CATALYSTS RECYCLING THE WAY TO A SUSTAINABLE FUTURE

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Abstract

Auto catalysts that have been discussed hold significant amounts of platinum-group metals such as platinum, palladium, and rhodium, depending on the specific type of catalyst. This makes them a potential reservoir of these precious metals. This discussion aims to introduce individuals to catalysts in a broader context, including their historical significance and, importantly, the potential methods for extracting and utilizing these noble metals further. The article primarily delves into the theoretical aspects of processing spent catalysts, exploring both pyrometallurgical and hydrometallurgical techniques. Platinum-group metals (PGM) are exceptionally rare and notoriously difficult to acquire elements on our planet, presenting a significant risk of potential supply shortages. Despite this, their importance remains paramount for both the European Union (EU) and the automotive sector. It's important to note that not every catalyst used in the market can be effectively recycled, primarily due to the absence of these valuable metal components.

Keywords: Precious metals, catalyst, recycling, PGM

1. INTRODUCTION

In the dynamic environment of modern industry and technological advancement, the concept of sustainability has emerged as a primary aspect. As societies strive to achieve a harmonious balance between economic growth and environmental care, the critical role of recycling processes becomes increasingly evident. Among these processes, catalytic recycling stands out as a key player on the path to a more sustainable future.

The necessity for catalysis recycling becomes even more apparent when considering the intricate composition of modern catalysts. Numerous industrial catalysts are designed with complex structures that incorporate rare and precious metals like platinum, palladium, and rhodium, collectively known as Platinum Group Metals (PGMs). These metals, acclaimed for their exceptional catalytic properties, confront a challenging paradox. While propelling the development of sustainable technologies, their scarcity and associated geopolitical intricacies pose significant supply chain risks. This dual nature of PGMs intensifies the urgency to implement effective recycling procedures that ensure the responsible and efficient utilization of these valuable resources.

The need for catalytic recycling goes beyond the scope of resource conservation. It deeply resonates with the global effort to reduce the ecological footprint of various industrial sectors. Given that catalytic processes are an integral part of sectors such as energy production, transportation, and chemical manufacturing, the effective recycling of catalysts contributes to reducing energy consumption, lowering emissions, and minimizing waste generation. These outcomes align with international sustainability goals and regulatory frameworks aimed at mitigating climate change and promoting a circular economy [1].

1.1 Auto catalyst history

Environmental pollution results from various sources, including the release of harmful substances into the air from industrial activities, oil extraction, agriculture, and waste disposal, among others. As the automotive industry expanded, emissions from vehicle exhausts into the atmosphere also increased, leading to a worsening of environmental pollution. To combat this issue, efforts were initiated to address pollution through legislative means, specifically through the implementation of emission standards.

2. IMPORT AND DEMAND OF VALUABLE METALS IN THE WORLD

Metals from the platinum group find applications in various industries, including dentistry, jewelry, and chemical processes. However, their primary and most crucial role stems from their catalytic properties. Roughly half of the platinum and palladium produced are utilized as catalysts in automotive and industrial processes. In the case of rhodium, an even more significant proportion (around 80-90%) is employed as an alloying element in the active layer of different catalysts. The substantial quantity of ore required to yield just a small amount of PGM (approximately 300-900 kg to obtain 1 g) contributes to their high market prices. Typically, platinum and palladium ores contain 5-10 times higher concentrations than rhodium and ruthenium, and about 50 times higher concentrations than iridium and osmium [3].

Moreover, there is a notable geographical limitation of PGM sources, with a heavy reliance on South Africa and Russia as the primary suppliers. This creates a substantial imbalance between PGM supply and demand worldwide, making catalyst recycling essential from both ecological and economic perspectives. The industry is driven to enhance catalyst efficiency due to the high costs of PGM. This is achieved through improvements in wash coat technology, where the use of rare-earth elements like cerium oxide increases surface area and ensures oxygen supply. However, the inclusion of cerium in the recycling process of catalytic converters introduces an additional critical element, posing a significant challenge for conventional pyrometallurgical recycling methods [3].

The geographical mismatch between PGM suppliers (predominantly Africa and Russia) and consumers (Europe, China, Japan, and North America) is evident. A substantial portion of global PGM reserves, approximately 95%, is concentrated in South Africa, with Russia holding about 1.6%, and the remaining 2.8% distributed elsewhere. This underscores the heavy reliance on African supply, particularly due to the cost-intensive processing of ore in regions like Russia with permafrost soil and deep mines in Africa. Addressing a sudden surge in demand, as seen in Russia, is not straightforward, as PGMs are by-products of nickel production. Increasing PGM output would require a boost in nickel production, potentially leading to oversupply and reduced prices for the primary product, nickel.

A similar, and even more pronounced, situation can be observed with rare-earth elements, with particular interest in cerium, which is integral to catalyst wash coats. China has historically dominated global rare earth production, accounting for a significant share. Efforts to diversify resources outside of China, especially for heavy rare earths, have been challenging due to the complexity of the chemistry involved.

Another factor contributing to price fluctuations is the significant role played by the automotive industry in utilizing platinum, palladium, cerium, and rhodium in the form of catalytic converters. Statistics reveal that approximately 55% of palladium and platinum, or 40% of platinum and 67% of palladium, are used in automotive catalysts. This heavy reliance on the automotive market makes the PGM supply highly susceptible to automotive industry dynamics. As you can see in **Figure 1** [3].

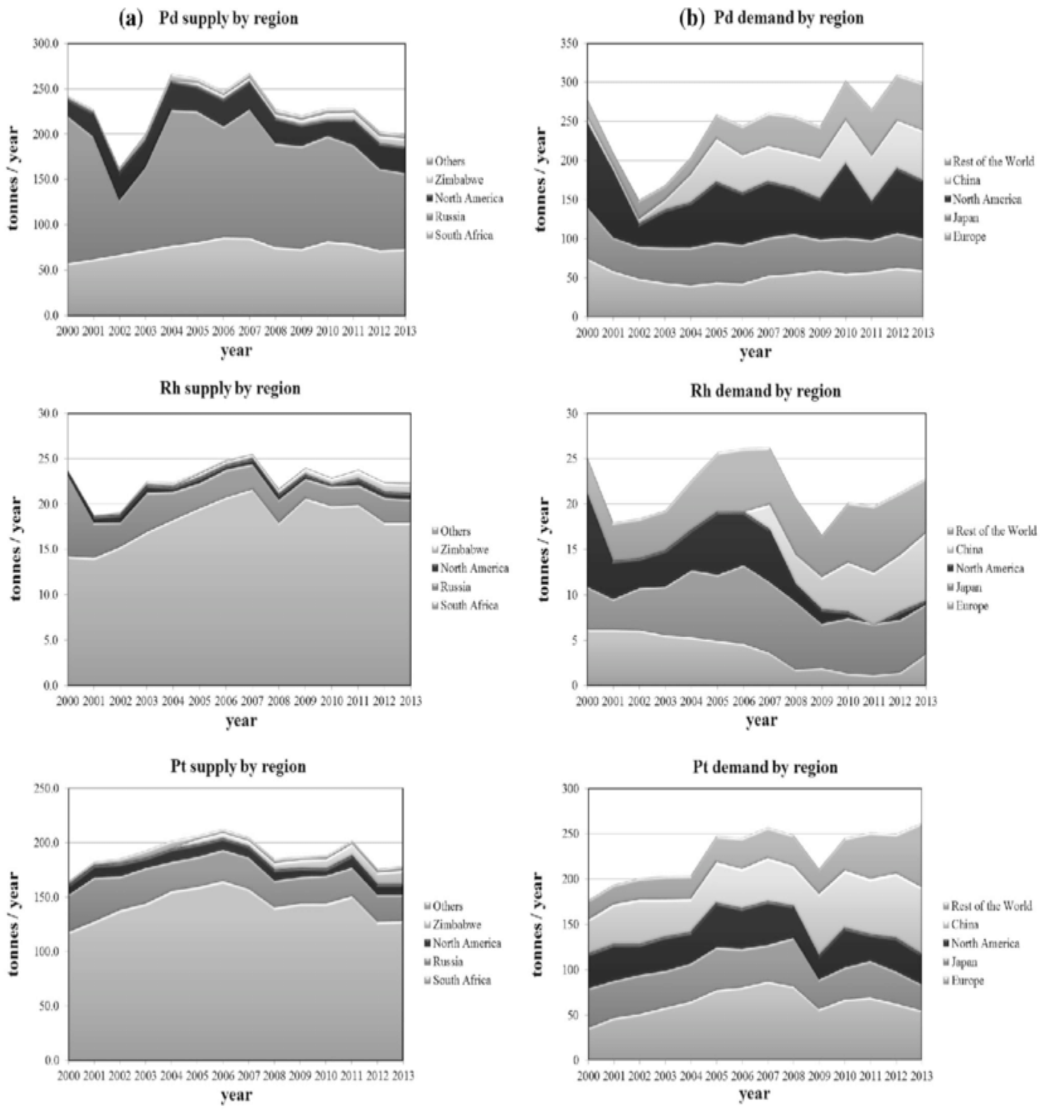

Figure 1 Platinum, palladium, and rhodium supply (a) and demand (b) by region and their development since 2000 [3]

3. PREPARE OF IDENTIFICATION OF SUSTAINABLE CATALYST

The determination of the specific catalyst used relied on the container code, with key attributes of each catalyst being the vehicle model and catalyst type, see **Table 1** and **Table 2**. To confirm the catalyst type, a chemical analysis was conducted to assess the metal content [4].

Table 1 Identification of 3 catalysts on market [6]

Number	Canister code	Model Car
1	13106917	Opel Astra H
2	8200358551, C114	RENAULT ESPACE, 2200CC, DIESEL
3	3B0131701Q, 8D0178E, GLH	AUDI A6, 2400CC, DIESEL

The process involved the disassembly of every catalyst, extracting the metal container, and acquiring the ceramic catalyst, which was then prepared for a physicochemical analysis. Great care was taken during the decanning process to avoid damaging the ceramic monolith, ensuring that weight and dimensions could be assessed [5].

Tab. 2 Dimension of catalyst [6]

Number	Weight, g	Height, cm	Diameter, cm
1	952.30	9.7	20.1
2	1026.75	14.4	10.7
3	573.50	11.9	11.4

The dimensions of each catalyst were determined based on their specific shape. In the case of cylindrical catalysts, measurements included weight, height, and diameter. Each ceramic catalyst was prepared for microscopic examination and elemental analysis (XRF). This preparation included a series of steps like grinding, milling, and sieving to reduce the particle size to less than 250 µm. During the grinding process, small samples were extracted from each catalyst for optical microscopy analysis, enabling the observation of cell structures and measurement of their dimensions.

3.1 Process of identification of sustainable catalyst via optical microscopy

- **Catalyst number 1:**

To capture images from different areas under the optical microscope, two small pieces were collected from the spent catalyst see **Figure 2**. These fragments were used to evaluate both the cell density and the thickness of the ceramic monolith walls [5].

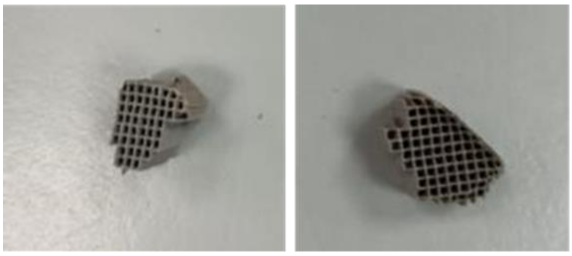

Figure 2 Pieces from catalyst number 1 [6]

By examining images captured with an optical microscope, an assessment was made regarding the cell density and the thickness of the wash coat on the monolith. The results obtained through optical microscopy indicated an approximate cell density of 527 cells per square inch (cpsi). Additionally, measurements and computations determined a cell wall thickness of 0.193 [mm] and a wash coat thickness of 0.049 [mm] **Chyba! Nenalezen zdroj odkazů.**.

- **Catalyst number 2**

To visually examine various areas under the optical microscope, two small sections were collected from the spent catalyst, as shown in **Figure 3** on left side. This allowed for the evaluation of both cell density and the thickness of the ceramic monolith walls. The images captured via the optical microscope were also employed to measure the cell density and the wash coat thickness of the monolith. Specific regions were selected, as depicted in **Figure 3** on right side, to quantify the catalyst's cell density.

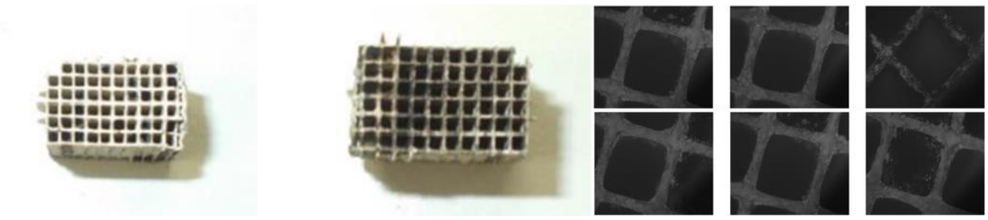

Figure 3 Pieces from catalyst number 2 and optical microscope images from catalyst number 2 [6]

- **Catalyst number 3**

To obtain a range of viewpoints under the optical microscope, two small fragments were collected from the spent catalyst, as illustrated in **Figure 4** on left side. The primary objective of this process was to assess both the cell density and the thickness of the ceramic monolith's walls. The cell density and the wash coat thickness of the monolith were ascertained by analyzing the images captured using the optical microscope. Specific areas, as indicated in **Figure 4** on right side, were selected for the purpose of quantifying the cell density of the catalyst **Chyba! Nenalezen zdroj odkazů.**.

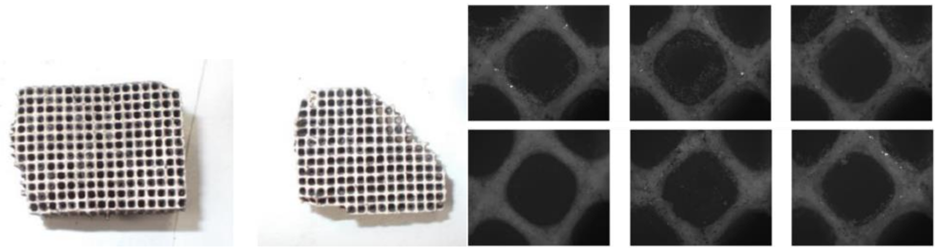

Figure 4 Pieces from catalyst number 3 and optical microscope images from catalyst number 3 [6]

3.2 X-ray Fluorescence (XRF) analysis and Calcination process

The determination of PGM (Platinum Group Metals) loading was accomplished using X-Ray Fluorescence (XRF) spectroscopy. XRF analysis is characterized by its precision, speed, non-destructive nature, and repeatability, eliminating the necessity for chemical preparation. Consequently, there is no requirement for chemical reagents, which helps minimize costs. The XRF spectrometer used comes with a built-in calibration provided by the manufacturer, ensuring precise measurement of Pt, Pd, and Rh in used catalysts with average PGM concentrations of 1000 [ppm], 1700 [ppm], and 300 [ppm], respectively.

In addition to the manufacturer's calibration, an extra calibration was conducted to further enhance the accuracy of XRF measurements. This supplementary calibration allowed for the calibration of Pd within a loading range of 1270-2730 [ppm], Pt within a range of 614-2760 [ppm], and Rh within a range of 237-322 [ppm]. The PGM content of two small samples from each catalyst was assessed, and their average was computed (**Table 3**). These measurements were used to confirm the uniformity of the catalyst samples [6].

As previously mentioned, the microscopic examination identified the presence of organic residues within the catalytic converter's structure. Consequently, a calcination procedure was carried out on small-scale samples to measure the mass of these organic deposits in each catalyst. Furthermore, the calcined samples were subjected to XRF analysis to assess how these organic compounds affected the detection of PGM concentrations. The quantification of organic deposits was based on comparing the sample mass before and after the calcination process, which was conducted at a temperature of 750°C for a duration of 5 hours. The impact of calcination was visually observable, particularly through changes in the color of the various samples [6].

4. CONCLUSION

In summary, a total of three used catalysts underwent a comprehensive physicochemical analysis. This involved the identification of the catalysts, preprocessing, and XRF analysis to prepare the samples for chemical assessment and determine the PGM (platinum, palladium, rhodium) content. A calcination process was executed to detect any potential organic residues in each sample, and XRF analysis was conducted both before and after calcination to evaluate how organic compounds influenced PGM detection.

Regarding the final categorization of the provided used catalysts, those containing rhodium and platinum or/and palladium were classified as Three-Way Catalysts (TWC). Conversely, catalysts predominantly consisting of platinum or/and palladium were typically identified as Diesel Oxidation Catalysts (DOC). However, spent catalytic converters with low concentrations of platinum or/and palladium might be considered Dual-Function Catalysts, considering additional details like the vehicle model and year of manufacture. As you can see in **Table 3**.

Tab. 3 Conclusion table

Number	Pt [ppm]	Pd [ppm]	Rh [ppm]
1	-	1945	348
2	620	-	-
3	2434	-	-

As a result of this detailed analysis, the following research findings were obtained.

- Only catalyst number 1 is identified as a suitable for recycling thanks to the values of Pd and Rh.
- Only Pt was detected in the other catalysts.

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