Review

Recent Developments on Processes for Recovery of Rhodium Metal from Spent Catalysts

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Abstract: Rhodium (Rh) catalyst has played an indispensable role in many important industrial and technological applications due to its unique and valuable properties. Currently, Rh is considered as a strategic or critical metal as the scarce high-quality purity can only be supplemented by refining coarse ores with low content (2–10 ppm) and is far from meeting the fast-growing market demand. Nowadays, exploring new prospects has already become an urgent issue because of the gradual depletion of Rh resources, incidental pressure on environmental protection, and high market prices. Since waste catalyst materials, industrial equipment, and electronic instruments contain Rh with a higher concentration than that of natural minerals, recovering Rh from scrap not only offers an additional source to satisfy market demand but also reduces the risk of ore over-exploitation. Therefore, the recovery of Rh-based catalysts from scrap is of great significance. This review provides an overview of the Rh metal recovery from spent catalysts. The characteristics, advantages and disadvantages of several current recovery processes, including pyrometallurgy, hydrometallurgy, and biosorption technology, are presented and compared. Among them, the hydrometallurgical process is commonly used for Rh recovery from auto catalysts due to its technological simplicity, low cost, and short processing time, but the overall recovery rate is low due to its high remnant Rh within the insoluble residue and the unstable leaching. In contrast, higher Rh recovery and less effluent discharge can be ensured by a pyrometallurgical process which therefore is widely employed in industry to extract precious metals from spent catalysts. However, the related procedure is quite complex, leading to an expensive hardware investment, high energy consumption, long recovery cycles, and inevitable difficulties in controlling contamination in practice. Compared to conventional recovery methods, the biosorption process is considered to be a cost-effective biological route for Rh recovery owing to its intrinsic merits, e.g., low operation costs, small volume, and low amount of chemicals and biological sludge to be treated. Finally, we summarize the challenges and prospect of these three recovery processes in the hope that the community can gain more meaningful and comprehensive insights into Rh recovery.

Keywords: Rh catalyst; recovery; pyrometallurgical; hydrometallurgical; biosorption

1. Introduction

As strategic resource reserves, precious metals (rhodium (Rh), platinum (Pt), palladium (Pd), ruthenium (Ru), iridium (Ir), and osmium (Os)) are widely used due to their unique chemical and physical properties [1,2]. The application of precious metals can be deeply involved in many military high-tech fields such as aviation, navigation, missiles, rockets, atomic energy, microelectronics technology, as well as in chemical, optical, lubricating materials, instrumentation, petrochemicals, automotive exhaust purification,

biomedicine, etc. Nowadays the development of precious metals has already been emitting an indispensable, important, and valuable brilliance, which attracts a large amount of attention around the world. With a continuous combination of nanotechnology and deep processing technology, the application scope of precious metals is expanding, especially in the field of chemical catalysis, which plays an irreplaceable role. Almost all precious metals can be used as catalysts, but the most commonly used are Pt, Pd, Rh, Ag and Ru, among which Pt and Rh are more employed. Precious metal particles can easily adsorb reactive substances on their surface, facilitating the formation of intermediate "active compounds". They can act as important catalyst materials widely utilized in the chemical industry, biocatalysis, and environmental protection, due to their high decomposition activity. Precious metal catalysts play a key role in the petrochemical industry, which can accelerate the chemical reaction rates without participating in the reaction itself. Besides, they are regularly applied in hydrogenation, dehydrogenation, oxidation, reduction, isomerization, aromatization, cracking, synthesis, and other reactions. In addition, with the development of technology, precious metal catalysts are beginning to be employed in emerging environmental and energy fields [3]. As a clean energy carrier, hydrogen is known to be a very promising renewable energy source due to its high energy density, zero carbon emission, and earth element abundance [4]. However, the slow reaction kinetics and the excessive overpotential for the cathodic precipitation of hydrogen and the anodic precipitation of oxygen are becoming the main obstacles for large-scale electrolysis. Therefore, high-performance electrocatalysts are needed to reduce the overpotential and improve the efficiency of water cracking, and noble metal-based (PGMs) catalysts have been proved as the most advanced electro-catalysts owing to their high activity and stability in acidic solutions [5,6]. In particular, Ir and Ru and their oxides are the most advanced OER (oxygen evolution reaction) catalysts [7–9]. Moreover, the cost of storing hydrogen is extremely high, as it must be kept in pressurized tanks up to 700 bar or it should be liquefied, which means that it has to be cooled down to -253 °C. Note that these two procedures require additional energy consumption. Scientists at the German Electron Accelerator have proposed a new method of storing hydrogen in tiny nanoparticles made of the precious metal palladium, which is only 1.2 nm in diameter. They found that hydrogen adheres to the surface of the precious metal nanoparticles and barely penetrates the interior. Recovering the stored hydrogen requires only a small amount of heat to be given and the hydrogen is rapidly released from the surface of the particle, as the gas molecules do not have to push out from inside the cluster [10]. As precious metal nanoparticles are extremely sensitive to heat, light, humidity, and temperature in the environment, nanosensors are also one of the most promising application areas for metal-based nanoparticles. By varying the size, shape, and dielectric environment of precious metal nanoparticles, they can eventually be applied in preparing a variety of noble metal nanoparticle-based morphology/size-dependent colorimetric assays. They offer high sensitivity and selectivity compared to other conventional colorimetric sensors, based on excellent and sensitive LSPR offset optical properties for the recognition of different targets [11].

However, natural PGM reserves in the earth's crust are relatively low, with only 66 thousand tons available globally, distributed in North America, Canada, South Africa, Zimbabwe, and Russia. With the booming of the above-mentioned industries, the demand for precious metals is rapidly increasing [1,12–14], but the scarce resources of high-quality ores are unable to meet the market demand and can only be supplemented by refining in poor ores with a low content (2–10 ppm), which leads to an extremely high cost of extracting precious metals from minerals [15]. Moreover, due to the gradual depletion of these precious metal resources, pressure on environmental protection, and high market prices, increasing prospects for PGMs has become a matter of great concern and urgency. Metal wastes can be called precious metal secondary resources relative to precious metal mineral resources, which are mainly generated in the production process, deep processing, usage process, and elimination process of precious metals, mainly in the form of tailings from the production process of precious metals, waste liquid and slag from the deep

processing and use process, scrapped or eliminated industrial and civil electronic products, etc. Encouragingly, wastes such as waste catalysts, old industrial equipment, and electronic scrap contain higher concentration of precious metal content than natural minerals, and the energy consumption and other costs per unit mass of precious metal in the recycling process are significantly lower than those of the original mining, while the emissions of the three wastes generated are far less than those of the original mining process. Therefore, under the circumstances of the growing depletion of precious metal mineral resources, the high amount of pollution in the extraction and metallurgy process, and the increasing costs, it is of both economic and environmental significance to enhance the recycling of precious metal wastes [16]. Human society is currently facing two major challenges, i.e., resource scarcity and environmental pollution. To achieve social sustainability, it is necessary to simultaneously improve the efficiency of energy supply, conversion, and use, and the recycling of precious metal waste resources is an important way to transform the linear economic model into a circular economic model, stabilized into energy or other useful products. It has a strategic synergistic potential to reduce both resource consumption and pollution, thus reducing the environmental impact [17,18]. The vast majority of countries have placed the recycling of precious metal wastes [19] on par with (or even more important than) the development of mineral resources. Therefore, the recovery of precious metal catalysts is crucial, but the diversity and complexity of spent catalysts urgently require a variety of recovery technologies for the target species [20].

Affiliated as a member of the platinum group of metal elements, Rh not only has superior physical properties of high melting point and mechanical strength, good electrothermal stability, but also stable chemical properties, excellent corrosion resistance, strong oxidation resistance, and exceptional catalytic activity. As a result, Rh has expanded into numerous industrial applications. The main Rh consumption (80%) involves automobile catalytic converters which can dramatically reduce nitrogen oxides in exhaust fumes (Figure 1). With the rapid development of fuel cell technology as power sources for vehicles, the Rh amount used in the automotive industry will further increase. Moreover, Rh is greatly utilized as a catalyst in hydrogenation reactions [21,22], nitric acid [23] and acetic acid production [24] in the petrol-chemical industry. In addition, Rh is becoming increasingly important for scientific investigation; for instance, it can be used for optic fibers, optical mirrors coating, crucibles, thermocouple elements, etc. Besides, due to its high electronic conductivity and strong corrosion resistance, Rh is considered an excellent electrical contact material. Given the paramount significance of Rh in many fields, it has been recognized as a strategic commodity in most leading industrial countries, such as the United States, European Union and the United Kingdom [25,26].
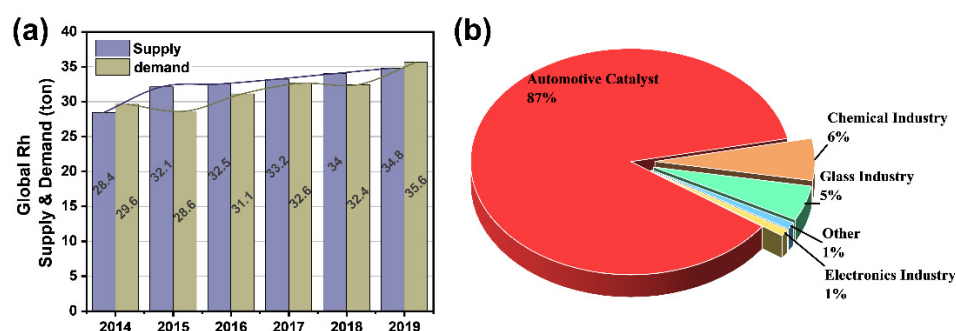
Figure 1. (**a**) Global Rh supply/demand from 2014 to 2019. (**b**) Global consumption profile of Rh in 2019.

Along with the boosted requirement for related industrial products and the heightened awareness of environmental protection, Rh-related demand has increased annually [27]. However, Rh is very rare, accounting for only one billionth of the crust content, which makes it a costly material in the market [28] (Figure 2). Although many new catalysts have been developed to substitute for Rh, none of them can fully meet the market

requirement [25,29]. Therefore, how to utilize the limited Rh resource rationally and effectively is crucial. For instance, the spent Rh-based catalysts in various forms are considered the most promising source of Rh secondary resource at present (Table 1). Among them, the spent auto-exhaust catalyst is the largest part (in 2018, approximately 84% of Rh (24.07 tons) was used in automotive catalytic converters) and is of the uppermost priority for recycling Rh in a green and economic manner.
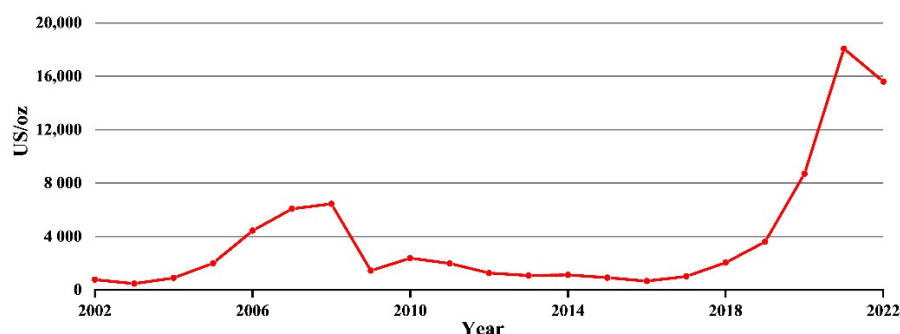

Figure 2. Average Rh price trend 2002–2022 (USD/oz).

Table 1. Composition of different types of spent catalysts in various applications.

Application Fields		Catalyst Carrier	PGMs	Content/wt.%	References
Automotive industry	Catalysts	Cordierite monolith ceramic Metallic monolith	Pt/Rh; Pt-Pd-Rh; Pt, Pt; Rh	0.1–0.5	[1,30] [31]
Bulk and specialties	Nitric acid HCN	Gauzes Al_2O_3, gauzes	Pt-Rh Pt/Rh	100 0.1, 100	[32] [1,33]
Fine Chemicals	Hydrogenation	Activated carbon Al_2O_3, SiO_2	Pd; Pd/Pt, Ru; Rh; Ir	0.5–10	[34]
	Oxidation	Activated carbon	Pd; Pd/Pt, Ru; Rh; Ir		[35]
	Debenzylation	Activated carbon	Pd; Pd/Pt, Ru; Rh; Ir		[36]
Glass industry	Glass fiber	Pt-Rh alloy	Pt-Rh	100	[37,38]
Homogeneous products	Acetic acid	SiO_2, Metallic monolith	Rh; Ir/Ru	0.01–5	[39]
Oil refining industry	Reforming	Al_2O_3	Ru; Rh/Ir	0.02–1.2	[40,41]

Over the past two decades, many efforts have been dedicated to the recycling of spent catalysts. By and large, there is no generally accepted criterion for classifying the existing PGM recovery methods from the spent catalysts. However, a common practice is to classify them as hydrometallurgical and pyrometallurgical methods. The spent materials are initially segregated, crushed, ground and then handled through pyro/hydrometallurgical processes to recover the PGM. This paper reviews the relevant technologies and methods for the recovery of Rh from spent catalysts, including various hydrometallurgical and pyrometallurgical methods and biosorption techniques [42–44]. We directly analyze the advantages and disadvantages of these processes, while briefly discussing the progress of these technologies in recent years. Among them, the hydrometallurgical process, which includes extraction, precipitation separation, adsorption separation and ion exchange [45–47], is commonly used for Rh recovery from auto catalysts due to its technical simplicity, low cost and short processing time. However, its overall recovery is quite low due to the still high content of Rh in the insoluble residue and the unstable and incomplete leaching. In contrast, higher Rh recovery, larger capacity and less effluent discharge can be ensured by pyrometallurgical processes. Pyrometallurgical processes then include incineration and melt enrichment. The spent catalyst can be melted at high temperatures by combining

fluxes and metal collectors to form PGM-containing alloys, from which precious metals can be recovered by appropriate re-refining techniques. Therefore, it is widely used in industry to extract precious metals from spent catalysts. Moreover, the whole process is quite complex, which leads to expensive hardware investments, high energy consumption, long recovery cycles, and difficulties in controlling contamination in practice. With the rapid development of biotechnology and the increase of human environmental awareness, biosorption technology has become an emerging field for metal recovery. Biosorption is the technology of adsorption, ion exchange, micro precipitate and coordination of metal ions with biomass [48]. Compared with conventional recovery methods, the biosorption process, with its low operating costs, small size, and a small number of chemicals and biological sludge to be treated, is considered a cost-effective biological method for Rh recovery, and it has great potential to replace the two conventional methods mentioned above. In this paper, several methods are described and evaluated by reviewing metallurgical processes that have been established for Rh recovery from spent catalysts (Table 2). It is hoped that this paper will provide the reader with an understanding of the advances and prospects associated with spent catalyst recovery and that researchers can gain additional meaningful and important knowledge and insights into Rh recovery.

Table 2. Advantages and disadvantages of various recycling methods.

Method		Advantage	Disadvantage
Pyrometallurgical process	Incineration	Simple process; no chemical additives required; high recovery rate.	The need to control the rate of incineration; prevent loss of fugitive material.
	Plasma melting	Short process flow; high efficiency; no wastewater and waste gas generation; high platinum enrichment.	Not very suitable for materials containing SiO_2; short service life of plasma guns at high temperatures.
	Metal trapping method	High adaptability of raw materials; low operating costs; weak reduction atmosphere; high capture efficiency; large production scale.	Rh recovery is low (65% to 70%); number of factors to consider when selecting a metal trap.
Hydrometallurgical process	Volatilization	Simple process; low reagent consumption; low energy consumption.	Corrosive; high equipment requirements; toxic gases to be handled.
	Extraction method	Good separation effect; simple operation; high safety; low energy consumption.	Requires large amounts of extractant and diluent; ingredients are mostly toxic reagents.
	Coprecipitation	Simple equipment; low investment; large processing capacity.	Inconvenient to operate; slow reaction speed; introduction of other elements; easy to produce secondary pollution.
	Adsorption separation	High separation efficiency; low cost; simple equipment and operation.	Rhodium is difficult to separate in resin; high cost of resin incineration; serious secondary contamination.
Biosorption		Cheap; easy to obtain; flexibility.	Immobilization of biomaterials, distribution of biosorbents; regeneration and recycling are also important issues to be solved.

## 2. Process of Rhodium Catalyst Recovery

Since the 1970s, research on Rh recovery from spent catalysts have been initiated in both academia and industry. In general, the recovery of platinum-group metals from spent catalysts generally consists of three major processes: pretreatment, crude extraction and refining. Pretreatment means the necessary crushing and fine grinding of spent catalysts; crude extraction is an important step to separate the carrier and platinum-group metals in spent catalysts; refining is to concentrate and purify the platinum-group metals in the leachate. The coarse extraction process is the most important part of the whole recovery process, which directly affects the recovery rate and cost. Given the complexity of the composition, morphology and the original manufacturing process of the spent catalyst, there

are various Rh recovery techniques, and the main methods can be classified as pyrometallurgical, wet enrichment and bioenrichment. The processes related to pyroprocessing are discussed separately in the later sections [49–53].

2.1. Pyrometallurgical Process

Pyrometallurgy is an important smelting method in the metallurgical industry. The basic principle is the separation of metallic and non-metallic substances in the molten state by high temperatures [54], followed by grinding, sieving and separation of the materials (Figure 3), and finally, further refining and purification of the metals. Pyrometallurgy is also a general solution for the recovery of valuable elements from industrial waste. In pyrometallurgical recovery of precious metals, the non-precious metals in the catalyst are heated at high temperatures to form slag with additional slagging materials in a molten state, and the slag is removed by floating in the upper part of the melt under the principle of density difference, while the precious metals are trapped by other base metals to form an alloy that sinks to the bottom of the solution for further processing after cooling. The main methods for recovering Rh from automotive catalysts by fire include incineration, plasma melting, metal trapping, pyro-chlorination and high-temperature volatilization.
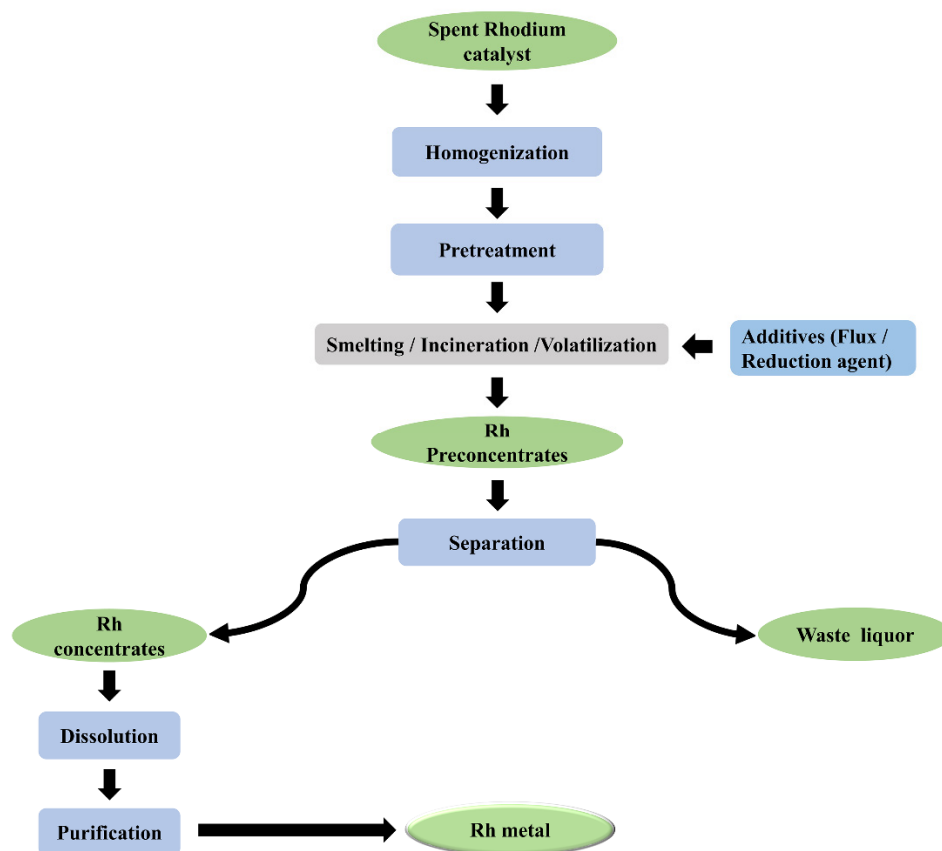
Figure 3. Flowsheet illustrating Rh recovery by the pyrometallurgical process.

2.1.1. Incineration

Carbonaceous carrier catalysts of platinum-group metals have been widely used in the petrochemical and chemical industries. Pt-C, Pd-C and Rh-C catalysts are commonly used in hydrogenation reactions such as hydrogenation, amination and hydrodesulfurization to remove sulfur from aromatic compounds in the petrochemical industry, and the carriers are mostly granular or flake coconut shell activated carbon. They are mostly distributed on the surface and in the pores of the carbon particles in a particulate metal state. They have a strong adsorption capacity, and the use of the direct leaching method is very unsatisfactory. The incineration method mainly focuses on the carrier of carbon material, using

the combustibility of carbon in the incineration method to destroy the carrier and collect the active component platinum-group metals. The principle of the incineration method is to recover the platinum-group metals from the burnt residue after decarburization by incineration, taking appropriate measures such as oxygen-enriched operation, adding combustion aid clay or slaked lime to make the activated carbon carrier ignite, so that the ash rich in platinum-group metals can be obtained after full combustion. The platinum-group metals are subsequently recovered by process steps such as reduction, dissolution, solution purification, and refining [53,55,56]. Incineration is a simple process, without the addition of any chemical additives. The corresponding recovery rate is also very high and the key to affecting the recovery rate of Rh needed for the above-mentioned characteristics of the various carriers, to take appropriate measures to speed up the incineration rate and prevent the loss of fugitives.

Mitsubishi Chemical Co. reported a method to prevent Rh loss during incineration. An alkaline compound, as an incineration inhibitor, was put into the mixture of organic solvent and Rh complex coordinated by organic phosphorous compounds. The incineration temperature was well controlled, and the final temperature was below 1000 °C. The Rh recovery rate was estimated to be more than 93% [57]. Wang et al. [58] used programmed heating to control the incineration rate to further improve the recovery of Rh. They concluded that the Rh recovery from the catalyst was related to the operating temperature during incineration and that gradual heating could greatly increase the recovery of Rh. In this study, the Rh catalyst with a boiling point of below 300 °C accounts for 70~80% of the composition. Below 300 °C, if fast heating is exerted, the spent catalyst easily evaporates with the volatilization of organic components. Therefore, programmed heating is usually applied. Before reaching 300 °C, the temperature is maintained for 1.5 h with an interval of 50 °C. When the temperature is above 300 °C, it is kept for 1 h at every 100 °C, before the ultimate temperature of 1100 °C is attained. It was found that the recovery rate can be as high as 99.9% under the optimum conditions.

2.1.2. Plasma Melting Method

The principle of plasma melting is to use the plasma arc to melt metals by providing a sufficiently high temperature and to intensify the melting of the furnace charge so that the platinum in the spent catalyst combines with the trap metal to form an alloy and sink to the bottom, while the carrier component enters the slag phase by slagging with the applied slagging material to achieve the mutual separation of platinum and catalyst carrier. The plasma melting method has the advantages of relatively short process flow, the high production efficiency of precious metals, no wastewater and waste gas generation, and high enrichment of platinum. The process is that the material melts and the alloy sinks while the slag floats, making the slag and metal separate from each other. Since the content of Rh in the spent catalyst is generally low, a good separation of slag and alloy is necessary to ensure a high recovery rate. In this method, the difference in specific gravity between slag and metal is large, and the separation of slag and alloy is excellent.

Li et al. [59] studied the melting enrichment of platinum-group metals in spent automobile exhaust catalysts by pyrometallurgical smelting technology. The research showed that when the smelting reaction time was 4 h, the amount of collector Fe_3O_4 was 20% of the material amount and the reducing agent dosage was 9%. When the amount of CaO was 40% and the temperature was 1450 °C, the comprehensive Rh recovery rate could reach more than 97%. The Kunming Institute of Precious Metals in China used a special process to treat imported platinum group metal mixtures obtained from plasma smelting. The main components of raw materials contained: Platinum (Pt) 5.12%, Palladium (Pd) 0.95%, Rhodium (Rh) 0.71%, Copper (Cu) 0.85%, Nickel (Ni) 9.66% and Ferrum (Fe) 55.41%. The platinum group metal mixtures were converted into a metal liquid by plasma melting, which contained 54.9 wt % Pt, 10.4 wt % Pd and 9.25 wt % Rh. And the experimentally comprehensive recovery rate can reach up to 98%.

Although the plasma melting method has irreplaceable advantages, it also has some disadvantages. For example, when the waste catalyst contains a certain amount of silica, SiO_2 will be reduced to mono silicon under the action of reducing agent during the melting process, and then mono silicon will form high ferrosilicon with the trapping agent, which will form an insoluble alloy phase with precious metal platinum, making the subsequent treatment more difficult and increasing the cost of the process. In addition, the plasma melting method also has many other problems that need to be solved, such as the plasma melting equipment needs to operate at special high temperatures, and the plasma gun at high temperatures in the very short service life, so that the application of the method in practice is limited, so in the future, further research can be higher temperature resistance, and easy to replace the plasma gun. At the same time, high-temperature refractory materials should be used as the lining of the equipment to solve the wear and tear problem caused by refractory materials in the high-temperature working environment.

2.1.3. Metal Trapping Method

Similar to plasma, metal trapping also employs a metal matrix to trap platinum group elements (Figure 4). The metal trapping method uses the special affinity of molten metals such as Fe, Cu, Pb, Bi, or molten cannon to PGMs to make PGMs enter the alloy phase. The base metal carriers and fluxes make slag, and the density of the alloy phase is greater than that of the slag phase and settles in the lower layer, thus achieving efficient enrichment of PGMs. The trapping process is as follows: the trapping metal is melted into droplets at high temperature and then uniformly distributed in the liquid slag; the reduced PGMs particles are attracted to the metal droplets and attached to the metal droplets; due to gravity, the metal droplets gather and settle to the bottom of the vessel, thus achieving the purpose of enrichment and separation. Metal trapping method can deal with insoluble carriers, and low-grade platinum group metal waste catalysts, with the advantages of strong adaptability of raw materials, low operating costs, weak reducing atmosphere, high trapping efficiency, and large production scale. It is especially suitable for treating poorly soluble carriers and spent catalysts with very low platinum group metal content. Nevertheless, it' low Rh recovery (65% to 70%) inevitably hinders the potential application. In terms of metal trap selection, this process requires consideration of the trap melting point, the solubility of the trap and platinum-group metals, slag and alloy separation, and metal loss.
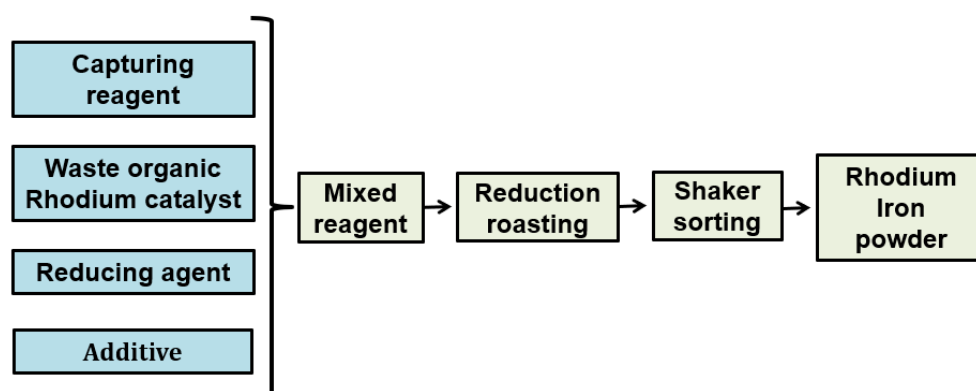
Figure 4. Flow chart for Rh recovery via metal capture.

Zhou et al. [60] proposed a process to recover Rh from waste organocatalysts by solid iron trapping. The effects of the reducing agent, trapping agent and reduction temperature on Rh recovery were systematically examined. It was shown that, after grinding and sorting, the solid-state reduction occurred at a reduction temperature of 1200 °C, a reduction time of 6 h, a coal dust ratio of 9% and an additive ratio of 8%, the Rh recovery was 96.53%. Zhao et al. [61] utilized the copper trapping method to recover

platinum-group metals from the failed auto catalysts. The results showed that, upon increasing CaO/SiO_2 mass ratio, the amount of trap and reductant, melting temperature and processing time, the recovery rate increased gradually and saturated after reaching a threshold value. The corresponding recovery rates of Rh, Pd and Pt were 97.6%, 99.2% and 98.2%, respectively, at a condition of CaO/SiO_2 mass ratio = 1.05, trap ratio of 35–40%, reducing agent ratio of 6%, melting temperature of 1400 °C and melting time of 5 h. In literature published in 2012, He et al. [39] developed a new process for the treatment of Rh-containing organic wastes in the acetic acid industry. Taking full advantage of the specific affinity of metal sulfides (CuS, FeS, Ni_2S_3, etc.) for platinum-group metals, Rh is recovered from the organic waste incineration slag using high nickel rhenium-aluminum thermal activation. High-activity Rh can be achieved with low demand for equipment. Compared with the wet treatment, which produces a large amount of harmful wasted water, the pyrometallurgical concentration can avoid the above problem with a short process flow. In addition, in the case of high-temperature metallurgical enrichment process, the Rh recovery rate can reach 94.65%.

The metal trapping method is based on the same principle as the plasma melting method, except that the equipment providing the required temperature for melting is different and the melting temperature is much lower than that of plasma melting. The metal trapping method involves the separation of the precious platinum from the molten catalyst by trapping the molten platinum into the metal melt at high temperatures, while the other carrier material and the additional slagging agent form a slag that can be easily separated from the metal melt. The main considerations in this method are the type of melt and the choice of trapping agent. The trapping agent should take into account its mutual solubility with platinum, melting point, loss of slag-entrained metal, and chemical properties. Various metals have certain advantages and disadvantages as trapping agents.
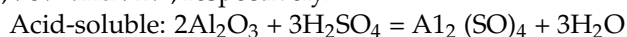
2.1.4. Volatilization

The treatment of spent catalysts with chlorine gas and chlorinating agents at high temperatures results in the formation of soluble chlorides or gaseous chlorides of platinum-group metals. Depending on this property, the platinum-group metals can be enriched from some failed auto exhaust catalysts by using chlorinated gas phase volatilization. Then, it is absorbed using water, alkaline solution, chloride complexes, or adsorbents, and then further recycled for processing. In a Japanese patent [62], platinum-group metals from exhaust gas cleaning catalysts of the failed automobile were recovered by high-temperature chlorination and volatilization method. At first, a chlorinating agent (e.g., NaCl, KCl, CaCl, NaF, and CaF_2) was added to the crushed failed auto exhaust catalyst. Then, a gaseous oxidizer such as Cl_2 or CCl_4 was passed into the closed high-temperature furnace and chlorinated at high temperature of 1000~1200 °C and absorbed by NH_4Cl solution, and the Rh recovery rate can reach 85~90%. In addition to the recovery of platinum-group metals by chlorination, some carriers of failed auto exhaust catalysts can be removed by volatilization and chlorination, thus enriching platinum-group metals.

The chlorination gas phase volatilization method has the advantages of a simple process, low reagent consumption and low energy consumption, but the high temperature chlorination in the production process has a corrosive effect on the equipment, resulting in high requirements for the equipment; the waste catalyst has the phenomenon of adsorption of chlorine gas and the need to wash the waste catalyst with N_2 before feeding, as well as the need to deal with a large amount of toxic gas in the whole recovery process, thus limiting its technical application. In addition, attention should be paid to chlorination treatment in production to prevent it from causing harm to human body and environment.

Overall, thermal recovery has significant advantages over the wet process in terms of platinum recovery rates and environmental aspects. As the environmental impact of the wet process becomes more severe and the grade of platinum in the spent catalyst becomes lower, the wet process can no longer meet the current recovery production situation. The thermal process has many advantages due to its shorter process flow, less wastewater, lower environmental impact and a wide range of raw material grades. Thermal recovery technology will be the main technology for secondary resource recovery of platinum in the future. Therefore, the research work on pyroprocessing for platinum recovery will be continued in the following process.

2.2. Hydrometallurgical Process

In the late 1960s, the hydrometallurgical process began to be applied in recycling precious metals and gradually became one of the prevailing methods in this field [63,64]. Wet metallurgy relies on solutions such as acids or bases to dissolve metal components, which are then concentrated and purified to recover the involved metal [14,65]. The wet process mainly includes pretreatment, leaching and extraction processes. Catalysts are mainly composed of two parts: the carrier and the active material, and the catalysts of different industries have different applications and different carriers. For example, most of the catalyst carriers for the automotive industry are α-Al_2O_3 and ceramic cordierite; for the petroleum industry, the catalyst carriers are generally alumina; more commonly used industrial carriers are silica, activated carbon, molecular sieves, etc. During the catalytic reaction, the platinum group metal particles in the carrier are in a dynamic equilibrium moving inside and outside, and due to thermal diffusion, the temperature rises and the γ-Al_2O_3 around the metal particles turns into α-Al_2O_3. The catalyst may sometimes adsorb organic matter and bring in other impurities, resulting in carbon accumulation on the catalyst surface. Therefore, according to the physicochemical properties of different types of catalysts, corresponding pretreatment measures, such as grinding, roasting and leaching, are used to improve the leaching rate of platinum-group metals. Huang et al. [66] used cyanide to recover platinum-group metals from automotive exhaust gas catalytic systems by means of pressurized leaching. The pretreatment effect on the subsequent cyanide leaching rate of platinum-group metals was investigated by analyzing the material size, solid content, alkali dosage, leaching temperature, leaching time and pressure in the reaction process. The results demonstrated that the encapsulation of platinum-group metals by catalyst carrier could be destroyed during the pretreatment procedure, which facilitated cyanide leaching. The optimized process conditions are determined as follows: 90% of spent catalytic particles with a size less than 74 μm, slurry solid ratio 4:1, alkali content 10%, reaction temperature at 160 °C for 2 h and total pressure of constant system at 2.0 MPa with initial oxygen partial pressure of 1.0 MPa. Under the above optimal experimental condition, the cyanide leaching rates of platinum-group metals, Pt, Pd and Rh can reach 96%, 98% and 92%, respectively.

Acid-soluble: $2Al_2O_3 + 3H_2SO_4 = Al_2(SO)_4 + 3H_2O$

Alkali-soluble: $Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$

Dissolution is one of the most important steps in separating the carrier from the platinum-group metals in spent catalysts, and three methods are commonly used: carrier dissolution, active component dissolution and total dissolution. The carrier dissolution method is to dissolve the failed catalyst carrier so that the platinum-group metals are enriched in the insoluble slag, which has stable chemical properties and is difficult to be eroded by common mineral acids. The spent catalyst carrier alumina, however, is an amphoteric oxide that is both soluble in acids to produce aluminum salts that are easily soluble in acidic solutions (pH < 4) and soluble in bases to produce partial aluminates that are easily soluble in alkaline solutions (pH > 13). Therefore, acid-soluble or alkali-soluble methods are used to treat alumina carrier catalysts so that they are transferred into solution and separated from the active component to enrich platinum-group metals. The carrier dissolution method is suitable for the treatment of catalysts with γ-Al_2O_3

carrier, but if the carrier is α-Al$_2$O$_3$, the dissolution rate is not high and other methods must be used to separate α-Al$_2$O$_3$. In addition, the alkali dissolution method requires much equipment and the operation of solid-liquid separation is difficult, so it is not used much in practice. The active component dissolution method, which is the opposite of the carrier dissolution method, is the use of one or more oxidant hydrochloric acid solutions to dissolve the platinum group metal components in the waste catalyst, so that the PtCl$_6^{2-}$, PdCl$_4^{2-}$, RhCl$_6^{3-}$ ion form into the solution, and are then extracted from the solution. With the active component dissolution method, the reagent consumption is low, the recovery cost is low, and the recovery rate is high, but the leaching residue still contains a high level of platinum-group metals, which will cause a lot of waste if not recovered reasonably. In contrast, the total dissolution method is to dissolve both the carrier and the active component of the spent catalyst into solution in the presence of an oxidizing agent, mixed with one or two acids, and then extract the platinum-group metals from the solution. High recovery of platinum-group metals can be ensured, but the acid consumption is high, the treatment cost is high and, like the carrier dissolution method, it is only suitable for the treatment of catalysts with γ-Al$_2$O$_3$ as a carrier. In order to concentrate and purify the platinum-group metals in the leachate, suitable methods must be used. The main methods currently used are reduction precipitation, solvent extraction and ion exchange. They are described in detail below.

2.2.1. Extraction Method

In 1971, International Nickel Corporation (INCO) first employed solvent extraction for the recovery of the precious metal gold. At that time, dibutyl carbitol (DBC) was used as an extractant, while oxalic acid was subjected to stripping to recover solid gold until the 1980s. Afterward, INCO had a fairly complete range of extraction processes which were gradually applied to the recycling of secondary resources, such as waste catalysts in the automotive or chemical industries and precious metal scrap in the electronics industry. The extraction efficiency is a measurement of the activity of the Rh catalyst and is related to the ease of extraction and the degree of deactivation [67]. Among the processes for extracting Rh, most studies focused on the choices of extractant and stripping agents. Extractants were applied to the extraction of platinum-group metals, primarily oxygen, sulfur, phosphorus and nitrogen-containing extractants. American Eastman Kodak company disclosed a process for the recovery of Rh catalysts from the carbonylation of methyl esters to acetic anhydride systems. After adding an equal amount of dichloromethane and HI solution to tar containing the Rh catalyst, 28% ammonia water was added, followed by vigorous shaking for 30 s. The as-obtained mixture was allowed to stand for 10 min, layered and finally repeatedly extracted to obtain the Rh. The Rh recovery rate in the above process can reach 98%. In addition, the aqueous solution containing the catalyst can be returned to the reactor for recycling [68]. As reported by Fuchs et al. [69], for the first time, an effective reactive extraction method was successfully developed; that is, adopting acetic acid aqueous solution for ectopic reaction extraction of *bis*-hydroaminomethylation (*bis*-HAM) products formed a water-soluble ammonium salt. The generated ammonium salt was primarily present in the aqueous phase, while the Rh complex remained in the nonpolar organic phase, so that Rh could be successfully reused in a three-cycle operation.

Yang et al. [70] reported the development of a novel thermoregulated polyethylene glycol (PEG) biphasic system consisting of PEG-400/1,4-dioxane/n-heptane. By applying this system to the hydroformylation of 1-dodecene catalyzed by a phosphate-containing modified Rh complex TMPGP (P[O(CH$_2$CH$_2$O)$_n$CH$_3$]$_3$, n = 8)(Figure 5), the conversion of 1-dodecene and the yield of aldehyde reached 96% and 94%, respectively. The catalyst showed no significant loss of catalytic activity after 23 cycles with an average Rh loss per run of 0.65%.
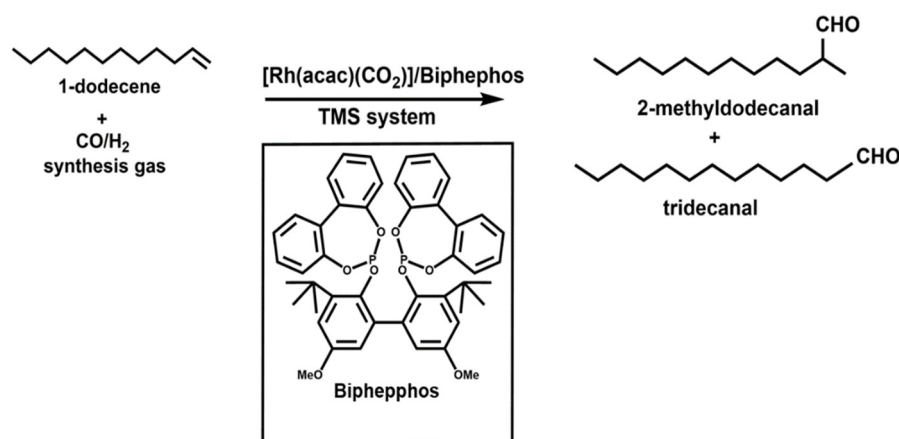
Figure 5. The hydrotormylation of 1-dodecene [70].

In recent years, the rapid development of catalysis technology and homogeneous catalysis reaction has also made a significant impact in this field. Although homogeneous operation mode generally shows high selectivity and mild reaction conditions, it is challenging when effectively separating and recycling metal catalysts [71]. The first industrial-scale application of homogeneous transition metal catalysts in the chemical industry is hydroformylation; however, two-phase extraction techniques were unable to recover the catalyst used for this reaction. Researchers have found that when two or more extractants are used to extract platinum-group metals or their compounds simultaneously, a co-extraction effect can be produced and the extraction rate can be improved. Yu et al. [72] designed a triple-liquid-phase system (TLPS) to study the extraction and separation of Pt, Pd and Rh, which allows the extraction of different target components into three different liquid phases in a single-step operation. His research system consists of polyethylene oxide-polypropylene oxide random block copolymer (EOPO), diisopentyl sulfide (S201), H_2O and Na_2SO_4. The results showed that the salt concentrations, salt type and the coexisting H^+ and Cl^- concentrations in Na_2SO_4 aqueous solution significantly affect the phase separation of Rh, Pt and Pd. Under optimized operating parameters, Pt (IV) and Pd (II) can be selectively separated from Rh (III).

Ionic liquids have been considered as excellent alternative solvents in platinum-group metals (PGM) extraction due to their low toxicity, low volatility and high thermal stability. Yan et al. [73] presented a route for the extraction and separation of Pt, Pd, Ru and Rh from the mixed imidazolium-based ionic liquids. It was mentioned that the separation of Pt from the other three platinum-group metals was achieved using a mixture of three different ionic liquids. Secondly, the concentration of ionic liquids was adjusted to achieve the separation of Pd and Ru from Rh. This result provides more insight into extracting and separating metals.

Brunsch et al. [74] utilized the concept of temperature-controlled multicomponent solvent systems (TMS) in the hydroformylation of long-chain olefins (Figure 6). The principle of TMS essentially depends on temperature-dependent phase behavior. Because TMS is a homogeneous phase during the reaction, mass transfer restrictions will not occur. As the temperature decreases, a miscibility gap appears in the system leading to two liquid phases: nonpolar and polar liquid. Organic products are dissolved in the nonpolar phase, while the catalyst is dissolved in the polar phase. The products and catalysts can be separated by different solubilities in their phases. The reacted and separated non-polar product phase can be purified in down-streaming process, while the polar catalyst phase will be recycled. However, if the product phase dissolves the catalyst, the loss of catalyst cannot be avoided. For the first time, Behr et al. [75] performed an effective catalyst recovery of these long-term stable nanoparticles in a heat-set multi-component solvent system. In his study, the catalyst phase was recycled three times without significant degradation in activity. After cycling, Rh nanoparticles remain active catalysts.
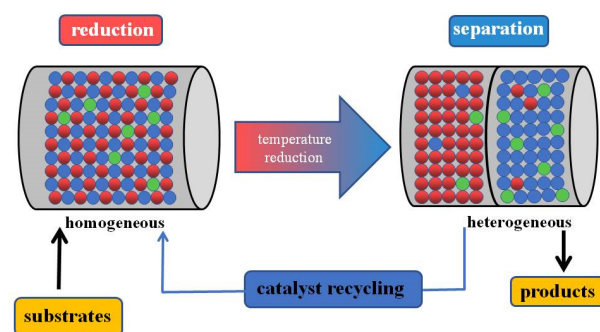
reduction

separation

temperature
reduction

homogeneous

heterogeneous

substrates

catalyst recycling

products

Figure 6. TMS catalyst recycling concept [74].

Solvent extraction is an efficient separation method with the advantage of good separation effect, simple operation, high safety and low energy consumption in the process.

2.2.2. Coprecipitation

Precipitation is the most common method for recovering platinum-group metals from spent catalysts and has been used for a long time and is still being developed and refined. The precipitation method can be divided into precipitation separation and co-precipitation separation. The precipitation separation method is suitable for the separation of macronutrient components (above the order of milligrams), while the co-precipitation separation method is mainly suitable for the separation of trace components (less than 1 mg/mL). Co-deposition is a method of enrichment by simultaneous deposition of a substance and the substance to be enriched. In the precipitation separation method, on the one hand, high recovery of the trace component to be separated and enriched is required, and on the other hand, the co-precipitant does not interfere with the determination of the component. It is required to select the appropriate co-precipitant and precipitation conditions in order not to interfere with the determination of the component. The co-precipitant and precipitation conditions should be selected according to the specific requirements in order to obtain a satisfactory separation and enrichment effect. The co-precipitation method is one of the effective methods to enrich trace precious metal components. After the addition of co-precipitant and reducing agent in the sample solution, the co-precipitating carriers precipitate out of the solution together with the carriers during the precipitation process through adsorption, entrapment and mixing crystals, thus separating them from the matrix elements. Commonly used precipitating agents include tellurium, thiourea, etc. In recent years, the use of new precipitating agents has effectively shortened the analysis time. Co-precipitation or precipitation of trace precious metals using inorganic or organic trapping agents to separate them from a large amount of matrix material is one of the common methods used for precious metal analysis and enrichment separation. Since rhodium is much more difficult to dissolve than other platinum-group metals, solutions or metal salts containing rhodium obtained during the refining process should not be readily reduced to metal without confirming their purity to the required level. In order to co-precipitate trace precious metals, the co-precipitating substances used are generally amorphous precipitates with a large active surface area, such as thiourea, sodium sulfide, sodium nitrite, ammonium chloride, etc.

(1) Thiourea precipitation method

The thiourea precipitation method is based on the fact that all the chloride complexes of the precious metals can generate a variety of complexes with a molecular ratio of 1:(1~6) with thiourea, such as $[Pt(Tu)_4]Cl_2$, $[Pt(Tu)_2]Cl_2$, $[Ph(Tu)_3]Cl_3$, $[Ph(Tu)_5]Cl_2$, etc. These complexes are destroyed when heated in concentrated sulfuric acid medium to produce the corresponding sulfide precipitates, while the base metals do not undergo similar reactions and continue to be retained in solution, thus achieving the separation of precious and base metals. In operation, 3~4 times of the total amount of precious metals are added to the solution to be treated, then sulfuric acid of the same volume as the solution is added, heated

to 190~210 °C and then held for 0.5~1 h. After cooling and diluting in 10 times the volume of cold water, the precious metal concentrate is obtained after filtering and washing. This method is good for the separation of precious and base metals, especially for a variety of complex solutions, but the operating conditions are poor, and usually less used.

(2)　Sodium sulfide precipitation method

The sodium sulfide precipitation method is to add Na_2S to the capacitated solution containing platinum-group metals, so that the precious and base metals in the solution under certain operating conditions are generated by sulfide precipitation, and then to dissolve the base metal sulfide with hydrochloric acid or controlled potential chlorination to achieve the separation of precious and base metals. At room temperature, sodium sulfide can directly precipitate gold (III) and palladium (II) from their chlorine complexes and rapidly form the corresponding sulfide precipitate in the solution. However, when reacting with Rh(III), only ligand exchange occurs first, and the reaction rate is slow; at boiling temperature, if sodium sulfide is added quickly and the dosage is too much, it can generally generate the corresponding thio-salt. In order to separate the precious and base metals, the following operation can be used: add an excess Na_2S to the mixed solution of precious and base metals, keep the pH value at 8~9, and boil for a while, so that the precious metal chloride ligands are converted into various thio-salts. Then acidify the solution with hydrochloric acid to pH = 0.5~1 and boil for 0.5 h, at which time the precious and base metals are all converted into easily settled and filtered sulfides. Submit the filtered mixed sulfide into hydrochloric acid, heat them and add appropriate oxidant into the above mixture to leach base metals, and the produced slag is the enriched precious metal sulfides with aqua regia dissolving for the subsequent separation and purification. This method is rarely used now because the precious metal sulfides are often not easily destroyed, and the reaction is often abnormal in the subsequent separation and purification process.

(3)　Sodium nitrite with hydrolysis precipitation method

Sodium nitrite with hydrolysis precipitation method is the use of platinum-group metals and chlorine with an acid salt solution, which after treatment by sodium nitrite can be converted into more stable soluble nitrite complexes, while the base metals other than Ni and Co do not form nitrite complexes. By adjusting the pH of the solution, the base metals can be precipitated out as hydroxides, achieving the separation of precious and base metals.

The nitrite complexes of Pt, Rh and Ir can exist stably in a solution of medium alkalinity. Even if the pH is 10, boiling still does not decompose them; the other base metals have been hydrolyzed and precipitated at pH < 8. In the precious/base metal separation process, gold is directly reduced to metal and can be recovered by the dissolution of the base metal hydroxide precipitates and filtration. In addition, the base metal hydroxide can adsorb precious metal complexes, which is not easy to be washed. Because the resulting precious metal nitrite complexes need to be converted into chlorine complexes through hydrochloric acid destruction, the process is also a relatively complicated operation and is now rarely used.

(4)　Ammonium chloride precipitation method

Ammonium chloride can generate corresponding ammonium precipitates of different colors with chloride complexes of precious metals, which have low solubility in water and even lower solubility in ammonium chloride solution, and can fully wash out the entrapped base metal ions with a certain concentration of ammonium chloride solution, to achieve effective separation of precious and base metals; this method is widely used in the refining of platinum-group metals. George et al. [76] studied the mechanism and kinetics of Rh^{3+} co-precipitation with CuS upon adding excess aqueous thiosulfate to metal sulfate solutions. First, a homogeneous reaction occurs before nucleation, followed by the growth of heterogeneous crystals. During this process, metal sulfides are automatically catalyzed. At the initial stage of ionic precipitation, there is competition between Rh^{3+} and Cu^{2+} within the hydrogen sulfide aqueous solution, resulting in precipitation of most

of the Rh. When $[Rh^{3+}]$ falls below $[Cu^{2+}]$, the total reaction rate of Rh^{3+} will be much lower than that of Cu^{2+}, which can deplete available sulfides and restrain the amount of ionic Rh^{3+} precipitation. Eventually, the concentration of Rh^{3+} is two orders of magnitude lower than that of Cu^{2+} and the temperature ranges from 50 to 150 °C. The heterogeneous cationic substitution reaction has been identified as a new precipitation path in metal sulfide co-precipitation. According to this study, the concentration of metal ions and the reaction temperature are confirmed as the main factors affecting the precipitation rate of metal sulfide.

Researchers [77] investigated different precipitants, providing H-, Cl-, CO- and acac-source reagents, along with fresh triphenylphosphine (TPP), to produce easily precipitated substances such as $RhCl (CO)(TPP)_2$, $HRh (CO)(TPP)_3$ and $Rh (CO)(acac)(TPP)$ (acac is an acetylacetonate base), to separate Rh from the spent catalyst. The process is simple and mature and the partially deactivated catalyst is activated directly. However, the higher the degree of catalyst deactivation, the more difficult it is to form precipitates. As a result, the recovery rate is greatly reduced, indicating that it depends heavily on the activity of the Rh catalyst in the spent catalyst solution. Japan Mining Metal Co. Ltd. invented a way to refine Rh-containing hydrochloric acid solution, wherein the solution also contains Ag, alkaline earth metals and other heavy metal impurities [78]. First, alkali is added to the solution to adjust the pH within the range of 7 and 12. After all components other than Rh are neutralized and precipitated, the solution is then filtered and separated. Then, hydrochloric acid is added to control the molar ratio of Cl: Rh in the solution. Ag is removed by a heating and cooling treatment. In the final step, the previously obtained solution was extracted with bis(2-ethylhexyl) phosphate acid (DEHPA). Through the above steps, the recovery of Rh from the aqueous phase can be ensured, while heavy and alkaline earth metals can be removed. Hermann et al. [79] developed a process for the recovery of noble metals from dilute aqueous and non-aqueous solutions, which contain salts of non-noble metals and other less volatile inorganic or organic compounds. At first, the Rh-containing catalyst solution is mixed with elemental tellurium or a reducible tellurium compound. Then the solution is stirred at a temperature of 100 °C to 250 °C for 1 to 3 h. Finally, the Rh precipitate is acquired via precipitation. The recovery rate of the above method is higher than 98%. Except for a slight entrainment loss, tellurium is not absorbed by organic waste streams, so its consumption is very small. The U.S. Patent (No. 5256188) provides a method by which Rh is separated from an organic solution, organic water mixture or aqueous solution complexing agent by reacting with bismuth or a reducible bismuth compound to form precipitates [80]. In this method, bismuth in the homogenous catalysis is added to the residue of a homogeneous catalytic aqueous solution containing Rh. After sulfuric acid is added to adjust the pH to about 2, the solution is refluxed at a temperature of 200 °C for 12 h. Finally, Rh recovery can be achieved after filtering out the precipitate.

The advantages of the reduction precipitation method are simple equipment, low investment and large treatment capacity. Inconvenient operation and a slow reaction speed, however, limit its applications. In addition, the introduction of other elements when adding precipitating agents, especially those containing metal elements, increases the difficulty of post-treatment. The amount of sludge generated is large and difficult to recycle, and it is easy to produce secondary pollution of sludge.

2.2.3. Adsorption Separation

Recently, adsorption separation has emerged as a new technology, based on adsorption of certain elements or ions by an adsorbent. This method separates dissolved Rh-phosphorus complex catalysts from high-boiling-point organics by adding adsorbent for pure physical separation (Figure 7). In particular, it benefits from the application of ion exchange resin technology for adsorption. The ion exchange method is a method of separation by using ion exchange agents to exchange ions in solution. Depending on the nature of the functional groups they contain, ion exchange resins can be classified into seven categories: strongly acidic, weakly acidic, chelating, redox, weakly basic, acid-base

amphoteric and strongly basic [81]. Since ion exchange occurs between similar ions, and platinum-group metals tend to form complex anions, anion exchange resins are the majority of resins used in platinum group metal separation. Compared with conventional hydrometallurgy, adsorption separation is more promising by its high separation efficiency, low cost, simple equipment and operation [25,82–87]. We believe that it will gradually become the most desirable option for the recovery of low concentrations of PGMs.
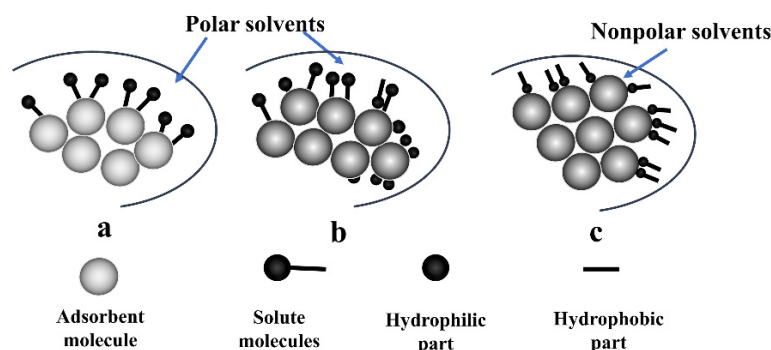
Figure 7. Schematic diagram of adsorption action of large-grid adsorbent. (**a**) In polar solvents, the adsorption of non-polar adsorbents. (**b**) In polar solvents, the adsorption of moderately polar adsorbents. (**c**) In non-polar solvents, the adsorption of moderately polar adsorbents.

Japanese patent (No. 51-048519) provided a method for a complete separation of Rh-phosphine complexes from high-boiling-point or gelatinous distillation residues formed by organic reaction [88]. The Rh phosphine complex catalyst is adsorbed and separated by adding a selective adsorbent material to the mixture. The adsorbents used are carbonates and alkaline earth metal silicates, with magnesium silicate being preferred. The surface area of the adsorbent generally covers the range from 100~1000 $m^2 g^{-1}$, with a recovery rate of Rh > 90%. In 2018, Ibrahim et al. [89] reported a selective and efficient Rh recovery process under modest working conditions. This method utilizes CO to extract Rh nanoparticles on a variety of polar solvent carriers. In comparison with traditional recovery technologies, it operates at a low temperature and does not require strong acids. In the presence of other precious metals, the newly reduced sample is still very selective for Rh with a leaching rate exceeding 90%. The metals are obtained in the form of highly reduced multi-core clusters. Similar to CO, as a leaching agent, formic acid is also able to extract Rh from the spent catalysts under milder conditions. A.C.R. Brown et al. [34] recovered Rh from a spent catalyst solution with the aid of ion exchange resins that bonded with metal components. After calcination and purification processes, the Rh powder was obtained. Using this method, the Rh catalyst can be recovered from the homogeneous catalytic hydroformylation reaction of olefins with CO. Panster et al. have successfully recovered Rh by suspending an organosiloxane-based absorbent in HNBR solution via the stirred kettle method [90]. The absorbent was removed from the solution after a suitable residence time. Alternatively, by employing a column method in which the catalyst is fully absorbed in an absorbent, the combustion residue was collected by incineration or by extraction with a suitable solvent. Li et al. [91] investigated the direct adsorption of catalysts from HNBR mastic with a macroporous ion exchange resin and analyzed the adsorption capacity of Ru and Rh precious metals in hydrogenated nitrile rubber (HNBR) chlorobenzene mastic. The resin was pretreated with 2 wt% NaOH and 5 wt% HCl solution and then soaked in ethanol and acetone solution in turn to load the column. A certain amount of HNBR mucilage was slowly added to the column to control the effluent rate, which was substituted by chlorobenzene. At 90 °C, the adsorption rate of metal Rh was over 95% using A40, R01 and R02 resins, while the recovery via resin incineration can exceed 98%. A Chinese Patent (No. CN102923796A) developed a technique to recover Rh from the spent catalysts of carbonyl synthesis [92]. The researchers first added silica adsorbent into the waste containing Rh catalyst after the carbonyl synthesis reaction. Then, a high-temperature dry

distillation and roasting were performed, before adding concentrated hydrochloric acid to the resulting residue. Ozone was passed into the system until there were no black particles in it. After performing filtration and washing, rhodium chloride acid solution was acquired. Finally, impurities such as Fe, Ni and Ca were removed by ion exchange and the solution was concentrated and dried to get hydrated rhodium chloride. The described procedure combines incineration and liquid phase digestion, which overcomes the low efficiency arising from the all-liquid phase method and large loss stemming from the incineration method. Additionally, this approach has the characteristics of high efficiency, simple operation and low loss. Benefiting from this process, the recovery rate of Rh is greater than 99% and the content of total impurities within the produced rhodium chloride hydrate is less than 0.5% [93]. Although the adsorption method is straightforward, a deeper insight is still required to gain a high and stable recovery of Rh. Apart from the Rh dissociation problem from adsorption resin, the introduction of resin incineration is not only costly but also brings a risk of serious secondary pollution.

Compared with the pyrometallurgical process, the hydrometallurgical approach provides the following merits: (a) suitable for small-scale treatment at a low cost; (b) excellent quality of recycled precious metals; (c) mild reaction conditions and low energy consumption [47]. However, it is obsessed by the following problems: (a) the process is complicated and a certain amount of precious metals is lost; (b) the alkaline or acid leaching agent is highly corrosive, causing inevitable secondary pollution to the environment; (c) the extractant and diluent in the extraction are highly toxic, resulting in a potential threat to environment and human health; (d) a huge amount of wastewater is generated, containing spent chemical solvents that are difficult to treat or recycle [64].

2.2.4. Other Methods

The oxidation method [77] employs oxidizing agents to disrupt the coordination of ligands with Rh metal in catalyst under appropriate conditions, resulting in Rh as Rh^{3+} or solid particles, which are then separated from the catalyst waste stream. Though the hardware requirement of oxidation method is simple, the overall recovery rate is low. Chen et al. [94] invented a way to refine Rh-containing waste catalysts out of a hydroformylation reaction by treating them with hydrogen peroxide. As a result, nearly 90% of total Rh is recovered in the form of precipitation by keeping the reaction temperature at 100~150 °C for 1 h~3 h. The remaining solution is concentrated and processed into Rh slag. Then the as-obtained slag is incinerated for 2~4 h to remove the residual carbon. Owing to the existence of other metal impurities, the final rhodium trichloride hydrate merely serves as crude material.

Yang et al. [95] provided a method to recover Rh from the spent catalysts in carbonyl synthesis reactions. The carbonate of alkali metal or alkaline earth metal was added to the waste catalyst and incinerated at 650 ~700 °C. The residue after incineration was crushed and then dissolved by adding an appropriate amount of alkali metal acid sulfate at an elevated temperature. The waste Rh species converted into soluble $Rh_2(SO_4)_3$. When the as-obtained solution was poured into the cathode chamber of an electrolysis device at a controlled potential, Rh powder was plated at the cathode. The single process recovery rate can reach more than 96% with a purity as high as 99.95% in the final powder.

Photocatalytic reactions produce free radicals with high reactive properties, which can interact with other substances. In addition, photocatalysis has the advantages of low energy consumption, simple operation, high efficiency and zero emission of hazardous waste. Chen et al. report a photocatalytic process for the selective recovery of elemental Rh from spent circuit boards, spent catalysts and ores [96]. The whole process does not involve strong acids or bases or toxic cyanides, but only the addition of a photocatalyst, (e.g., TiO_2) in a MeCN-DCM solvent and exposure to light. By a simple reduction reaction, more than 99% of the target elements can be dissolved with a purity of 98% and the catalyst can be reused more than 100 times by experiments.

2.3. Biosorption

As mentioned earlier, both pyrometallurgical and hydrometallurgical processes are widely adopted to recycle precious metals from waste. Unfortunately, the corresponding time and labor costs of both methods are relatively high. At the same time, from the process point of view, because many chemical reagents are added during the treatment process, a large amount of secondary waste is generated. The reprocessing of these wastes is also tricky. Therefore, it is necessary to develop a low-cost and environmentally friendly precious metal recovery process for Rh recovery from wastewater.

Biosorption is based on the usage of active or inactive microorganisms and their metabolites, (including yeasts, bacterial active matter, bacteria, fungi, algae and some biological wastes) [97], to adsorb metals through physical interactions and/or chemical reactions (including complexation and deposition, redox and ion exchange, etc.) [54,98]. The mechanism of metal biosorption is relatively complex. The state of the biomass (active or inactive), type of biomaterial, chemical nature of the metal solution, and the environmental conditions, affect the mechanism of metal biosorption on the basis of physicochemical interactions in the form of chelation and complexation of metal ions, ion exchange, and electrostatic interactions, between functional groups on the cell surface and metal ions (Figure 8). The process parameters affecting the biosorption of precious metals are listed as follows [99].
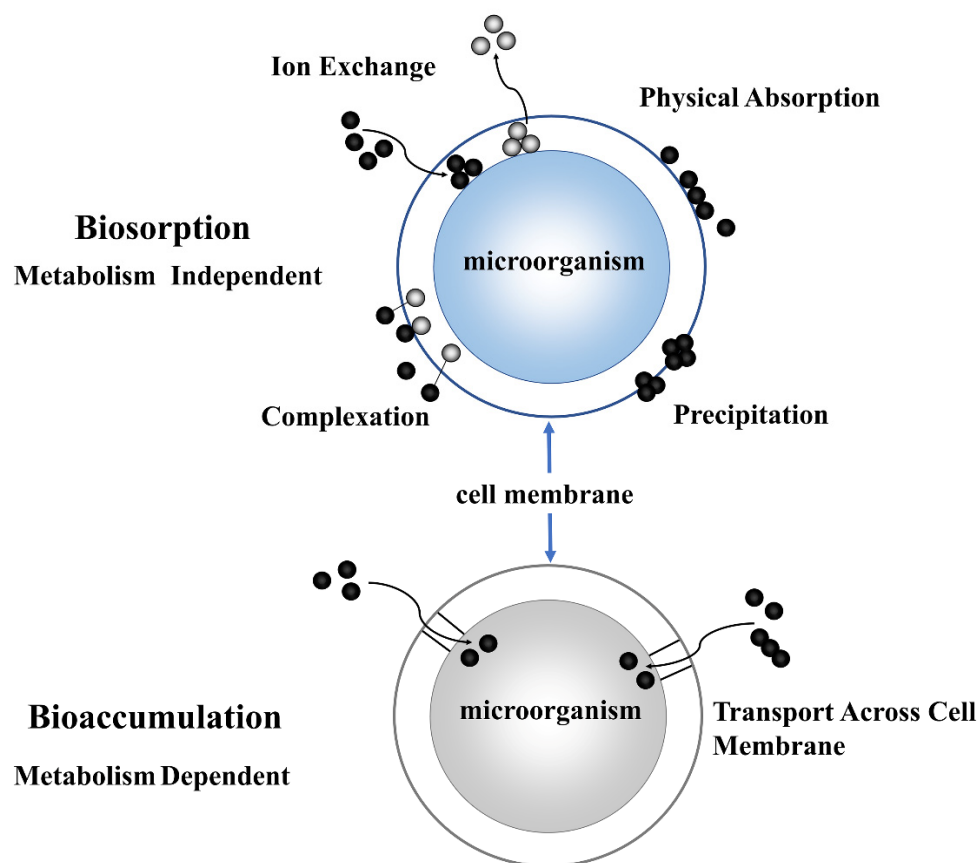
Figure 8. Mechanisms of biosorption and bioaccumulation of metal ions by microorganisms.

(a) Solution pH serves as the most important factor influencing both adsorption process [100] and the exposure of the adsorbent binding sites. The optimal adsorption pH (1.0–3.0) for platinum-based metals is generally low [101].

(b) Biosorbent dosage. Decreasing the surface area of the biosorbent increases the number of binding sites, while the number of solutes adsorbed per unit weight of biosorbent decreases with increasing biosorbent dosage.

(c) Initial solute concentration. The higher the concentration, the greater the solute uptake, which is due to the lower ratio of the initial molarity of the solute to the effective surface area at lower initial solute concentrations. Subsequently, the number of adsorbed solutes is independent of the initial metal concentration.

(d) Stirring speed and period. By adjusting the stirring speed, the mass transfer resistance of the system can be reduced.

(e) Reaction temperature usually affects the stability of the precious metal ions in solution [48], the stability of the ions with the adsorbent fit, and the ionization of the cell wall chemistry.

(f) Ionic strength also affects the solute adsorption on the biomass surface, which can be attributed to a competition between ions, i.e., other competing ions may compete with the major metal ions for adsorption sites or reduce the properties of the adsorbent.

The biosorption of precious metals could be governed by chemisorption and/or physisorption mechanisms. Considering the adsorption groups of microorganisms, the main mechanisms include complexation, ion exchange adsorption, electrostatic mechanism, micro-precipitation mechanism, enzymatic mechanism, redox mechanism, etc. [102,103]. (1) Complexation mechanism: the microbial cell wall (mainly sugars, proteins, lipids and pigments) contains a variety of functional groups, such as hydroxyl, carboxyl and phosphate groups, which can be ligand-binding with heavy metals [104,105]. (2) Ion exchange adsorption mechanism: some pre-existing ions such as Ga^{2+}, Mg^{2+} and OH^- ions are replaced by the target heavy metal ions in solution and exchange adsorption with heavy metals. (3) Electrostatic mechanism: some charged groups on the surface of microbial cells exert an electrostatic effect on the heavy metals in solution and thus adsorb on the surface. (4) Micro-precipitation mechanism: some microorganisms react with heavy metals in the cell wall or inside the cell to produce precipitates. (5) Enzymatic mechanism: microorganisms use their biomass enzymes to transport some of the precious metals into the cell, thus acting as recycling agents. (6) Redox mechanism: certain enzymes secreted by microorganisms undergo redox reactions with metal ions. One of the unique and effective ways of fabricating novel biosorbents is to enhance biosorption by cell surface engineering. Microorganisms are endowed with a large contact area with metal ions in the environment due to their small size and resultant large specific surface areas. The bounded metal ions can be easily recovered without disrupting the integrity of cells. Moreover, provided the metal-binding molecules anchored on the cell surface are functionally active, the biosorption capacity of the cells can be maintained, even if an inanimate biomass is used.

Garcia evaluated the biosorption of platinum-group metals (Pd, Ru, Ir, Rh, Pt) using plant powder of Eichhornia crassipes. The recovery adsorption capacity of Rh reached 67.6% at an initial concentration of 14 mg/L. By investigating the mechanism, they concluded that the high density of carboxylates in the root system is one of the main roles of biosorption [106]. Gao et al. used waste P. pastoris and recombinant P. pastoris as new adsorbents to study the adsorption of Rh (III). Under the adsorption conditions of pH 1.2, temperature 30 °C and adsorption time 2 h, the maximum adsorption rates of waste P. pastoris and recombinant P. pastoris were 55.69% (110.1 mg g^{-1}) and 75.03% (142.11 mg g^{-1}), respectively. They found that the absorption peaks of O-H, C-O, amide II band, amide III band and sugar were shifted after adsorption, indicating that hydroxyl, amino, protein and sugar on the surface of the cell wall of P. pastoris GS-R play an important role in the adsorption of Rh (III) [107]. Ngwenya et al. carried out a quantitative analysis of Rh (III) removal by stationary sulfate-reducing bacteria (SRB) under different biomass, initial Rh concentration, electron donor, temperature and pH conditions [108]. It has been shown that SRB cells have a stronger affinity for anionic Rh species compared with neutral species and cations. They found that SRB were indeed capable of recovering and subsequently reducing Rh from highly concentrated solutions (>200 mg L^{-1}). When the cells were exposed for 90 min, Rh-rich precipitates were observed inside SRB cells. After exposure for 9 h, high-density Rh zones existed at the exterior and periphery of SRB cells. Yousif

prepared a new chelating biosorbent with iminodiacetate functionality [109] and produced a resin (R-COONa) with better adsorption of Rh (III) in dilute solution. In the column experiments, the breakthrough points of Pd (II) and Pt (IV) were faster than those of Rh (III). This study suggests an immense potential for selective adsorption of Rh in spent catalyst converters containing palladium and platinum.

In recent years, a great deal of studies on biosorption have proven it to be a cost-effective biological method with great promise. This type of biomass is relatively inexpensive, readily available, and can be used in situ with proper designation. Notably, the immobilization of biomaterial is another key factor that needs to be addressed before applying biosorption. In addition to cost reduction, it is also important to reduce the distribution, regeneration, and recycling of biosorbents. The pursuit of a balance between energy cost and environmental impact is also one of the research directions for Rh recovery. With the rapid application of biotechnology in metal recovery, these problems are expected to be partially solved soon. However, there is still a long way to go before biosorption can be commercialized at a large scale [110,111].

3. Conclusions and Prospect

As precious metals are heavily used in industrial catalysts, functional materials, and electronic products, related applications are restrained by their insufficiency in nature. However, the above problem can be generally solved under consideration of the existence of many kinds of secondary resources of precious metals. As the content of precious metals from different sources varies greatly, the environmental pollution problem in processing puts forward higher requirements on the secondary resource enrichment technology of precious metals. This review provides an overview of the processes used to recover the spent catalysts. These are divided into hydrometallurgical, pyrometallurgical and biosorption processes, all of which have merits and demerits. In the current industrial practice, the pyrometallurgical process benefits from its short processing period, lower emission of wastewater, and lower economic cost. Nevertheless, it requires a lot of energy and investment and causes environmental pollution. In contrast, hydrometallurgy allows small-scale processing at a cost of mild reaction conditions and low energy consumption. However, the corresponding process is complicated and generates large amounts of wastewater containing spent chemical solvents. Bio-recycling processes are flexible and cost-effective while avoiding secondary waste generation. In addition, the bio-recycling process is sustainable compared to other conventional metal recovery methods. Nevertheless, it suffers from low Rh recovery efficiency. It is clear that current technology is deficient and still has a long way to go before industrialization.

Currently, the recovery of spent Rh catalysts relies mainly on a combination of pyro-processing, wet metal separation, and subsequent purification processes. With the growing demand for avoiding large-scale disposal and the requirement of environmental protection, in addition to developing new recovery processes, it is necessary to further optimize the existing recovery process and improve the industrial chain of spent catalyst recovery. We suggest that we can start from the special characteristics of secondary resources of precious metals, increase the investment in developing secondary resources recovery technology, and gradually establish a robust and efficient recovery system for precious metals. Secondly, in the future, we shall be able to use secondary resources efficiently without increasing the environmental burden while keeping certain economic benefits. Finally, since there are many valuable metals in secondary resource waste, we hope to achieve simultaneous recovery and comprehensive utilization of other valuable resources while enhancing the recovery rate of precious metals.

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