Heliyon 10 (2024) e25283

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Review article

# Extraction of platinum group metals from catalytic converters

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ARTICLE INFO

*Keywords:*
Platinum group metal (PGM)
Catalytic converter
Spent catalysts
Recovery
Pyro/hydrometallurgy
Magnetic separation

ABSTRACT

Platinum group metals (PGMs) assume an important role within the chemistry and chemical engineering due to their exceptional chemical stability in high temperatures and various environmental conditions. Their unique attributes make them highly demanded materials across an array of industries. Nevertheless, the gradual depletion of PGM reserves underscores necessitates of recycling PGM-containing waste as a means to ensure the reasonable utilization of resources. Recycling of catalytic waste, in particular, presents a more cost-effective and environmentally sustainable approach acquiring these metals, in contrast to the conventional practice of mining from natural ores. Of particular importance are spent automotive catalysts, which represent a valuable source of platinum group metals, featuring substantially higher PGM concentrations than their naturally occurring counterparts. Conventionally, the recovering of PGMs from waste materials predominantly employs hydrometallurgical and pyrometallurgical processes. Unfortunately, these established techniques entail the utilization of potent oxidizing acidic solutions, including aqua regia and hydrochloric acid with chlorine gas, which exert adverse ecological consequences. In recent years, there has been a growing focus on the development of alternative methodologies that are both environmentally friendly and economically viable for the recovery of PGMs from spent catalysts. Notable among these emerging techniques are solvometallurgy, molecular recognition technology, and magnetic separation. This comprehensive review endeavors to study and assess the latest advancements in the recovery of platinum group metals from spent catalysts, meticulously evaluating their respective advantages and disadvantages. Through an analysis, this review aspires to identify the most promising method - one that combines environmental friendliness and economic feasibility.

## 1. Introduction

The platinum group metals (PGMs), which include platinum, palladium, rhodium, ruthenium, osmium, and iridium, have held a long-standing allure and have ascended to eminence across various industrial sectors. Historical accounts reveal that the discovery of significant PGM reserves in nations such as Russia, the USA, Canada, and South Africa between the 18th and 20th centuries served to establish the important role of platinum in the global industrial landscape [1]. Over the course of the past two centuries, platinum has

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https://doi.org/10.1016/j.heliyon.2024.e25283
Received 15 July 2023; Received in revised form 23 January 2024; Accepted 24 January 2024

showcased its remarkable versatility, finding utility not only in jewelry craftsmanship but also as a catalyst with wide-ranging applications [2].

Within the automotive industry, platinum group metals (PGMs) have found extensive utilization as catalysts for exhaust gas treatment, a practice that has gained prominence since the 1970s [3]. This surge in PGM application is primarily caused by the necessity to meet strict environmental requirements, exemplified by regulations like the Euro standards [4]. Conventional PGM extraction from ores involves labor-intensive processes, underscoring the need for more ecologically sustainable, convenient methodologies for obtaining catalytic systems. Consequently, the recycling of catalytic waste, including components like catalytic converters, has emerged as a highly promising approach. This article is dedicated to a comprehensive examination of recent breakthroughs in the development and implementation of techniques geared towards the recycling of catalytic converters, with the goal of obtaining functional catalyst systems.

The remarkable chemical stability exhibited by platinum group metals (PGMs) under extreme temperatures and various environmental conditions makes them exceptionally well-suited for industrial applications (Fig. 1), mainly as catalysts. These PGMs are instrumental in acceleration of chemical reactions and facilitating the selective advancement of particular chemical processes. They occupy a position of significant importance within the chemistry and chemical engineering [1].

In summary, this review focuses on the important role of platinum group metals (PGMs) within the chemistry and chemical engineering. It accentuates their historical significance, expansive utility across various areas, and high attention directed toward the recycling of catalytic waste as a means to acquire valuable catalyst systems.

Their most notable application lies in their role as catalysts, orchestrating chemical reactions and, in scenarios involving multiple concurrent reactions, selectively promoting the most critical ones [6–14]. PGMs function as catalysts in important processes, including ammonia and ammonium nitrate production [15–18], catalytic converters [1,12,19,20], hydrogen fuel cells [21–25] and various other areas of significance.

PGM catalysts constitute an category of mixed oxide catalysts, allowing for a comprehensive analysis of their chemical surface and catalytic properties under conditions equivalent to those experienced by operative oxide catalysts [8]. Within PGM catalysts, rhodium assumes the role of a reduction catalyst, palladium serves as an oxidation catalyst, and platinum functions as a redox catalyst [26]. The synthesis of PGMs involves a diverse array of methodologies, typically yielding microstructures and nanostructures with a rich spectrum of shapes, including spheres, pyramids, cubes, and dumbbells [27]. Of particular note, platinum catalysts have attracted significant attention due to their remarkable activity in catalyzing CO oxidation reactions.

The industrial market presents a significant demand for platinum, palladium, and rhodium, as illustrated in Fig. 2 [1].

Table 1 showcases the wide array of industrial applications where PGM catalysts find extensive use.

Within the realm of fine chemicals, various applications necessitate high selectivity despite producing relatively modest product volumes. Pharmaceutical production accounts for over 50 % of this sector, with agriculture making up 25 %, and the remaining 25 % distributed among flavors, dyes, pigments, and food additives [45]. Within this spectrum, hydrogenation reactions constitute a significant portion, spanning approximately 10–20 % of the product range. These reactions include the hydrogenation of nitro compounds, asymmetric catalysis, and the selective hydrogenation of double bonds. Predominantly, Pd catalysts are deployed in these processes, although other catalysts may also find applicability. One pivotal hydrogenation reaction pertains to the reduction of nitrobenzene, which plays a crucial role in the production of aniline dyes, explosives, and pharmaceuticals. Furthermore, a significant asymmetric reaction revolves around the production of menthol, which is facilitated by the utilization of an Rh catalyst.

In a study [53], it has been established that a catalyst containing just one percent rhodium supported on a mixed cerium-zirconium oxide (1 % Rh/$Ce_{0.75}Zr_{0.25}O_2$) demonstrates high activity over an extended period, maintains its purity, and facilitates conversion of

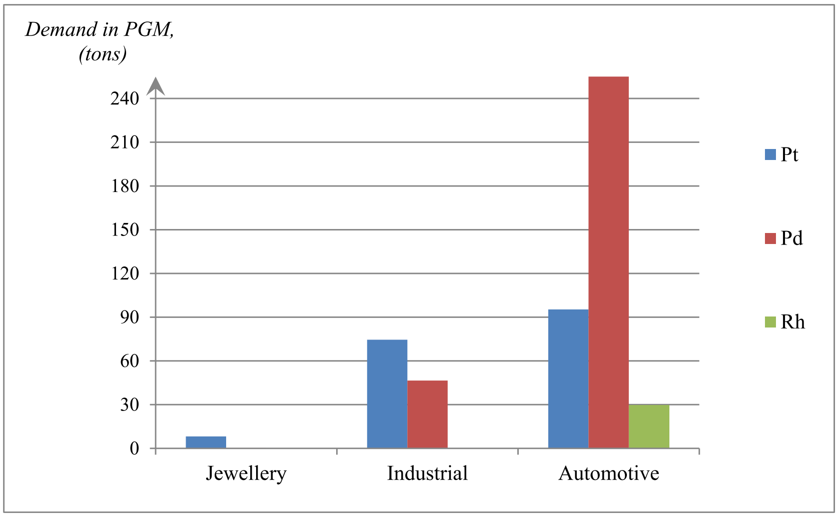

**Fig. 1.** – Net demand for Pt (178 tons), Pd (303.5 tons) and Rh (29.5 tons) for various industries (2023) [5].

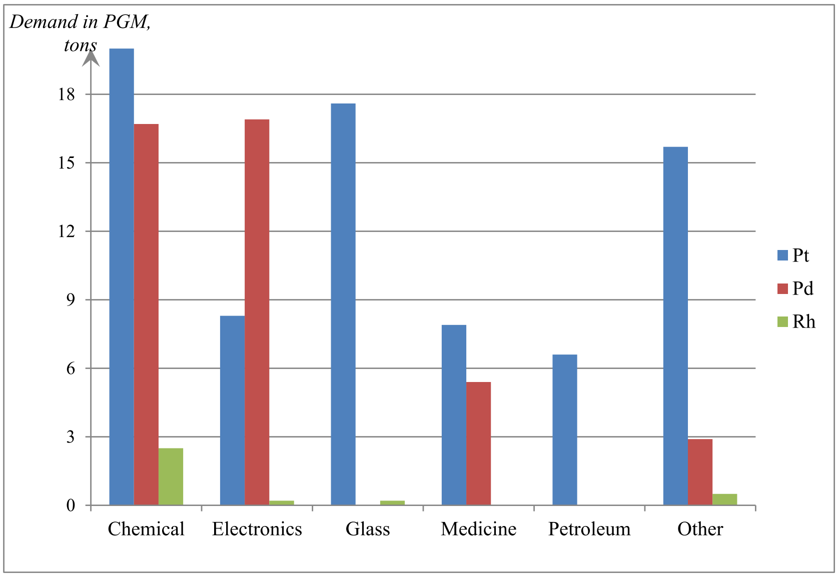

**Fig. 2.** Net demand in tons for PGM for the industrial sector, in 2023.

**Table 1**
Applications of PGM catalysts.

| Catalyst | Reaction | References |
|---|---|---|
| $Pt/Al_2O_3/SiO_2$ | Disproportionation of toluene to benzene | [28] |
| Pd/H–Y-Zeolite | Obtaining fuel by cracking of vacuum distillates | [29,30] |
| Pt/Zeolite | Xylene isomerisation | [31] |
| Pt/Pd/Rh | Industrial exhaust | [32–34] |
| Pt, Pd/oxide supports | Volatile organic compounds removal | [35–37] |
| Pt | Hydrodesulphurisation | [38] |
| Pt/Zeolite | Naphtha reforming | [39] |
| Pd | Caprolactam synthesis | [40,41] |
| Pd/supported oxides | Telomerisation of 1,3-dienes | [42] |
| Pd | Production of toluene diisocyanate | [43] |
| Pd suspension | Production of $H_2O_2$ | [40] |
| Pd | Bio-oils hydrogenation | [44,45] |
| Pt/Pd/Rh | Oxidation of ammonia | [46] |
| Pt, Pd | Ketones/aldehydes to alcohol | [47] |
| Pt/Pd/Rh | Production of nitric acid | [40] |
| Rh, $Pd/SiO_2$ | Acetic acid synthesis | [40] |
| Rh | Production of citronella | |
| $PdCl_2$ | Acetaldehyde synthesis | [40] |
| Pd | 2,5-dichloropyridine amidocarbonylation | [48] |
| Pt | Hydrogenation | [45,49] |
| $PdCl_2$ | Substituted alcohol carbonylation | [50] |
| Pd | Aldehydes and Ketones amination | [51] |
| Pd | Production of 1-octene | [52] |

$C_{2+}$-hydrocarbons into $CH_4$, $CO_2$ and $H_2$ at relatively low temperatures (300–400 °C). An interesting feature of rhodium catalysts lies in their unique ability to generate minimal amounts of ethane. This study underscores the potential of rhodium as an alternative to nickel due to its superior catalytic activity and stability. Importantly, rhodium catalysts can be deployed without the need for pretreatment in a reducing environment, enhancing their practicality and efficiency.

## 2. Structural properties of catalysts

The surface structure of platinum oxide catalysts showcases an extensive crystalline morphology. Fig. 3 provides a visual representation of the crystal structure of platinum oxide.

The catalytic performance of platinum oxide catalysts is fundamentally rooted in their capacity to provide surface oxygen as a reactant [8]. Oxygen vacancies located near the catalyst surfaces assume a central role in shaping the physical and chemical attributes of the system, consequently exerting an influence on catalytic reactivity. Fig. 4a,b elucidates these effects and their significance.

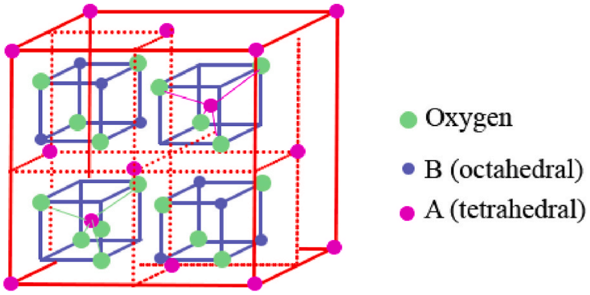

**Fig. 3.** – The position of oxygen in the platinum oxide catalyst [8].

The prevailing structural characteristic observed in most platinum oxide catalysts arises from the occupation of semioctahedral sites by cations, forming a hexagonally close-packed arrangement with oxygen anions [8]. The strength and nature of the oxygen-metal bond are tied to the specific arrangement of metal cations and oxygen anions within the catalyst system.

Automotive catalytic converters, as illustrated in Fig. 5, frequently utilize platinum (Pt), palladium (Pd), and rhodium (Rh) as PGM catalysts (Table 2).

A surface coating with a smooth texture is applied to the walls of the cordierite structure, constituting approximately 20–30 % of the total catalyst weight. This coating is expected to possess specific characteristics, which include the capacity to support noble metals in an ordered manner and demonstrate chemical inertness when exposed to the reaction environment. These prerequisites are met through the utilization of various substances, such as gamma alumina ($\gamma$-$Al_2O_3$) (Fig. 6), alkaline earth metals, and oxides like $CeO_2$, $La_2O_3$, $ZrO_2$, BaO, $TiO_2$, $Y_2O_3$, NiO, $WO_3$, and other similar compounds [57].

The process of depositing platinum group metals onto the $\gamma$-$Al_2O_3$ surface involves impregnation using solutions containing hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), palladium chloride ($PdCl_2$) and rhodium chloride ($RhCl_3$). Following this impregnation step, these metals are subsequently reduced to their metallic forms by reduction under proper concentrations of carbon monoxide or hydrogen, preceding their practical utilization [59]. On occasion, the freshly obtained metallic catalyst undergoes a mild partial oxidation procedure to temper its inherent reactivity toward oxidation during the phases of transportation and storage. It is worth noting that this reduction process typically generates heat as an exothermic reaction, warranting precise temperature control to prevent any inadvertent overheating.

Additionally, it is imperative to be mindful of the fact that elevated temperatures can induce undesired phenomena such as sintering and the formation of salts when these metals interact with supporting materials like aluminates. These conditions pose substantial challenges in terms of their subsequent reduction into their metallic forms. Excessively rapid heating rates or excessively high reduction temperatures can lead to the undesirable aggregation of metal particles into larger crystal structures. This aggregation substantially diminishes the extent of dispersion and the available surface area for catalytic activity [60].

Metallic elements in this aggregated state exhibit heightened reactivity and are susceptible to spontaneous combustion upon contact with atmospheric oxygen. Consequently, it is imperative to safeguard these materials by encapsulating them within inert gases or liquids to prevent unintended reactions with the surrounding air.

The production of automotive catalysts hinges on the use of ores as the primary source material (net demands for Pt (95.3 tons), Pd (256.7 tons), and Rh (29.5 tons) for the automotive industry are high [5]), subject to beneficiation techniques aimed at extracting platinum group metals from the concentrated ore.

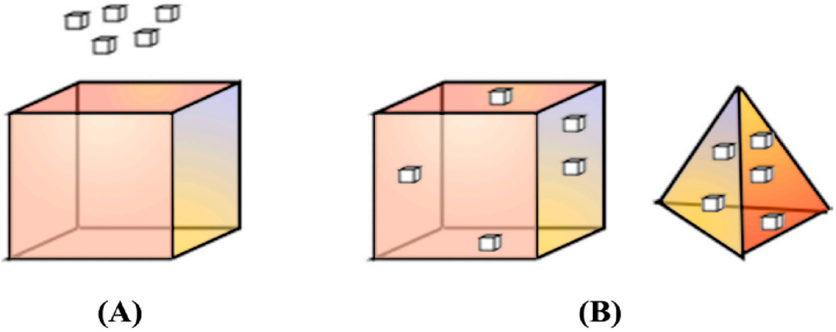

**Fig. 4.** – Molecular structure of platinum oxide catalysts. Pt, platinum; Pd, palladium: (a) Pt or Pd nanoparticles (10 nm and 20 nm) and (b) particles on particles [8].

**Fig. 5.** A used 1995 Toyota Mark II catalytic converter with 200,000 km mileage (gasoline).

**Table 2**
Properties of platinum, palladium, and rhodium catalysts.

| Property | Platinum | Palladium | Rhodium |
|---|---|---|---|
| Melting point | 1768.3 °C | 1554 °C | 1963 °C |
| Boiling point | 3825 °C | 3213 °C | 3727 °C |
| Atomic number | 78 | 46 | 45 |
| Relative atomic mass | 195 | 106 | 103 |
| Density | 21.5 g/cm$^3$ | 12.02 g/cm$^3$ | 12.41 g/cm$^3$ |

These catalytic converters are typically composed of a cordierite shell ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), which adopts a honeycomb structure with cell densities ranging from 60 to 120 cells per square centimeter. The dividers between the cells possess an approximate thickness of 150 μm [54–58].

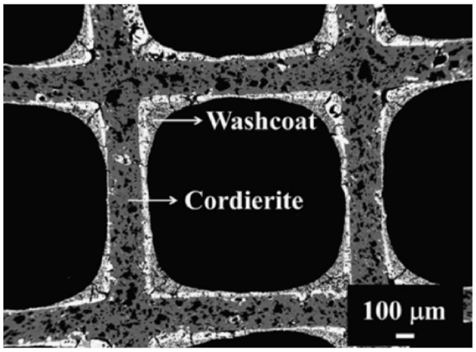

**Fig. 6.** – Cordierite shell of a catalytic converter coated with γ-$Al_2O_3$ [55].

## 3. Beneficiation of ores of platinum group metals

Ores containing platinum group metals are subjected to various preliminary beneficiation methods tailored to accommodate their distinctive textural and mineralogical characteristics. The processing of these PGM-containing ores includes mechanical separation, high-temperature smelting, primary processing, and the application of hydrometallurgical techniques [61,62].

In contrast to other metals, there exists a comparatively limited literature addressing the beneficiation of platinum group metal ores [63–66]. Nonetheless, specific scientists have made noteworthy contributions to the exploration of PGM ore beneficiation [67–73].

The choice of beneficiation techniques for the extraction of PGM minerals from ores is contingent upon a multitude of factors, including mineralogical composition, the nature of mineral deposits, and attributes of the host rock. In Table 3, a comprehensive overview of the various categories of beneficiation methods employed for the preliminary treatment of PGM-containing minerals is provided.

The beneficiation process for platinum group metal (PGM) ores involves a sequence of grinding, gravity separation, and flotation treatments. Achieving the best possible recovery hinges on attaining the desired level of liberation of PGM minerals. Consequently, the choice of the grinding process and its specific stages is informed by the mineralogical attributes of the ore. Sulfide minerals containing PGMs, known for their favorable liberation properties, are enriched through a combination of gravity and flotation techniques. In some instances, PGM ores related to chromospinelides can undergo magnetic separation, while gravity separation serves as a method for pre-

**Table 3**
Methods of beneficiation of PGM ores.

| Ore/deposit | Beneficiation method | Identified minerals | References |
|---|---|---|---|
| Chromite ore (PGM-containing) | Hydro separation | Ruarsite, erlichamanite | [74] |
| Alaskan or Dunite type ore | Gravity separation, jigging, panning | Sperrylite, osmiridium, platiniridium, cooperite, etc. | [67,75,76] |
| Raglan, Clarabelle ores | Gravity concentration | Sperrylite, moncheite | [63,77] |
| Ferrochrome host (PGM-containing) | Gravity and magnetic separation | Braggite, sudburyite, laurite | [63,78] |
| Sulfide-hosted ores (PGM-containing) | Crushing, flash flotation, froth flotation | Cooperite, braggite, Kotulskite etc. | [63,67,79] |
| Cu–Ni sulfide ore | Hydro separator, gravity concentration | Tetraferroplatinum, cooperite, sperrylite | [80] |
| PGM minerals associated with Fe | Gravity and magnetic separation | Nickelferroplatinum, retraferroplatinum, tulameenite | [81] |
| Chromite-hosted ore (PGM-containing) | Crushing, flash flotation, froth flotation | Cooperite, malanite, laurite, braggit, etc. | [63,64,66,67,82] |
| Cu–Ni sulfide deposit in Noril'sk | Flotation | Rustunbergite, isoferroplatinum, cooperite, etc. | [63,67,83] |
| BMS-hosted ore (PGM-containing) | Crushing, flotation, micro flotation | Palladium, sperrylite, Isoferroplatinum, etc. | [84,85] |
| Alaskan type ore | Milling, magnetic separation, hydro separation | Platiniridium isoferroplatinum, laurite, etc. | [86–88] |
| Ferrochrome hosted deposit | Crushing, milling, gravity concentration | Braggite, sudburyite, laurite | [68] |
| Sulfide-hosted fine PGM minerals | Milling, flotation | Moncheite, braggite, vysotskite, etc. | [63,89] |
| Low-grade placer deposit | Flotation | Isoferroplatinum, sperrylite | [90–92] |
| Cu–Ni sulphide deposit in Yunnan | Flotation, leaching | Serpentines, chlorites, pyroxenes | [93] |

concentration. Nonetheless, in the case of exceedingly low-grade PGM ores marked by minute grain size and inadequate liberation before flotation, advanced gravity separation techniques are utilized [61]. Due to the finely dispersed nature of PGM minerals in such scenarios, conventional gravity separation methods may prove less efficient. Consequently, researchers have delved into the development of enhanced gravity separators capable of effectively managing these fine particles [68,77]. The next step involves subjecting the flotation concentrates to pyrometallurgical procedures aimed at generating PGM-containing PGM-Ni-Cu matte. Hydrometallurgical methods are employed to segregate the base and noble metals from the matte, culminating in the isolation of individual noble metals in their pure state via the refinement of PGM concentrates [94]. Concurrently, a series of studies have explored diverse milling media to isolate PGM minerals and have developed reagents aimed at increasing flotation recovery rates [71,95,96]. For instance, in a study [71], a series of experiments was conducted using various grinding media, and the most robust recovery of platinum group metals was achieved via flotation utilizing ground products from ceramic media. Another research [96] endeavor, it was demonstrated that the inclusion of lime during the grinding process resulted in favorable flotation recovery outcomes.

As a result of ore beneficiation, the opportunity for direct extraction of PGMs becomes feasible.

## 4. Extraction of platinum group metals from concentrates

As shown in the data outlined in Table 4, platinum group metals are characterized by their rarity, placing them among the most uncommon elements within the periodic table.

To facilitate a comparison, the table incorporates iron, and the mention of cerium is warranted due to its pivotal role as an auxiliary metal in the production of automotive catalytic converters. This industry stands out as the largest consumer of platinum (95,3 tons) and palladium (256,7 tons) [1,5,97,98].

Platinum group metals are found in two forms: either as pure metals or alloys in the siderophilic state, or as ores in the chalcophile state. The most extensive reserves of PGM-containing ores are situated within ultramafic and mafic igneous rock formations, primarily in nations including Canada, the Russian Federation, South Africa, the United States, and Zimbabwe [99–101]. According to calculations presented in a study [1], the projected "lifespan" of platinum group metals is approximately 200 years, except for palladium, which is estimated to endure for approximately 100 years.

**Table 4**
Prevalence of PGMs.

| Metal | Atomic number | Prevalence (Atoms/$10^6$ Si atoms) | Prevalence in the upper continental crust ($bn^{-1}$) | World resources (tons) |
|---|---|---|---|---|
| Fe | 28 | 600000 | 5.2 % | $110 \bullet 10^9$ |
| Ru | 44 | 1.49 | 0.03 | 5000 |
| Rh | 45 | 0.214 | 0.018 | 3090 |
| Pd | 46 | 0,675 | 0.526 | 24302 |
| Os | 76 | 1 | 0.05 | 580 |
| Ir | 77 | 0.821 | 0.022 | 1074 |
| Pt | 78 | 1.625 | 0.599 | 32896 |
| Ce | 58 | 2.26 | 65 | $299 \bullet 10^6$ |

### 4.1. *Extraction of PGMs from sulfide ores*

The primary source of PGMs is sulfide ores (Table 5) [102], with a smaller fraction obtained from placer deposits of metallic platinum in Russia. However, the most significant reservoir of these ores is found in South Africa [103]. Typically, South African ores contain an average of around 3–4 g of platinum group elements per ton of ore.

The recovery of PGMs is a costly process, underscoring the imperative of optimizing the extraction efficiency to obtain the concentrate.

PGMs are primarily situated within sulfide minerals within the ore deposit, either as soluble constituents within pentlandite [$(Ni,Fe)_9S_8$] or as discrete mineral grains, such as braggite [(Pt,Pd)S]. Typically, minerals containing PGMs are encompassed by grains of pentlandite, pyrrhotite [$Fe_8S_9$], or chalcopyrite [$CuFeS_2$] [79,104,105]. The extraction of platinum group elements is a highly expensive process, emphasizing the need to achieve maximum extraction efficiency into the concentrate.

The process of extracting PGMs involves several key steps.

- crushing and grinding of the ore;
- obtaining a sulfide concentrate rich in platinum, primarily through froth flotation;
- melting and converting the concentrate into matte;
- purification of PGMs from the matte using hydrometallurgical techniques (adsorption, chelation, ion exchange, leaching, precipitation, solvent extraction).

Following the smelting and conversion of the concentrate, the resulting matte contains roughly 0.3 % of the entire PGM. Subsequently, this matte undergoes a leaching process with sulfuric acid and oxygen, leading to the formation of an insoluble solid residue that contains approximately 60 % of the total PGM content.

The initial step in the purification of PGMs includes dissolving the solid residue in hydrochloric acid, employing chlorine as an oxidizing agent. This procedure results in the dissolution of all precious metals except silver. Osmium takes the form of $OsO_4$, a volatile compound that can be captured in the gas phase.

The separation and refinement of PGMs into discrete metals involve the following steps.

- sequential removal of each element from the leached solution via precipitation, ion exchange, and evaporation processes;
- purification of each element in solution using a similar set of processes (precipitation, ion exchange, and evaporation processes);
- conversion of these purified elements into metallic forms through either calcination or reduction.

The final product typically attains a level of purity within the range of 99.9 %–99.99 %.

### 4.2. *Gravity Separation [103]*

Platinum-containing minerals exhibit higher densities in comparison to the surrounding host rock and iron. For instance, $Pt_3Fe$ isoferroplatinum and PtFe tetraferroplatinum possess densities of 18 g/cm$^3$ and 16 g/cm$^3$, respectively. In contrast, the densities of pentlandite $(Ni, Fe)_9S_8$, chromite $(Fe, Mg)Cr_2O_4$, pyroxene $(Mg,Fe)_2Si_2O_6$, and quartz $SiO_2$ are 5 g/cm$^3$, 5 g/cm$^3$, 4 g/cm$^3$, and 3 g/cm$^3$, respectively. This density contrast is exploited to obtain a gravity concentrate containing approximately 20 % PGM. The remaining ore undergoes further flotation processes.

Due to their widespread use across diverse industries, PGMs are found in higher concentrations within industrial sources in contrast to their occurrence in natural ores [106,107]. Given the substantial value of these metals, there exists a notable interest in the recycling of waste materials, such as catalytic converters, employing environmentally friendly and economically viable approaches [108–115].

## 5. Recycling of catalytic converters

### 5.1. *Poisoning of catalytic converters*

Three-way catalytic converters, an integral component of modern vehicle emission control systems, are engineered to address two primary objectives: reducing $NO_x$ emissions and facilitating the oxidation of unburned hydrocarbons and carbon monoxide. The core chemical reactions taking place within these catalytic converters are as follows (Equations (1)–(8)) [116]:

Oxidation reactions

**Table 5**
Minerals containing PGM.

| Sulfides | Braggit (Pt,Pd)S, cooperite PtS, laurite $Ru,[Os,Ir]S_2$ and unnamed Pt, Rh, Cu, S minerals |
|---|---|
| Pt–Fe | Isoferroplatinum $Pt_3Fe$, tetraferroplatinum PtFe |
| Arsenides | Sperrylite $PtAs_2$ |
| Tellurides | Moncheit $PtTe_2$ |

$$CO+\frac{1}{2}O_2 \rightarrow CO_2 \tag{1}$$

$$H_2+\frac{1}{2}O_2 \rightarrow H_2O \tag{2}$$

$$C_xH_y+\left(x+\frac{y}{4}\right)O_2 \rightarrow xCO_2+\frac{y}{2}H_2O \tag{3}$$

Steam reforming

$$C_xH_y+xH_2O \rightarrow xCO+\left(x+\frac{y}{2}\right)H_2 \tag{4}$$

Reduction of $NO_x$ emissions

$$2CO+2NO \rightarrow 2CO_2+N_2 \tag{5}$$

$$C_xH_y+\left(2x+\frac{y}{2}\right)NO \rightarrow xCO_2+\frac{y}{2}H_2O+\left(x+\frac{y}{4}\right)N_2 \tag{6}$$

$$H_2+NO \rightarrow H_2O+\frac{1}{2}N_2 \tag{7}$$

Water gas conversion

$$CO+H_2O \rightarrow CO_2+H_2 \tag{8}$$

The decrease in catalytic efficiency observed during the lifespan of a vehicle is a widely recognized phenomenon. As a catalytic converter undergoes aging, sulfur compounds present in diesel fuel can accumulate on its surface, leading to a decline in its catalytic performance [117]. Additionally, elevated operating temperatures can contribute to the clustering of platinum nanoparticles, resulting in a reduction of their effective surface area (agglomeration). This reduction in the surface area of precious metals involved in catalytic reactions with exhaust gases directly corresponds to a decrease in conversion efficiency [118].

Both gasoline and diesel fuels may include significant amounts of organic sulfur compounds, which undergo combustion within the engine, resulting in the production of various sulfur dioxide gases [116]. These sulfur compounds can rapidly impede the catalytic performance of palladium-based catalysts, as illustrated in Fig. 7.

In the high-temperature environment of a gasoline engine, there is often a natural process of sulfur compound removal: sulfates that have formed on the catalytic surfaces desorb at elevated temperatures, effectively recovering catalytic activity [120]. Unfortunately, in the lower temperature settings typical of diesel engines, such desorption events are infrequent, making palladium-based catalysts susceptible to deactivation due to sulfur contamination.

The utilization of catalysts constructed from Pt–Pd alloys notably increases their resistance to oxidation and sulfur-induced deactivation, consequently extending the longevity and preserving the effectiveness of the catalytic converter [121].

Sulfur species can manifest as both $SO_2$ and $SO_3$ forms [118]. When exhaust gases traverse through the catalytic converter, $SO_2$ molecules adsorb onto the catalyst's surface, thereby retarding the rate of chemical reactions. In the presence of abundant oxygen, adsorbed $SO_2$ can undergo oxidation, transforming into $SO_3$ and subsequently being released as a gas. $SO_2$ molecules adhered to the catalyst's active sites can also undergo decomposition into $SO_4$.

The conversion efficiency of $C_3H_6$ (Fig. 8a), CO (Fig. 8b), and $NO_x$ (Fig. 8c) was examined across a temperature range of 450 K–950 K at various levels of adsorbed $SO_2$.

The experimental findings demonstrate that an increase in the concentration of adsorbed $SO_2$ results in a significant decline in conversion efficiency, necessitating a higher temperature to reach 50 % of the conversion value.

### 5.2. *Condition of vehicles in the Republic of Kazakhstan*

In 2022, Marat Akhmetzhanov, who serves as the Minister of Internal Affairs of the Republic of Kazakhstan, emphasized a noteworthy surge in the vehicle count, which rose from 3.9 million to 5 million units spanning the period between 2019 and the current year [123]. Nevertheless, the minister also acknowledged a considerable degree of vehicle depreciation.

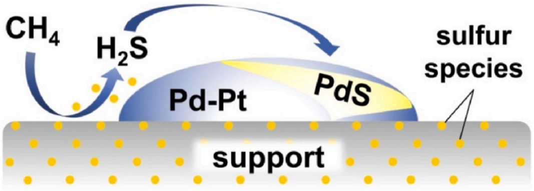

**Fig. 7.** - Sulfur poisoning of bimetallic Pd-Pt [119].

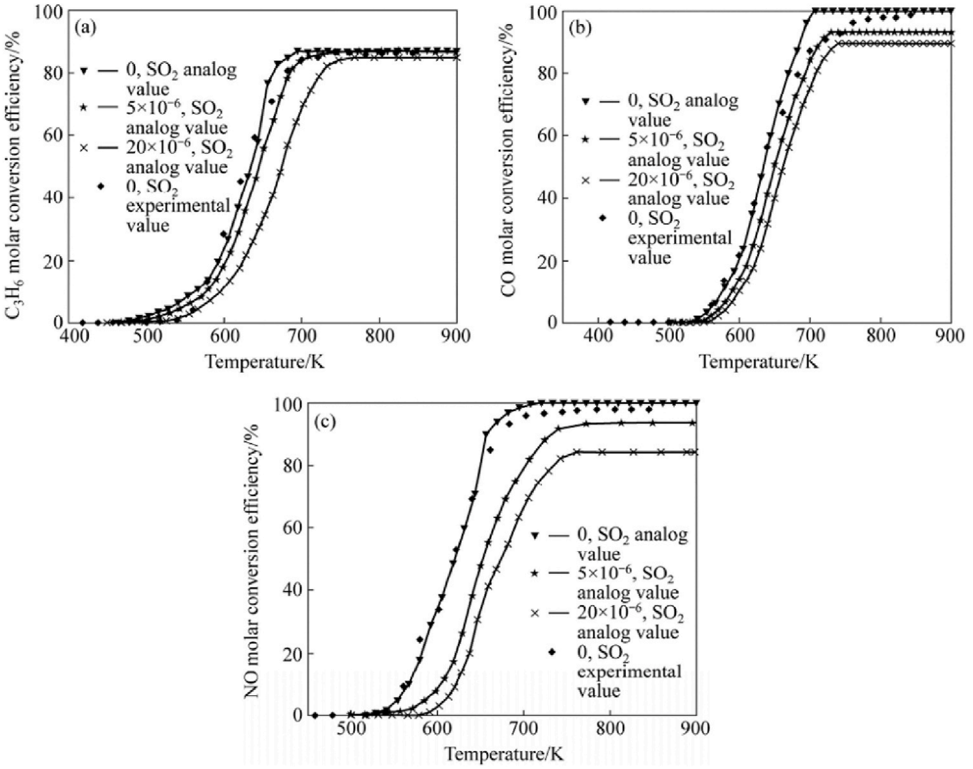

**Fig. 8.** – Conversion Efficiency Curves $C_3H_6$ (a), CO (b) and $NO_x$ (c) at various values of adsorbed $SO_2$ [122].

As of 2022, data published by the Bureau of National Statistics in the Republic of Kazakhstan reveals a noteworthy distribution within the passenger car fleet. Remarkably, vehicles aged 20 years or older dominate the landscape, comprising 50.3 % of the total. Meanwhile, cars spanning the age range of 10–20 years account for 21.1 % of the fleet, followed by those between 7 and 10 years at 14.5 %. A smaller proportion, 6.4 %, represents vehicles aged between 3 and 7 years, with a mere 7.6 % having a lifespan of less than 3 years, as depicted in Fig. 9 [124]. Regarding trucks, an even more substantial portion, 60.8 %, consists of vehicles manufactured over 20 years ago, while for buses, this figure stands at 42.2 %.

Over the course of January to November that year, a total of 50,005 vehicles were collected from the population, including 37,495 automobiles, 5271 buses, and 7239 trucks. Considering the average content of 1.5 g of platinum, 1.3–1.4 g of palladium, and 0.15 g of rhodium per kilogram of catalytic converter, the potential recycling of catalytic converters from these retired vehicles could yield an estimated 75 kg of platinum, 70 kg of palladium, and 7.5 kg of rhodium. This haul carries an approximate market value of $8.5 million.

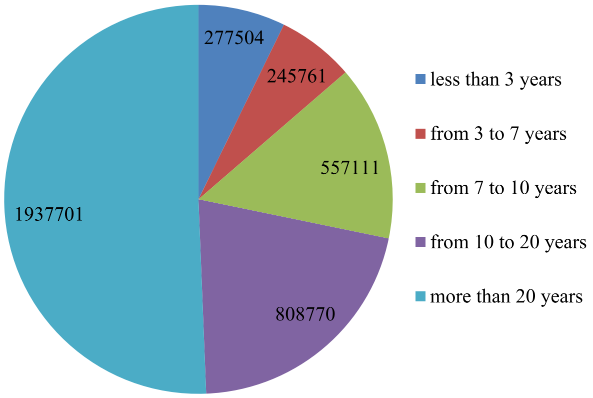

**Fig. 9.** Number of passenger vehicles by year of manufacture.

### 5.3. Methods for PGM extraction

Various techniques are applied to extract PGMs from catalytic converters [114,125–128], including pyrometallurgical and hydrometallurgical methods with subsequent element recovery [55,106,110,129–138], biological methods [139,140], leaching methods [109,141–146], solvometallurgical methods [147–151], molecular recognition technology [152–157] and biometallurgical methods [158–166]. These methods collectively ensure effective and eco-friendly processing of PGMs. The selection of a specific method primarily hinges on factors such as PGM concentrations and the presence of other substances. Nonetheless, the prevailing methods employed in practice are hydrometallurgical and pyrometallurgical techniques, which have garnered widespread adoption within corporations and industries such as Umicore, Johnson Matthey, Heraeus, and Nippon [167]. The procedure entails the initial steps of separating, drying, and comminuting the waste catalyst, followed by subsequent hydrometallurgical and pyrometallurgical procedures. For instance, the British firm Johnson Matthey utilizes a combination of melting, leaching, and refining processes to recover PGMs alongside other associated metals [106]. The Belgian company Umicore employs high-temperature furnace melting of a blend of catalyst waste and electronic waste to obtain a concentrate containing platinum, palladium, copper, and other metals, which are subsequently subjected to hydrometallurgical treatment [168].

#### 5.3.1. Hydrometallurgical method

In the hydrometallurgical process (Fig. 10), pre-treatment of catalytic waste is required to eliminate organic residues.

Pt–Re/γ-$Al_2O_3$, Pt–Sn/γ$Al_2O_3$ and Pd/γ-$Al_2O_3$ catalysts can be subjected to treatment involving dissolution, thanks to the amphoteric properties exhibited by γ-$Al_2O_3$. The finely ground catalyst is dissolved in sulfuric acid, resulting in the concentration of platinum (Pt) and palladium (Pd) in the residual solution. To recover some of the dissolved PGMs, the cementation process is applied, employing aluminum powder as a reducing agent [169]. In a study [170], autoclave leaching utilizing sulfuric acid was implemented for processing the catalytic converter. Alternatively, alkali dissolution follows the Bayer method, wherein γ-$Al_2O_3$ is dissolved in NaOH or KOH [170]. Nevertheless, it is important to note that this approach entails certain disadvantages, including high energy consumption and the necessity for complex equipment, including elevated temperatures and pressures for the leaching of γ-$Al_2O_3$.

PGMs present in the catalysts can undergo leaching in hydrochloric acid with the aid of oxidizing agents, including $HNO_3$, $Cl_2$, NaClO, $NaClO_3$, and $H_2O_2$ [171–173]. Within this leaching system, the generated chlorine contributes a formidable oxidizing capability and a substantial concentration of chloride ions. Consequently, the PGMs exist in the form of chloro complexes ($[PtCl_6]^{2-}$, $[PdCl_4]^{2-}$, $[RhCl_6]^{3-}$) (Equations (9)–(11)):

$$3Pt + 18HCl + 4HNO_3 \rightarrow 3PtCl_6^{2-} + 6H^+ + 4NO + 8H_2O \tag{9}$$

$$3Pd + 12HCl + 2HNO_3 \rightarrow 3PdCl_4^{2-} + 6H^+ + 2NO + 4H_2O \tag{10}$$

$$Rh + 6HCl + HNO_3 \rightarrow RhCl_6^{3-} + 3H^+ + NO + 2H_2O \tag{11}$$

The process often yields a modest quantity of PGMs. As a result, it requires pre-treatment procedures that encompass fine grinding, roasting, reduction, and pressure leaching. Several studies [55,174–176] have explored various pre-treatment techniques, including oxidative roasting, reductive roasting, and pre-leaching, to eliminate organic compounds from the catalyst's surface. As demonstrated in a study [176], it has been observed that the leaching efficiency of Pt(IV) exhibits an augmentative trend when subjected to a blend comprising 30 % HCl along with varying proportions of $H_2O_2$. This enhancement in efficiency is conspicuously discerned with the elevation in the temperature of the catalyst's roasting process, spanning the range from 700 to 900 °C, while maintaining a consistent $H_2O_2$ concentration. Furthermore, this study unveiled that pre-treating the catalyst leads to a remarkable boost in the leaching efficiency of Pt(IV), ameliorating it from an initial value of 84 % to a complete extraction rate of 100 %.

Moreover, the leaching of platinum group metals is conducted using appropriate acid or alkali solutions, depending on the specific

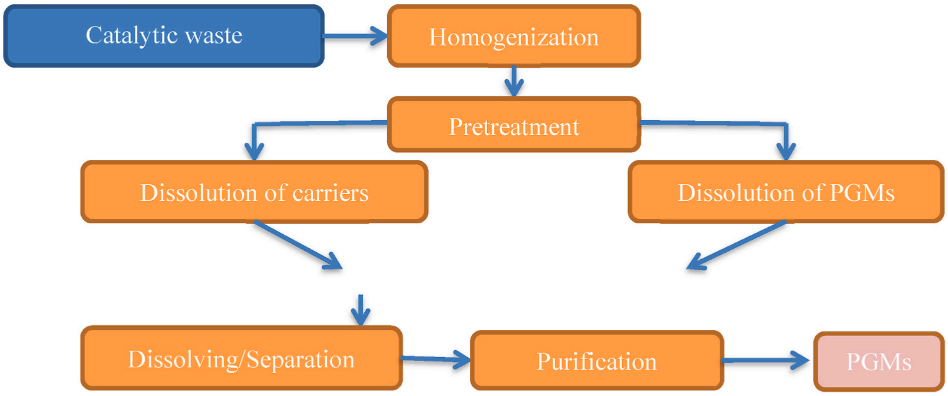

**Fig. 10.** Scheme of processing PGM by hydrometallurgy.

conditions. These solutions may include aqua regia, sulfuric acid, sodium chlorate, sodium hydroxide, and others [108,110,113,142,177–182]. After the leaching process, the metals are concentrated through either precipitation or liquid extraction, followed by subsequent purification steps.

While hydrometallurgical methods have garnered substantial attention, their advancement faces constraints primarily stemming from low extraction efficiencies, notably for rhodium. Additionally, these methods result in the production of substantial volumes of hazardous waste, and entail lengthy processing durations. Moreover, the inherent scarcity of platinum group metals in catalytic converters presents its own set of challenges during the extraction process [55,108,183].

### *5.3.2. Pyrometallurgical method*

Pyrometallurgical processes, illustrated in Fig. 11, serve as one of the primary methods for processing platinum group metals from catalyst waste [106,183–186].

These procedures include both melting and chlorination techniques for the retrieval of PGMs. In the smelting concentration phase, the catalyst is melted in the presence of flux, an auxiliary metal, and a reducing agent. This fusion results in the formation of an auxiliary metal-PGM alloy, which is subsequently subjected to a purification step for platinum group metals [187]. The choice of an auxiliary metal necessitates careful consideration of factors such as mutual solubility, melting point, and chemical compatibility with the PGMs. Commonly utilized auxiliary metals include nickel, copper, lead, and iron, known for their effectiveness in this role. The pyrometallurgical method, including stages like crushing, pelletizing, smelting, and separation, represents the conventional methodology for recuperating PGMs from recycled catalysts [185,187].

The lead metal collection technique stands as one of the earliest methodologies [20]. It presents certain advantages, including straightforward implementation, a relatively low melting point, and a straightforward purification process. Nevertheless, it carries the disadvantage of providing a reduced rhodium yield (around 70–80 %) and the emission of lead oxide, a substance posing risks to both individuals and the environment.

The copper metal collection method [188] entails the treatment of the catalyst within an electric arc furnace, accompanied by the addition of fluxes ($SiO_2$, CaO), a collector ($CuCO_3$ or CuO), and a reducing agent. Under relatively low temperatures and within a mild reducing atmosphere, PGMs are effectively gathered. The Serbian Institute of Mining and Metallurgy [114] has applied this approach to reduce PGMs, employing a comprehensive process that combines pyrometallurgical stages with electrolytic refining. This multifaceted process includes crushing, grinding, homogenization, granulation, drying, melting, electrolysis, and refining. Pre-dried pellets are immersed in a pre-melted copper solution, where the PGMs are extracted into the copper-metal phase. This copper metal is subsequently processed into an anode plate, subjected to an electrolytic procedure, ultimately resulting in an anode residue containing 20–25 % of platinum group metals [114].

While the smelting process proves to be proficient in handling platinum group metals, the utilization of pyrometallurgy is constrained. This limitation primarily arises from the elevated expenses incurred in addressing equipment corrosion during the evaporation phase. Additionally, the utilization of perilous gases such as carbon monoxide and chlorine can contribute to air pollution and jeopardize the well-being of personnel [109,111,183].

### *5.3.3. Solvometallurgical method*

Solvometallurgy represents an emerging area in metallurgy, focusing on the extraction of metals from ores, industrial residues, and

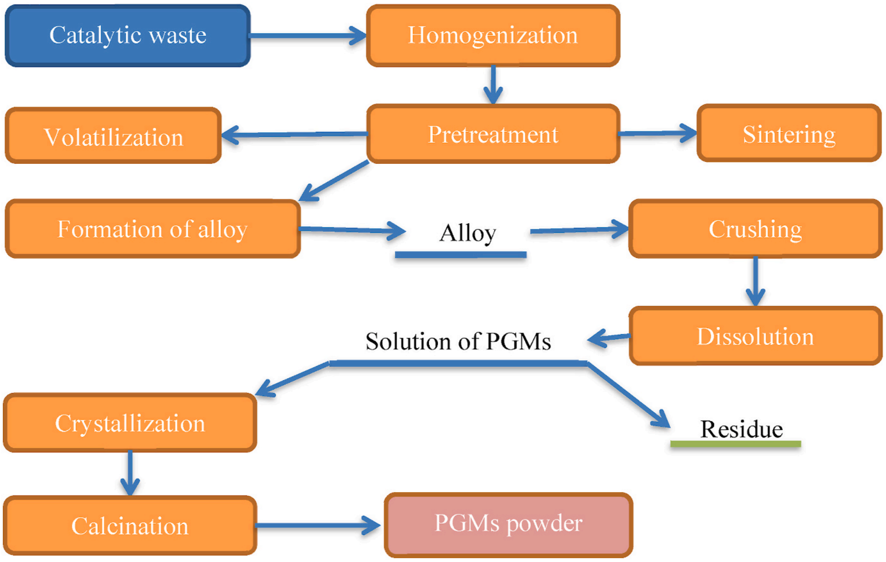

**Fig. 11.** Scheme of processing PGM by pyrometallurgy.

recyclable materials. Unlike traditional methods that rely on water, solvometallurgy employs polar organic solvents to achieve similar process mechanisms as hydrometallurgy. Notably, this innovative approach has demonstrated effectiveness in the selective leaching of metals [189].

Several researchers [147–149] have highlighted the ability to dissolve various metals, including precious ones, using halogens and halides in polar organic solvents. However, it's crucial to note that the high reactivity of halogens can lead to the formation of unintended by-products. For instance, a combination of $SOCl_2$ with pyridine or DMF has proven effective in dissolving noble metals like silver, gold, and palladium.

The process of isolating dissolved PGMs into their constituent elements (Fig. 12A) has its disadvantages, including the yielding of waste, the consumption of reagents, sluggish processing rates, and limited selectivity [150]. Consequently, a solution has been put forth in the form of non-aqueous solvent extraction (NASX), where a chemical reaction unfolds between two immiscible organic phases, as illustrated in Fig. 12B [151].

The phase structure includes two main elements: the polar phase, which encompasses solvents such as ethylene glycol (EG), poly (ethylene glycol) (PEG), and dimethyl sulfoxide (DMSO), housing the targeted metals for extraction, while the non-polar phase holds the extractant (such as LIX 984, Cyanex 923, TOA) and a diluent (such as kerosene, dodecane, *p*-cymol). The choice of solvents is of utmost importance, as they must exhibit specific attributes, including.

- low mutual solubility between the two phases;
- good solubility of the metal salt in the more polar phase and the extractant in the less polar phase;
- rapid phase separation for efficient extraction;
- minimal environmental impact to ensure sustainability.

The solvometallurgical method is illustrated in Fig. 13, depicting the overall process and its key components.

It is noteworthy to emphasize that solvometallurgy presents a notable disadvantage, limiting its practical application to laboratory-scale processes. This limitation arises from the inherent high viscosity of the majority of organic compounds employed, rendering the scale-up of solvometallurgical procedures unfeasible. Another disadvantage worth considering is the environmental unfriendliness and high volatility of pyridine and DMF. This characteristic poses a substantial concern, as it can lead to significant losses of these compounds during the process.

### 5.3.4. *Molecular recognition technology*

Molecular recognition technology (MRT) stands as a promising approach for achieving remarkably selective metal separation. This technique entails the chemical bonding of metal-specific ligands onto solid matrices, such as polymer substrates or silica gel. Subsequently, solid-phase extraction is conducted, eliminating the need for organic solvents. MRT boasts several notable advantages in comparison to conventional methods [152,153].

- high reaction speed, allowing for efficient and rapid metal separation;
- remarkable selectivity, enabling the specific binding of target metals;
- strong binding energies between the ligand and the target metal, ensuring effective extraction;
- environmental friendliness, as it eliminates the need for organic solvents.

MRT achieves remarkable selectivity through.

- using precisely tailored recognition molecules with specific shapes and functional groups that fit the target molecule;
- strong interactions between the recognition molecule and target molecule;

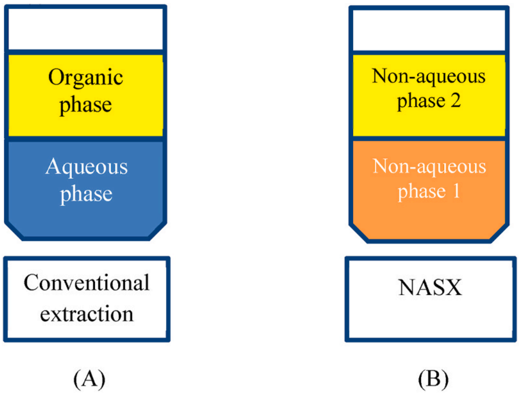

**Fig. 12.** Conventional extraction (A) end extraction with NASX (B).

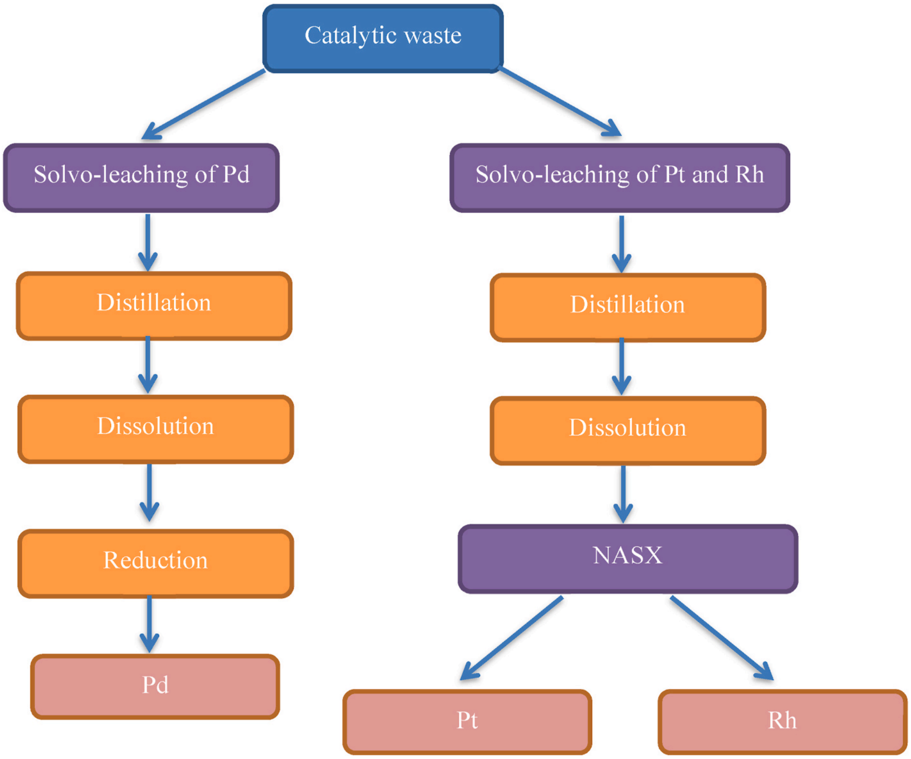

**Fig. 13.** – Scheme for the separation of PGM from catalytic converters by solvometallurgy [151].

- three-dimensional alignment of atoms and complementary functional groups;
- control over parameters like temperature and pH

In 1987, the work of Pedersen marked a significant milestone in the application of molecular recognition to this field, earning him the Nobel Prize [154]. Pedersen's initial research centered on the selective binding of alkali metal ions using specific cyclic polyesters [190]. Subsequent efforts by researchers further propelled the advancement of molecular recognition technology [155,156], giving rise to the development of SuperLig® systems [191]. These innovative systems involve the attachment of metal-specific ligands to solid supports through tethers [157].

SuperLig® systems employ a variety of ligands tailored to specific needs, including: aminophosphonic acid ligands, carboxylic acid ligands, crown ethers, imidazolium ligands and etc.

SuperLig® systems are notable for their small particle sizes, approximately 0.5 mm, and their installation in fixed-bed columns. The complete cycle of molecular recognition technology processes can be summarized as follows (see Fig. 14).

The SuperLig® technology stands out for its remarkable ability to selectively target specific metals, facilitating the direct extraction of these metals when loaded into the column at elevated concentrations [191]. In MRT, selecting the right eluting solution for recovering adsorbed PGMs is crucial. Common eluents for PGM recovery include strong acids (HCl, $HNO_3$), complexing agents ($NH_4SCN$), reductive eluents ($NaBH_4$), and ammonium hydroxide ($NH_4OH$). Efficiency in the adsorption-desorption process depends on several factors: metal loading, ligand affinity, adsorbent properties and etc.

A practical application of this approach can be observed in a refinery located in Houston, specializing in the recovery of platinum group metals from catalytic waste [192]. In this process, recycled catalysts undergo a transformation into an acidic solution containing PGMs, which is then channeled through the Molecular Recognition Technology (MRT) system. Within the MRT system, individual metals form selective bonds with the SuperLig® resin. The resultant PGM-enriched fractions can subsequently undergo further reduction to yield pure forms or be marketed as is.

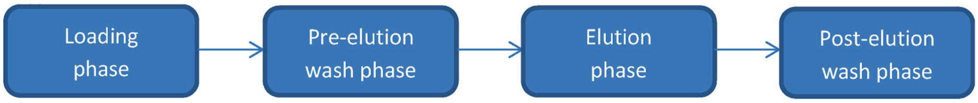

**Fig. 14.** Phases of molecular recognition technology.

### 5.3.5. Biometallurgical method

Biometallurgy is a term encompassing biotechnological procedures involving the interaction between microorganisms and metallic substances or minerals containing metals. Bioleaching, a prominent facet of biometallurgy, has garnered extensive global attention and implementation at a large scale [158–160]. It plays a pivotal role in the extraction and retrieval of metals from both ore deposits and waste materials. In this context, microorganisms, along with their metabolic byproducts, serve as instrumental agents for extracting metals from spent catalysts. This biologically mediated extraction process stands out for its eco-friendly characteristics and cost-efficiency, particularly when used with alternative leaching methodologies [158].

Bioleaching can be executed through two distinct ways: the direct one-step approach and the direct two-step approach. In the one-step process, fermentation and leaching transpire concurrently, signifying that both metal leaching and microorganism cultivation occur simultaneously [161]. Conversely, the two-step direct method commences with cultivation preceding the leaching step, albeit both processes transpire within the same containment vessel. On the other hand, the indirect method entails the leaching process transpiring within a medium that is devoid of microorganisms, a medium that is obtained through the prior process of fermentation [162].

In a series of studies [163–165], automotive catalytic converters and electronic scrap underwent a grinding process, resulting in finely ground particles. Subsequently, the metals contained within these materials were extracted through the application of strong mineral acids. It is noteworthy that the resulting leachates, enriched with metals, often exhibited limited compatibility with biological systems due to their low pH and elevated concentrations of toxic metallic elements. Consequently, an essential step involving dilution or pH adjustment was necessitated [165]. Alternatively, direct contact between the active biomass and these aggressive leachates was passed by employing either the off gases generated during bacterial fermentation or the premetallization of the biomass. These strategies facilitated an autocatalytic reduction process specifically tailored for the recovery of precious metals, such as Pd, Pt, Cu, and Au. The most remarkable outcome of this research lies in the selective and sequential retrieval of PGMs with an almost complete recovery of each individual metal species. This remarkable capability of the biometallurgy process to discriminate among PGMs represents a significant advantage when contrasted with conventional chemical recovery techniques.

In a study [166] an experimental investigation aimed at recovering platinum via the bioleaching method was conducted. Within this study, various bioleaching approaches were explored, encompassing both direct (including one-step and two-step processes) and indirect methods (involving spent medium bioleaching with and without pH control). Their findings revealed that the utilization of pH control led to enhanced Pt recovery. The optimal operating conditions were identified as follows: a pH of 0.5, a pulp concentration of 1 wt%, and a bioleaching temperature of 70 °C, culminating in a Pt recovery rate of 37 %.

It is noteworthy that the recovery of PGMs through bioleaching tends to be comparatively modest in comparison to traditional recovery methodologies. However, it is crucial to underscore the environmental and energy-related merits of bioleaching, which

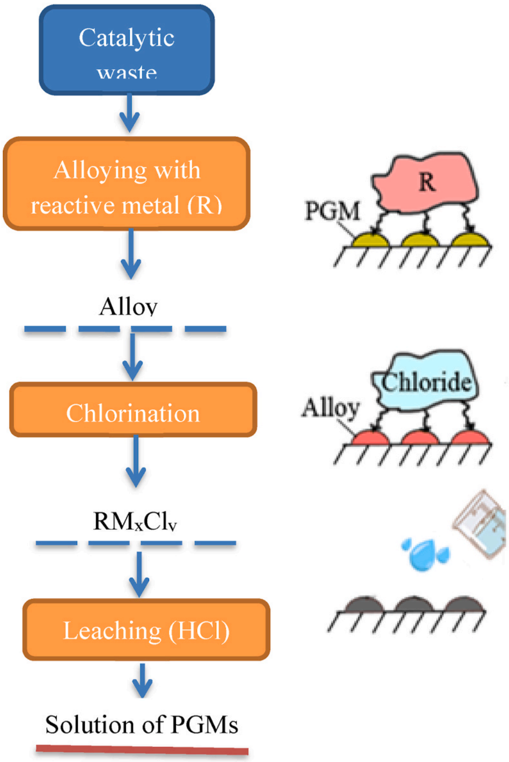

**Fig. 15.** – Scheme of processing by the PGM method [56].

emerges as an eco-friendly and energy-efficient alternative [193].

### 5.3.6. *Method of dissolution of platinum in aqueous solutions*

Furthermore, novel methods have been developed for catalyst processing that aim to be more cost-effective and environmentally friendly [111,112,194–196]. For instance, one such method [56] involves the dissolution of platinum in aqueous solutions without the need for toxic chemicals (Fig. 15).

The process involves the interaction between platinum group metals and magnesium vapor, leading to the creation of alloys referred to as PGM-Mg alloys. Following this, the alloy undergoes chlorination using metal chlorides like copper chloride. Platinum-containing compounds can be effectively dissolved in a hydrochloric acid (HCl) solution without the requirement for additional oxidizing agents.

### 5.3.7. *Magnetic concentration method*

An alternative technique for recovering platinum group metals from catalytic waste is detailed in a distinct study [112]. This method revolves around the direct magnetic concentration of these metals from catalytic converter waste (Fig. 16).

This procedure entails the application of ferromagnetic iron onto PGM particles via exposure to ferric chloride vapor, a process that involves a disproportionation reaction (Equation (12)).

$$FeCl_{2(g)} + Fe_{(s)} \rightarrow FeCl_{3(g)} \tag{12}$$

Consequently, the PGMs acquire magnetic properties, facilitating their efficient separation from non-magnetic components like the ceramic shell of the catalytic converter [195]. The concentrated PGMs yielded through this technique possess substantial worth and occupy considerably less space compared to untreated waste. Furthermore, these procedures can be carried out in compact installations with low energy consumption and devoid of the release of hazardous pollutants [111,112,194,196,197].

### 5.3.8. *Summary table of methods*

A summary of methods for PGM extraction is provided in Table 6.

In order to assess the composition and physical-chemical characteristics of the resulting catalytic systems for future utilization, it is imperative to conduct an examination employing a range of physicochemical techniques.

## 6. Physicochemical methods for studying catalysts

Physicochemical techniques hold a pivotal role in the analysis of catalysts, enabling the exploration of their physical and chemical attributes that dictate their catalytic effectiveness concerning both activity and selectivity. Various analytical methods find application in the characterization of solid catalysts [198–205].

### 6.1. *X-ray phase analysis (XRD)*

X-ray phase analysis (XRD) stands as a highly efficient and invaluable technique employed for the determination of a sample's crystal structure. Its functionality relies on the interference of coherently scattered X-rays, where the crystal lattice behaves like a diffraction grating, owing to its interplanar distances that align with the wavelength of the radiation. XRD holds widespread utility in the examination of bulk crystal structures and phase composition (Fig. 17). It particularly shines in identifying phases within unknown samples and can effectively distinguish between crystalline and amorphous states. The areas of chemistry, biochemistry, physics, materials science, and mineralogy frequently harness XRD across a range of applications [206–208].

In a study conducted by researchers [210], the physicochemical properties of a catalytic converter with the following composition were investigated: a cordierite shell, a Ce–Zr mixed oxide, and Pd nanoparticles.

Nanoparticles possess a distinct identity discernible through their interplanar spacing, a characteristic contingent on the specific element at hand. To illustrate, the gap between two crystallographic planes, denoted as (111) for Pd, measures 2.23 Å, while for Pt, it registers at 2.26 Å. In our investigation, we observed Pd nanoparticles exceeding 10 nm in size, whereas Pt nanoparticles consistently exhibited dimensions smaller than 5 nm. The absence of Pt in the diffractogram (Fig. 18) can be attributed to both their smaller size (5 nm compared to 15 nm) and lower concentration (0.014 % versus 0.046 %). It's established knowledge that nanoparticle agglomeration accelerates once they surpass their Tammann temperature, a threshold that can be proximate to half the melting point when considering absolute temperature. For Pt, this critical temperature stands at 750 °C, which is 110 °C higher than Pd's Tammann

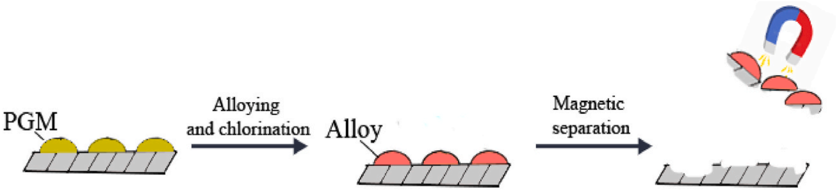

**Fig. 16.** Scheme of PGM separation by magnetic concentration.

**Table 6**
Methods for PGM extraction.

| Method | Advantages | Disadvantages | References |
|---|---|---|---|
| Hydrometallurgy | Energy efficiency;<br>Processing flexibility; | Scale-up challenges;<br>Management of solid byproducts | [55,106,129,133] |
| Pyrometallurgy | Established technological maturity;<br>High recovery efficiency | Significant capital outlay;<br>Elevated energy consumption | [137,184,186] |
| Solvometallurgy | Selective metal extraction;<br>Reduced energy demands;<br>Processing flexibility | Solvent management and disposal;<br>Solvent environmental impact;<br>Scale-up challenges | [147–151,189] |
| Molecular Recognition Technology | Selective metal extraction;<br>Environmental gains;<br>High reaction speed | Limited applicability;<br>Financial implications | [152–157] |
| Biometallurgy | Moderate recovery efficiency;<br>Low toxicity;<br>Versatility;<br>Energy efficiency | Low extraction rate; pH and temperature sensitivity;<br>Scale-up challenges | [158–166] |
| Magnetic concentration | Low toxicity;<br>Energy efficiency;<br>Moderate recovery efficiency | Selective challenges;<br>Scale-up challenges | [111,112,194,196,197] |

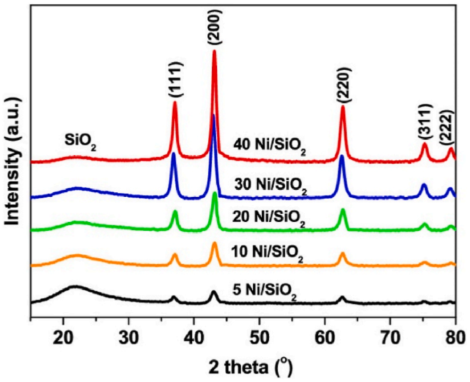

**Fig. 17.** – X-ray diffraction pattern of Ni/SiO$_2$ catalyst [209].

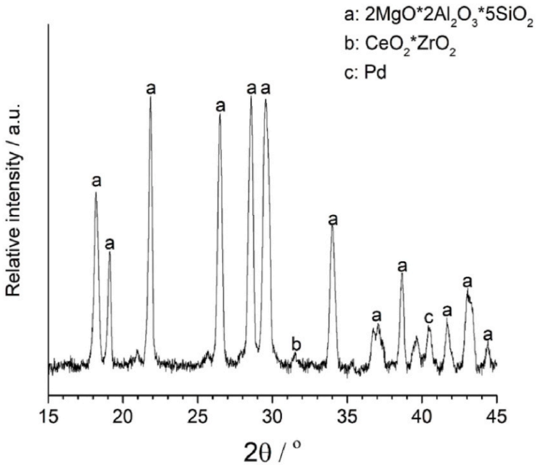

**Fig. 18.** – X-ray diffraction pattern of the utilized catalytic converter [210].

temperature of 640 °C. Given that catalytic converters can reach temperatures of 700 °C, this could account for the larger Pd nanoparticles we observed.

In the conducted study [211], a catalytic converter sourced from South Africa was investigated (Fig. 19).

The X-ray diffraction (XRD) analysis conducted on the gasoline catalyst sample confirmed the presence of distinct reflections,

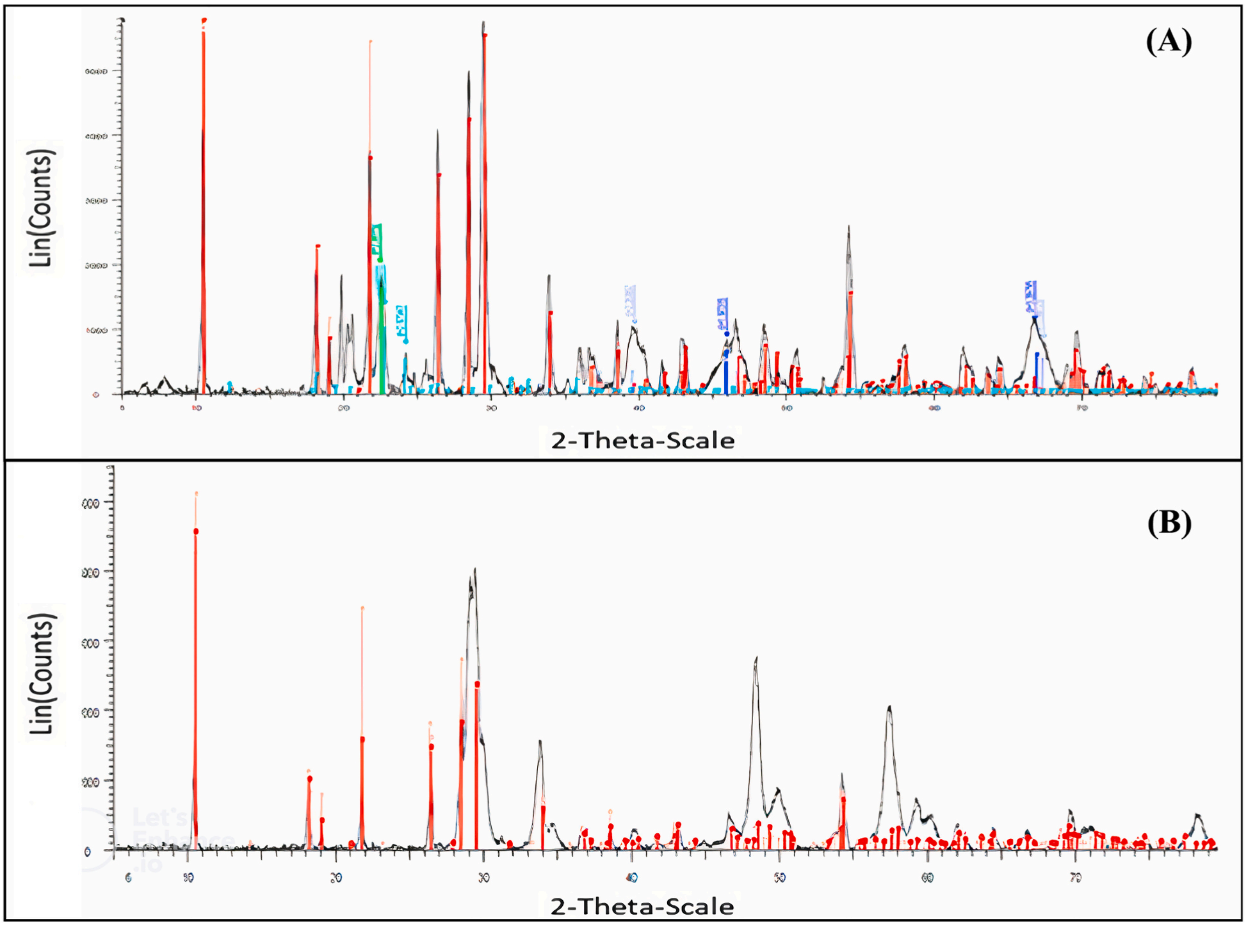

**Fig. 19.** – X-ray diffraction pattern of the utilized diesel (A) gasoline (B) catalytic converters confirming the presence of cordierite [211].

indicating the pure cordierite phase characterized by an orthorhombic $Mg_2(Al_4Si_5O_{18})$ structure (Fig. 19B). Conversely, the diesel catalyst sample (Fig. 19A) exhibited cordierite as the primary component (highlighted in red), along with minor phases including aluminum phosphate hydrate (depicted in turquoise), alumina (represented in blue), gamma alumina (shown in light blue), and aluminum silicate (illustrated in green). Notably, XRD did not detect any PGM phases, likely attributed to their small particle size and potential overlap with the dominant cordierite phase.

### 6.2. *Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)*

The investigation into the samples' morphological attributes was conducted through the utilization of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methodologies. SEM serves as a valuable tool for examining the physical attributes, including dimensions, crystalline nature, and phase interactions, manifesting on the sample's surface. By scanning the surface using a precisely focused electron beam, it becomes feasible to capture high-resolution images. The variations in contrast within these images unveil disparities in composition, a result of the emission of distinct electrons characteristic of the various elements constituting the sample [198,212,213].

Transmission electron microscopy (TEM) functions analogously to conventional light microscopy, wherein the optical system aids in the visualization of surface topography and morphological attributes, encompassing features such as particle geometry and dimensions. In the context of powder samples, such as catalysts, the initial step involves the reduction of particle size through precision grinding until a fine consistency is achieved. This fine particulate matter is subsequently dispersed within a volatile solvent, commonly isopropanol. A droplet of this suspension of particles is delicately deposited onto a thin carbon foil, which is firmly supported by a specialized microscope grid. Once the solvent undergoes evaporation, the powder particles are primed for size quantification and in-depth analysis.

Employing these methodologies provides an extensive comprehension of the catalyst samples' morphology, dimensions, and structural properties [198,214,215], as shown in the study of surfaces of $Fe_3O_4$ (Fig. 20a,c) and $SiO_2$ (Fig. 20b,d) [207].

The research study [210] included a thorough examination of the catalytic converter's physical structure, illustrated in Fig. 21. This image unveils spherical particles, distinguishably rendered in a deep black hue, conspicuously adhering to the cordierite substrate,

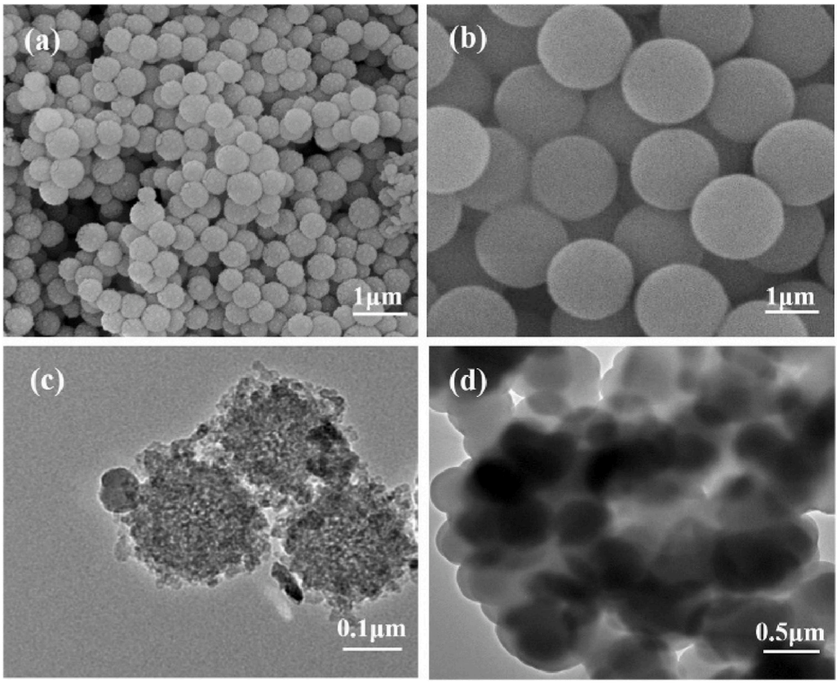

**Fig. 20.** – SEM and TEM images of $Fe_3O_4$ (a,c) and $SiO_2$ (b,d) [216].

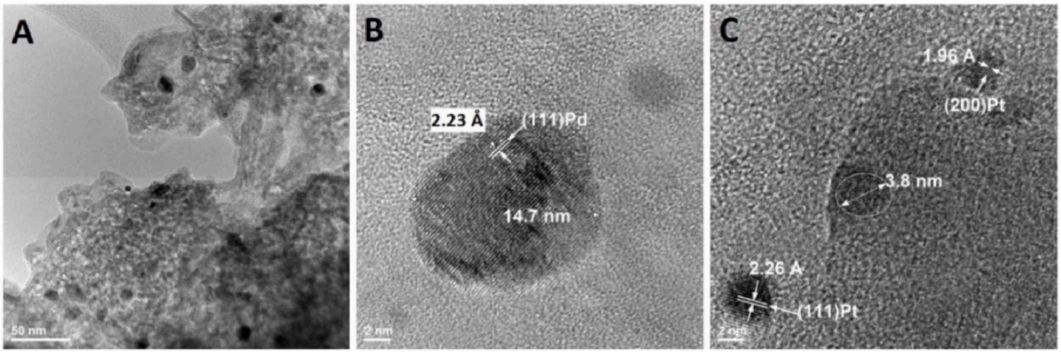

**Fig. 21.** – TEM micrographs of an utilized catalytic converter [210].

resplendent in a luminous gray tone (Fig. 21A). Delving deeper into the investigation through the utilization of transmission electron microscopy (TEM), the subsequent scrutiny disclosed the existence of two discrete categories of nanoparticles, each distinctly showcased in Fig. 21B and C.

The investigation detailed in the research study [211] delved into the morphological attributes of diesel (Fig. 22A–D) and gasoline (Fig. 22E–H) catalytic converters, and the findings are portrayed through the lens of scanning electron microscopy (SEM). This SEM analysis corroborated the presence of PGM ensconced within the honeycomb-like structure of cordierite, $2MgO–2Al_2O_3{\cdot}5SiO_2$ type. The morphology unveiled a unified configuration, characterized by a network of parallel channels, wherein the catalytically active material was conspicuously deposited along the inner walls of these conduits. This profound discovery resonates with prior research findings in the field [211,217].

### 6.3. *Brunauer-Emmett-Teller (BET) method (theory of polymolecular adsorption)*

The Brunauer-Emmett-Teller (BET) technique is a highly valuable analytical method employed for the examination of physical adsorption phenomena involving gas molecules on the surface of solid materials. It serves as a crucial tool for quantifying both the surface area and the distribution of pore sizes within the material under investigation. The BET theory, which underpins this method, exhibits remarkable efficacy when it comes to unraveling the intricacies of multilayer adsorption systems. In this method, gases that do not engage in chemical interactions with the material's surface are utilized as adsorbates. The primary goal is to ascertain the specific

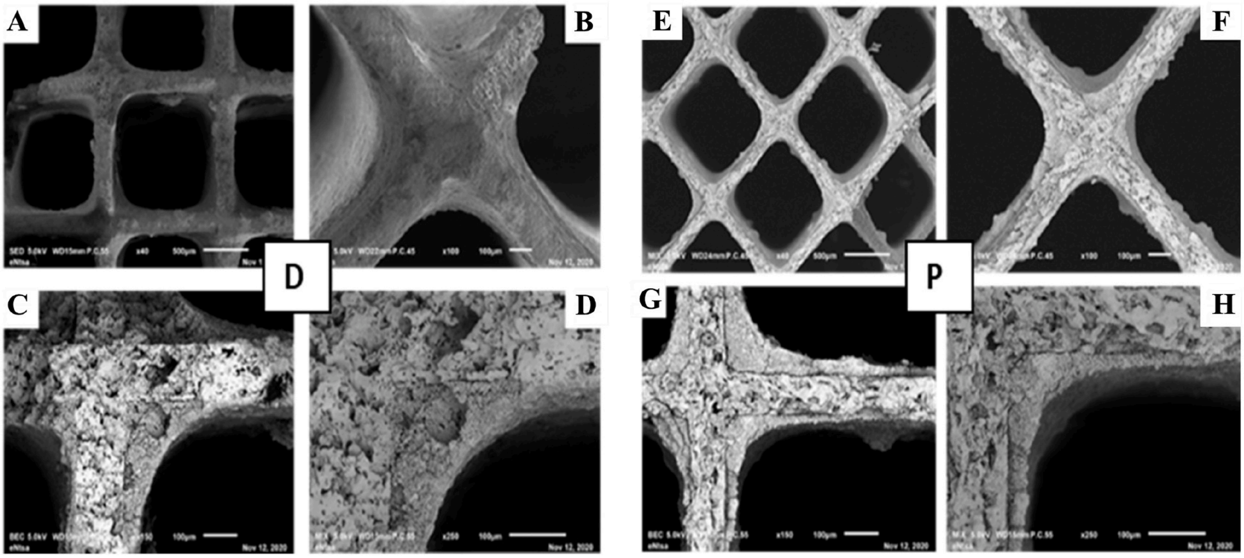

**Fig. 22.** – SEM micrographs of utilized diesel (D) and gasoline (P) catalytic converters at various magnifications [211].

surface area of the material. Typically, this analytical process unfolds under the conditions of liquid nitrogen's boiling point, which stands at 77 K. By using BET analysis to deduce the surface area and pore characteristics of catalysts, researchers gain insights into the potential dispersion of active metals within the catalyst material (Fig. 23a,b). This knowledge contributes significantly to understanding of catalytic processes and their optimization [198,218].

### 6.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) stands out as a prominent and indispensable technique in the realm of surface analysis and unraveling the intricate chemical compositions of materials. Its lies in furnishing insights into not only the elemental composition but also the empirical formula, chemical configuration, and electronic disposition of the elements residing on the material's surface. The operational principle underpinning XPS hinges on the stimulation of electronic states within the atoms at the sample surface via photons endowed with specific energies. Through the meticulous detection and examination of the ensuing emission of photoelectrons, XPS empowers scientists to tease apart distinctive chemical states across diverse samples (Fig. 24). This method serves as a base in the determination of characterizing surface attributes and delving into chemistry of materials [198,220].

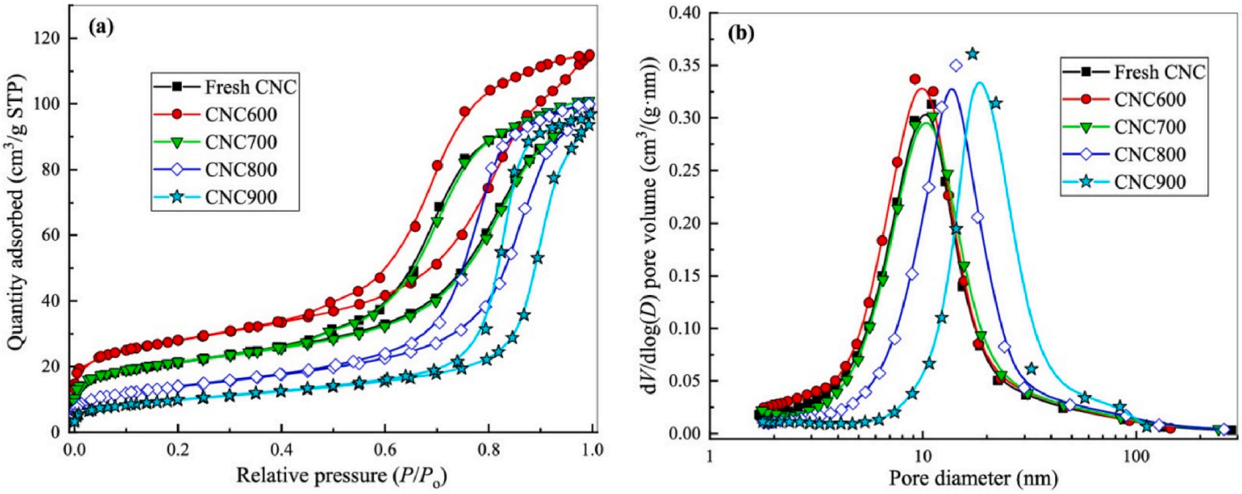

**Fig. 23.** – $N_2$ adsorption-desorption isothermal curve (a) and pore size distribution diagram (b) of a Ni-based catalyst [219].

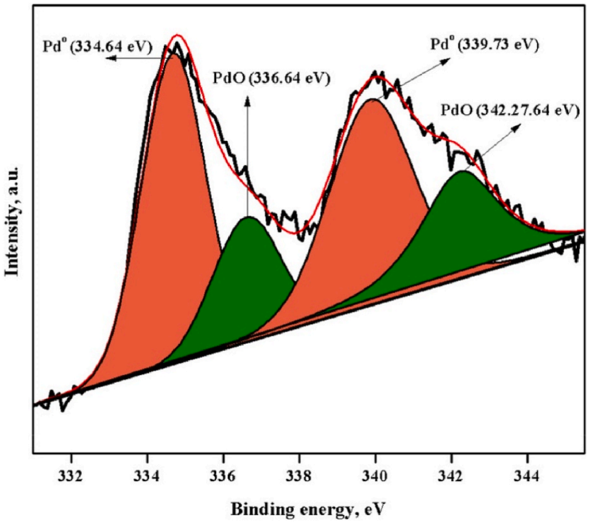

**Fig. 24.** – XPS spectrum of Pd/f-$SiO_2$ catalyst [221].

### 6.5. *FT-IR spectroscopy*

FT-IR spectroscopy, a powerful tool in the realm of vibrational spectroscopy, opens a window into the molecular composition of samples. This technique leverages the absorption of infrared radiation by molecular vibrations, enabling the elucidation of the intricate molecular structures within these samples. Whether one opts for the KBr method or the powder method, FT-IR spectra can be acquired with a high-resolution capability of 4 $cm^{-1}$, spanning a comprehensive range from 4000 to 400 $cm^{-1}$, typically involving an average of 100–200 scans. The versatility of FT-IR spectroscopy extends its reach across a broad spectrum of materials, encompassing both inorganic and organic substances. In the area of heterogeneous catalysis, it assumes a pivotal role. It aids in the identification of functional groups and delves into the molecular intricacies that define the structure of catalysts [198,222].

## 7. Conclusion

Innovative methods are crucial for extracting platinum group metals (PGMs) from ores, driven by the challenging procedures involved. Recycling catalytic waste, especially from automotive catalytic converters, has become essential. Two primary recycling techniques, hydrometallurgy and pyrometallurgy, are prominent.

Hydrometallurgy involves treating catalytic waste to eliminate organic residues. Catalysts like Pt/$\gamma$-$Al_2O_3$ and Pd/$\gamma$-$Al_2O_3$ can be dissolved in sulfuric acid, concentrating platinum (Pt) and palladium (Pd). However, limitations such as subpar extraction rates for rhodium, high reagent costs, hazardous waste generation, and prolonged processing hinder its advancements.

Pyrometallurgy involves fusion and chlorination, resulting in an auxiliary metal-PGM alloy, purified to extract PGMs. Despite effectiveness, challenges include equipment corrosion expenses and environmental risks from gases like carbon monoxide and chlorine.

To address these challenges, solvometallurgy and molecular recognition technology offer environmentally friendly alternatives with high selectivity and swift reaction kinetics. Another promising approach involves magnetic concentration directly from catalytic converter waste, using ferromagnetic iron deposition onto PGM particles. This scalable method requires minimal energy and emits no harmful substances.

These innovative approaches, including solvometallurgy, molecular recognition technology, and magnetic concentration, provide advantages in selectivity, reaction speed, and environmental sustainability. The resulting catalytic systems have diverse applications in industries such as chemicals, energy, petroleum, jewelry, and healthcare. The continuous evolution of efficient methodologies is vital for the sustainable utilization of these valuable metals.

## Funding

This work was supported by Ministry of Science and Higher Education of the Republic of Kazakhstan AP23489158.

## Data availability statement

No data was used for the research described in the article.

## CRediT authorship contribution statement

**Irina Chidunchi:** Writing – review & editing, Writing – original draft. **Maxim Kulikov:** Writing – review & editing, Writing – original draft. **Ruslan Safarov:** Writing – review & editing, Writing – original draft. **Eldar Kopishev:** Writing – review & editing, Writing – original draft.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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