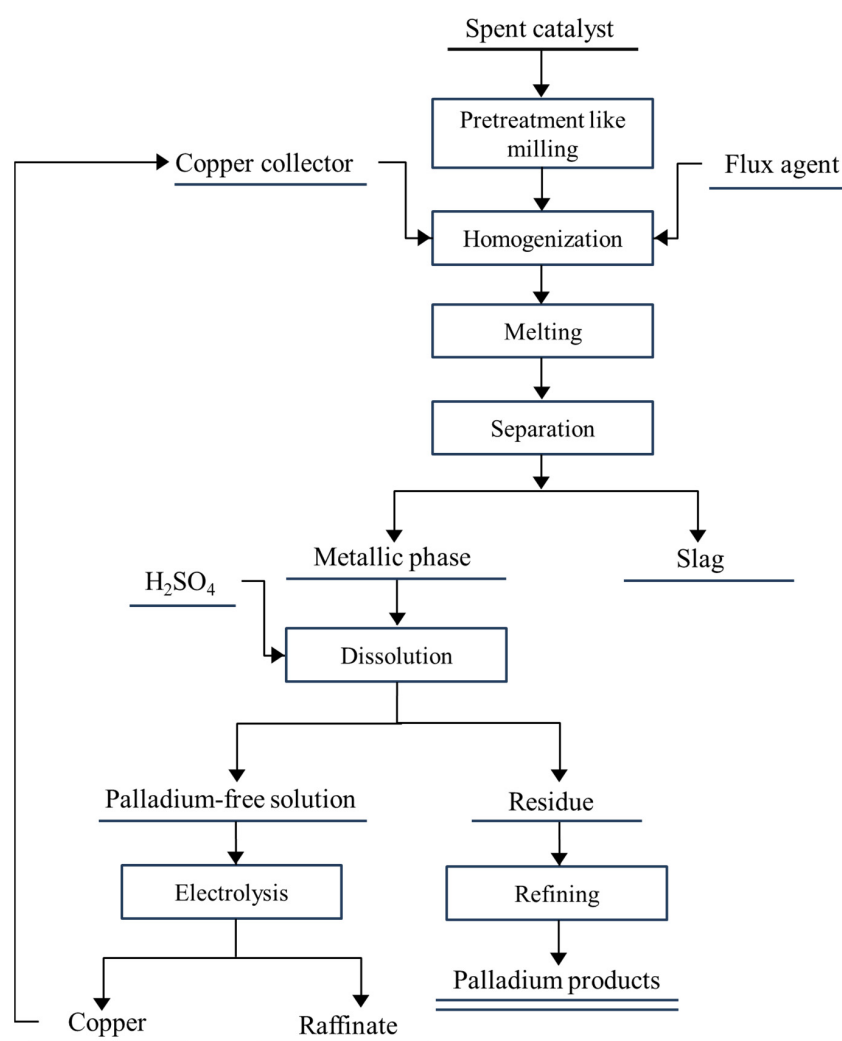


Figure 5. The flowchart of copper capture for recovering PGMs from spent catalysts.

The advantage of the copper capture method is that it can make full use of existing non-ferrous metal melting equipment, and thus the investment and processing cost can be saved. Besides, it has a large production capacity which makes it possess great competitiveness in industry. However, a large quantity of the anode slime containing both PGMs and copper is produced during the copper alloy electrolysis, which needs a complicated process to recover PGMs, causing the mechanical loss and low recovery ratio of precious metals [91].

Iron capture of precious metals from low-grade waste catalysts has been studied [24]. Because the melting point of iron (1538 °C) is high, iron capture of palladium from spent catalysts is in the plasma reactor. The heat generated by plasma made Al_2O_3 directly melt and there was no need to add other reagents to reduce its melting point. After the alloy was dissolved by H_2SO_4 , precious metals were enriched in residue. The recovery ratio of palladium by plasma smelting iron capture reached 98%. Plasma smelting possesses the advantages of a fast reaction speed and a controllable atmosphere. The plasma smelting furnace, however, as a kind of special equipment, is very expensive. Under the condition of extremely high temperature, the service life of the plasma gun is short (100~150 h) and the cost of maintenance and repair of the furnace body is high. Ding et al. [92] improved the economic feasibility of recovery of PGMs from leaching residue of spent auto-exhaust catalysts with iron capture by designing slag ahead to reduce slag volume and save cost. However, it is difficult to obtain stable technical indexes unless the operation is accurate enough and the spent catalysts are homogeneous.

The lead capture method of recovering PGMs uses an arc furnace or a blast furnace. C or CO is typically used to produce and maintain a reductive atmosphere in the furnace. Capturing happens during the reduction reaction by building the metallic bond between lead and PGMs. PGMs and lead transfer into lead alloy while the carrier of spent catalysts converts into slag phase, and then PGMs are concentrated. Compared with copper capture, the big problem of lead capture is the volatilization of Pb compounds, which are inevitable during high-temperature melting, resulting in great potential danger to labor health and environmental safety.

The matte serves as a collector due to the close affinity of matte for PGMs during the smelting of spent catalysts. By adding metal (e.g., nickel) and sulfur or metal sulfide (e.g., NiS) with flux (e.g., CaO, Na_2CO_3 , or their mixture), PGMs could be enriched in the matte phase at a relatively low temperature (1000~1450 °C). The smelting atmosphere should be well controlled because the oxidation of nickel will cause difficulty in refining after the separation of PGM-containing matte from slag. Besides, the silicon acidity of slag, defined as the mass ratio of oxygen in SiO_2 to that in Al_2O_3 and MgO, should be accurately controlled to avoid metal loss and optimize the smelting process. The equipment of matte capture can be directly combined with copper smelting equipment. However, the generated sulfur and its related oxides, which pose a threat to our environment, should be properly disposed of [13].

The existing advantages and disadvantages of pyro/hydrometallurgical methods introduced in this paper for recovering palladium from the spent automobile catalysts is shown in Table 7.

Table 7. Comparison of pyro/hydrometallurgical methods for the recovery of palladium from the spent automobile catalysts.

Methods		Advantages	Disadvantages
Hydrometallurgical methods	Cyanide leaching	Conventional technique and yields high recovery ratios >99% of Pd and Pt; low cost of reagents.	Cyano-compounds are highly toxic to living organisms; wastewater needs to be properly treated.
	HCl+oxidants leaching	High leaching ratio >99% of Pd; low investment of equipment.	Proper pretreatment is needed; extractants should possess high selectivity of Pd; equipment corrosion of high concentrated HCl.
	Bio-recovery	Low cost of reagents; no pollution to the environment.	Needs a long reaction period; main leaching mechanisms are unclear.
	Supercritical fluid process	High reaction speed of Pd recovery; no pollution to air and water.	Low recovery ratio of Pd; high temperature and pressure conditions.
	Electrochemical transient dissolution	Milder and safer.	Application is currently limited and needs further study.
Pyrometallurgical methods	Chlorination volatilization	Low melting temperature (1000–1200 °C); reusable carrier; high recovery ratios of PGMs.	Gases generated (Cl ₂ and COCl ₂) are toxic and corrosive.
	Iron collection	Low cost of collection iron; high recovery ratios of PGMs.	High energy consumption of plasma smelting (1500–1600 °C); Short service of the plasma gun. High investment for equipment.
	Copper collection	Collection copper can be reused; high recovery ratios of PGMs; moderate melting temperature.	A long production cycle; high energy consumption of smelting (1300–1400 °C).
	Lead collection	Simple operation; relatively low melting temperature.	Serious lead dust pollution, which is harmful to workers' health.
	Matte collection	Can be directly combined with smelting equipment of copper and nickel.	Generated sulfur and its corresponding oxides pose an environmental risk.

4. Summary and Conclusions

Due to the supply–demand imbalance of palladium, recovering palladium from the spent catalysts is important from the perspectives of the economic benefits and resource utilization. The high content of palladium in spent automobile catalysts and their increasing mass collection both attract a high interest in recovering palladium from the spent catalysts in these years. Pyrometallurgical methods are superior to hydrometallurgical methods in terms of the recovery efficiency and process capacity, which simultaneously means that pyrometallurgical processes are fit for those large factories which are able to continuously collect a large number of spent catalysts. However, the spent catalysts in China have dispersive distribution with a small volume of production at present, and hence hydrometallurgical technologies have strong adaptability since they are flexible enough in process capacity. Besides, pyrometallurgical technologies need a large investment for the high-temperature furnace which is currently import-based. It is risky to import the furnace under the situation of the COVID-19 pandemic.

Hydrometallurgical methods such as supercritical fluid process or bio-recovery both have their limitations at present and need further research. The most promising one, chloride leaching with oxidants, possesses the advantages of high selectivity and satisfying recovery ratio, and the process flow is flexible to serve palladium-containing spent catalysts of different types. Additionally, chloride leaching has no dust/harmful gas emission and its low energy consumption is beneficial for sustainable development from economic and environmental points of view. Due to the intensified scarcity of palladium, the recovery ratio of palladium from the spent catalysts should be further improved by developing/improving new kinds of extractants with high selectivity of palladium, especially for the complexed leachate with a low concentration of palladium.

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