

# The role and the recovery of Platinum-Group Metal catalysts in the pharmaceutical industry

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**KEYWORDS** - Recovery, precious metals, spent catalyst, platinum-group metals, catalysis, Peer Reviewed.

**ABSTRACT** - In terms of its history and chemistry, Platinum-Group Metal catalysis is one of the richest research areas. In the article, the authors describe the role of PGMs in pharmaceutical catalysis, from their industrial application through to their recycling.

## INTRODUCTION

As science and technology have progressed, the use of many elements of the periodic table has now become ubiquitous. However, the extensive use of some elements can be considered unsustainable from an environmental and economic point of view. Today, the critical depletion of known element reserves represents a hot topic for the global economy and for industry. These elements are frequently of strategic importance and associated with supply risks (1, 2). The "critical region" in the periodic table (figure 1) mainly involves the right-hand side of the transition metals (e.g. Au and Ag) and the post-transition metals (e.g. Sn, Pb and Tl). The Platinum-Group Metals (PGMs), which comprise Pd, Pt, Rh, Ir, Ru and Os, are included in the European Union's 2017 Critical Raw Material list.

This index represents a measure of how easy it is to substitute an element. The values range from 0, being the easiest case to substitute, to 1 for the hardest. In the case of PGMs, the substitution index is 0.93 regarding economic importance and 0.98 regarding supply risk (1).

Figure 2 depicts applications for Pt, Pd and Rh along with the individual share of production capacities excluding investments (3). The most important demand is catalysis, where the purification of automotive exhaust gases is the dominant use.

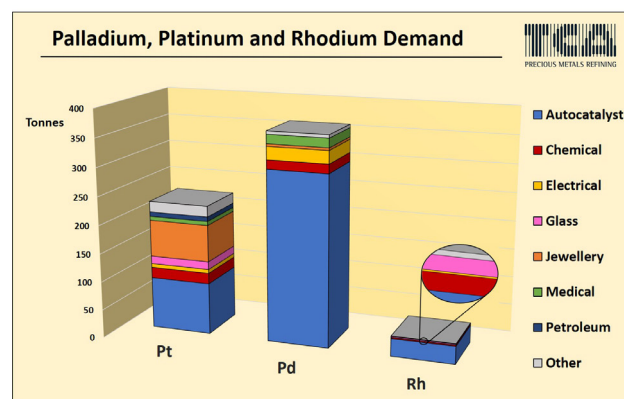


Figure 2. Palladium, platinum and rhodium demand (3).

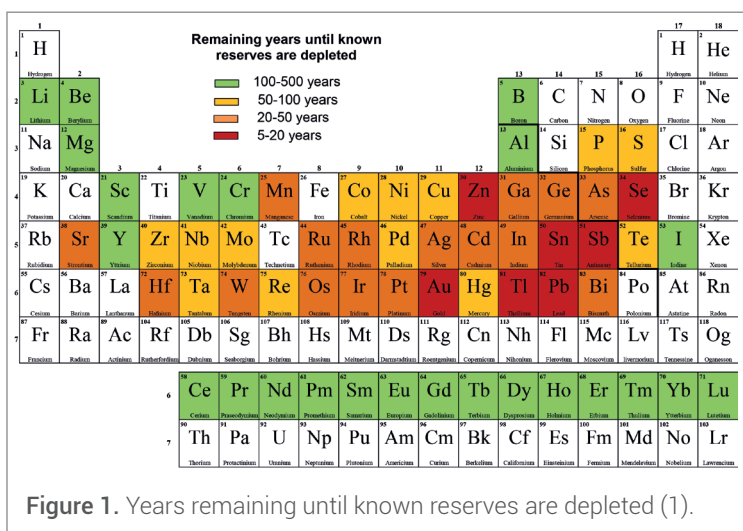
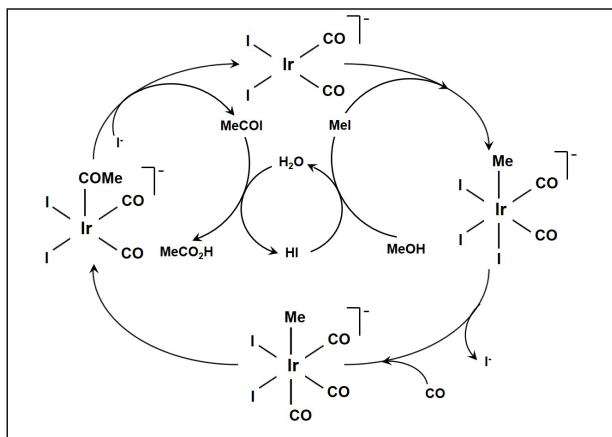


Figure 1. Years remaining until known reserves are depleted (1).

PGMs play a fundamental role in high-tech equipment, automotive emission control and chemical process catalysis. The driving force behind their extensive use comes from their peculiar – and sometimes unique – chemical-physical properties, as evidenced by the high substitution index (SI) value.

From a historical point of view, it is not surprising that price spikes recorded over the years are often linked to the catalysis industry. Indeed, when the scale-up of new processes to an industrial scale occurs, involving a large amount of PGM catalysts, the initial installation of fresh catalysts in the plants can increase net demand, having a substantial effect on the metal prices. This phenomenon is more likely for Rh, Ir and Ru due to their lower availability compared with Pd and Pt. For example, the price of iridium rose considerably during the three-year period 1996-1998 following substantial use of the complex  $(\text{Ir}(\text{CO})_2)_2^-$  in the Cativa process (4) for the production of acetic acid (figure 3) and, simultaneously, the introduction by Mitsubishi of an iridium-based catalyst for gasoline direct injection (5). Reliance on PGMs could be reduced by finding a suitable alternative. But even today, despite a green approach using enzymes and organocatalysts, catalytic reactions usually involve transition metals on an industrial scale. The use of PGM catalysts also leads to many disadvantages: PGMs represent a higher environmental burden (e.g. global warming potential, cumulative energy demand) than lighter metals in the first row of the periodic table (e.g. Fe, Ni) (6).



**Figure 3.** The reaction cycle for the Cativa iridium-catalysed carbonylation of methanol to acetic acid (5).

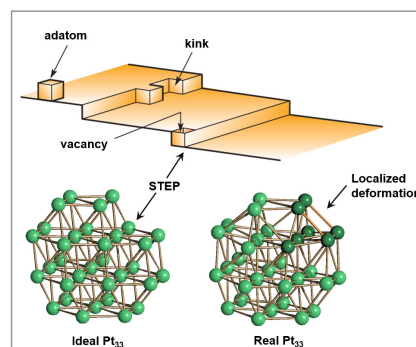
PGM recycling constitutes an attractive goal when it comes to avoiding the depletion of natural resources, as well as reducing the waste associated with mining (7).

### CATALYSIS IN THE PHARMACEUTICAL INDUSTRY

PGM catalysis has become fundamental to modern pharmaceutical design and manufacture (8, 9). In particular, palladium catalysts are most frequently used for cross-coupling reactions (*e.g.* Mizoroki-Heck reaction), while asymmetric hydrogenations involve the use of Rh, Ru and Ir. The ninth principle of green chemistry mentions the use of catalysts to increase selectivity and minimise waste, reaction time and energy demands (10). The cradle-to-gate life cycle assessment shows that the benefits of using PGMs as catalysts counterbalance their production (11).

In the pharmaceutical industry, as in fine chemistry, PGMs on activated carbon powder are most frequently used. Generally the main metal used is palladium in the form of highly dispersed nano-scale particles with a loading of 5 %. Zeolite, silica and alumina supports, like activated carbon, are characterised by a high surface area and constitute a suitable alternative in heterogeneous catalysis. Metal particle size and distribution, sintering control, support and doping effects are only some of many parameters that are investigated in order to synthesize tailor-made catalysts. Homogeneous catalysts have shown steady growth over the past few years. However, the subsequent separation (*e.g.* by distillation) of the catalyst from the reaction products represents the most important issue for industry (12). The advantage of homogeneous catalysts is that their reaction mechanisms are generally well-understood and their transition states are predictable. Therefore for these reactions it is generally possible to tune the chemo-, regio- and stereoselectivity. This knowledge gap is partly due to the faster development of solution spectroscopy compared with solid-state. From a historical point of view, this gap represented an important driving force for the synthesis and chemical-physical characterisation of suitable nano-structures as molecular models for bulky surface material. In this context, the Muetterties cluster-surface analogy from the 1970s represents an exciting example (13).

The analogy consists of finding parallels between ligand reactivity within a cluster (like homogeneous catalysts) and transformations of organic molecules on metallic surfaces (like heterogeneous catalysts). However, even if the metal cage of nano-clusters may be viewed as chunks of a metal lattice (14), the structural analogy is not necessary reflected in the associated catalytic properties (Figure 4).



**Figure 4.** Ideal and real  $\text{Pt}_{33}$  core of  $(\text{Pt}_{33}(\text{CO})_{38})^{2-}$  carbonyl clusters (14) compared to a step defect in bulky surface material of platinum particles in a heterogeneous catalyst.

Since precious metal-bearing catalysts are made in many sizes and configurations, identification of the best sampling and recovery technique is the key to an efficient and reliable recycling process. The next paragraph presents a brief overview of the main industrial treatments.

### RECOVERY OF SPENT PHARMACEUTICAL CATALYSTS

Owing to their high value, the recovery of PGMs from spent catalysts is crucial to the overall economic performance of chemical processes. A typical flowsheet of the metal recycling process can be split into three fundamental steps: pre-treatment, recovery and refining (figure 5). The pre-treatment process involves all the operations carried out to convert the spent catalyst into a suitable product for the subsequent sampling and recovery steps. Sampling should only be conducted with homogenised material, and performed as early as possible in the refining chain (15). Indeed, any treatment-manipulation prior to sampling entails an unavoidable, even if minimal, loss of material. Accurate and repeatable assaying procedures are guaranteed by spectrum analysis (*e.g.* X-ray fluorescence and inductively coupled plasma emission spectroscopy). In addition, classic volumetric, gravimetric and fire assay techniques (*e.g.* cupellation) (16) are involved. When all methods are used together, they provide the most thorough and most precise approach for determining precious metal content in spent catalyst materials, thus ensuring the highest possible returns.

The type of catalyst, like the nature of the solvent and substances in which is soaked, affects the choice of suitable pre-treatment. Generally, for pharmaceutical catalysts, **incineration** represents a widespread stage for most PGM refiners such as TCA. The incineration process can be simultaneously used to increase the PGM grade and to obtain a representative homogenised sample.

Incineration is conducted in special furnaces, whereby the organic content consisting of toxic and/or hazardous chemical compounds is destroyed.

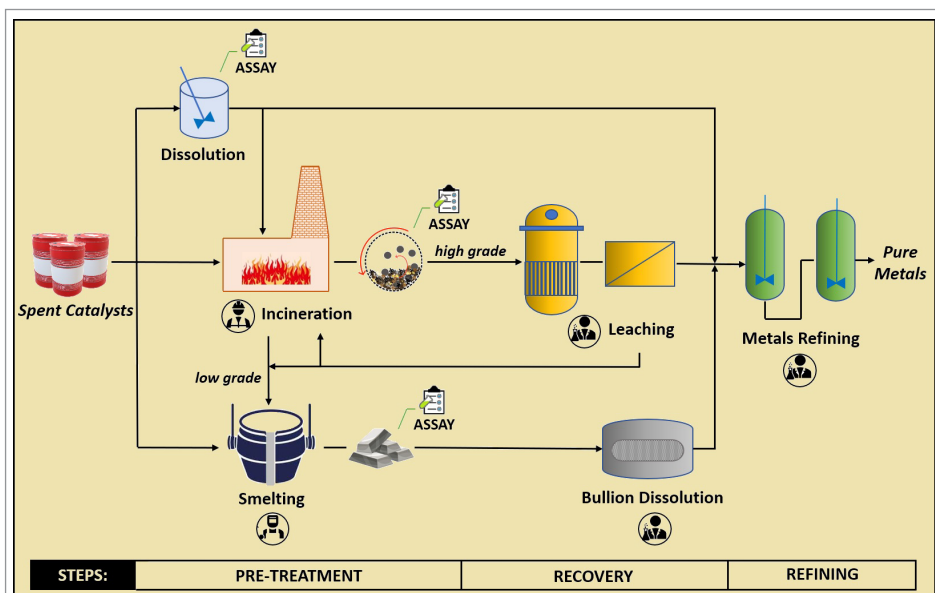


Figure 5. Basic flowsheet for spent catalyst recycling.

Alternatively, for heterogeneous catalysts, in the case of volatile organic substances separation can take place by means of simple drying. However, from a practical point of view, incineration represents a common choice even if in principle drying can be conducted. As a result of the concomitant presence of organic substrates, chloride compounds and metals, the incineration of spent catalysts gives rise to a high production of dioxins. It is therefore not surprising that the incineration plants for recycling catalysts are equipped with a large post-combustion chamber in order to destroy the dioxins and furans. The temperature and time of permanence of the smoke are the two most important parameters when considering the size of the plant. Moreover, a baghouse filter with activated carbon and/or lime for abatement of the physical particles is always present. In addition, a scrubber system may be involved in order to improve abatement of the particles and the chemical adsorption of acidic gases (*e.g.*  $\text{NO}_x$  and  $\text{HCl}$ ). After incineration, the burned spent catalyst is ground and the ash particle size selected by sieving. The granulometry represents a critical parameter in the subsequent homogenisation process (blending) which can be carried out using a batch mixer, roto-barrel machine or cyclonic vacuum cleaner. Finally, the homogenised ash is sampled.

Pyrometallurgical **smelting** may be involved in the catalyst recycling. However, this treatment is generally used as a recovery step rather than as a pre-treatment. This is due to the fact that, like incineration, the direct smelting of spent catalyst generates dioxins and furans, and the foundries of metal refiners are not necessarily equipped with a post-combustion chamber. Smelting treatment may be used after incineration when the PGM content is below 3-4 % and chemical recovery is not suitable. Metal collectors (*e.g.*  $\text{Cu}$ ,  $\text{Fe}$ ) can be used to improve the recovery yield (17) and to obtain a homogeneous bullion for the next assay stage (pre-treatment scenario).

Nevertheless, smelting treatment prior to the assay represents an issue when it comes to PGM quantification owing to material loss in the off-gas. On the basis of these features, pyrometallurgy treatment is systematically applied only in internal industrial recovery after the customer assay. The assay may be conducted on the bullion or in the homogenised molten metal. After the assay, in the latter case the molten alloy is poured into cold water with a thin stream moving the crucible in a circular motion or bubbling air into the water. This operation promotes the formation of shell-shaped grains with a high surface area for the subsequent metal recovery by chemical dissolution (*e.g.* aqua regia system).

Another pre-treatment approach for the quantification of PGM content consists of directly **suspending** as-received, spent catalysts in a batch vessel by adding water and surfactant agents. A homogeneous suspension is ensured by means of vigorous mechanical and/or air agitation and by using a pumped recirculation loop. A sample of the slurry mixture is removed from the recirculation loop and analysed. Suspension treatment may be followed by filtration and treatment via the traditional incineration route or by direct recovery of PGMs. A common recovery treatment, as in the case of incinerated spent catalyst, consists of chemical leaching (figure 5). However, after suspension treatment, a wet oxidation process may be involved using air or other oxidising agents (*e.g.* hydrogen peroxide). During the oxidation, the carbonaceous material is converted into carbon dioxide and nitrogen gas, without the formation of dioxins or furans, leaving PGMs and other metals as their oxides. Unfortunately, the drastic operating conditions involved in the process have prevented its widespread industrial development. Indeed, in the case of the **AcquaCat** process, a high temperature (above 370 °C) and pressure (above 220 bar) are required in order to ensure supercritical water oxidation (18). In classic hydrometallurgical processing, PGMs are **leached** directly or after pre-treatment using alkali or acid in the presence of a suitable oxidising agent (*e.g.* nitric acid, sodium chlorate). The formulation of the leaching solution varies from industry to industry and is mainly related to the subsequent refining process treatment. The leached PGMs in the solution are separated by filtration and the depleted matrix may be re-incinerated or melted.

Another chemical approach for the recovery of PGMs contrasting with leaching treatment consists of the hydrometallurgical dissolution of the matrix. For example, on the basis of their amphoteric properties,  $\gamma$ -alumina substrates can be dissolved by caustic soda or sulphuric acid, leaving PGMs as an insoluble residue (17).



In the case of the Lindlar catalyst, calcium carbonate can be separated by palladium with the simple addition of sulphuric acid releasing carbon dioxide.

Finally, after the recovery process, the final step consists of the **refining** of the PGMs by means of which high-grade (>99.95 %) PGM sponge is obtained. Indeed, for the pharmaceutical sector, PGMs are generally traded in sponge form due to its high surface/volume ratio which allows simple and rapid chemical dissolution, the first step for catalyst synthesis. Generally, the refining process consists of the repeated and selective precipitation of insoluble PGM salts.

Over the past decades, new sustainable recovery and refining approaches have been intensively investigated by academic researchers (19), although they have found it difficult to scale-up. However, there are several types of refining approaches, many of which are not reported in the literature – neither as an article nor as a patent. Development of unreported refining process and the optimisation of the conventional ones constitute the typical know-how of a refiner company.

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## ABOUT THE AUTHOR

**Iacopo Ciabatti** received his PhD in Chemistry from the University of Bologna in 2015 working on the synthesis and characterization of multivalent carbonyl nano-clusters. Currently, he is R&D manager in TCA S.p.A. He is author of 41 papers published in refereed international journals, one patent and more than 20 communications to scientific conferences.

# News

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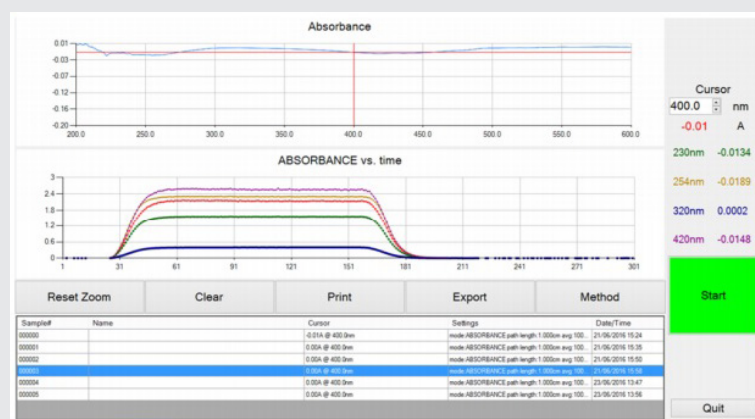
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