ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

RECOVERY AND OPTIMIZATION OF NANO-MATERIALS USED IN CATALYTIC CONVERTERS

M.Sc. THESIS

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Department of Nano Science and Nano Engineering

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KATALİTİK KONVERTÖRLERDE KULLANILAN NANO-MATERYALLERİN GERİ KAZANIMI VE OPTİMİZASYONU

YÜKSEK LİSANS TEZİ

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ARALIK 2019

Kadir Kıran, a M.Sc student of ITU Graduate School of Science Engineering and Technology student ID 513161015, successfully defended the thesis/dissertation entitled “RECOVERY AND OPTIMIZATION OF NANO-MATERIALS USED IN CATALYTIC CONVERTERS”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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RECOVERY AND OPTIMIZATION OF NANO-MATERIALS USED IN CATALYTIC CONVERTERS

SUMMARY

The demand for the platinum group metals (PGMs) has increased over recent years due to the fact that around 60% of the world's annual output of these metals, particularly platinum (Pt), palladium (Pd) and rhodium (Rh), is utilized to manufacture automotive catalysts, known as catalytic converters as well. In addition, the ratio of vehicles currently produced with PGM-containing automotive catalysts has risen to 98%. However, natural sources of PGMs are relative poor and it is therefore important to develop efficient methods both economically and environmentally for recovering PGMs from secondary sources, suchlike catalysts used in the vehicles.

In particular, the intended purpose of catalytic converters is to neutralise the toxic gases emitted by combustion process. They catalyse the reduction of NO_X and the oxidation of HCs and CO to N_2, CO_2 and H_2O with the percentage above 90%. As an instance, a vehicle sold in 1960 had higher emission values in contrast to 100 vehicles manufactured in 2014 with PGM-containing catalysts. While vehicle production continues to rise, the demand for PGMs is growing and the recovery from spent catalysts of these nanomaterials is gaining importance.

PGM recovery techniques from solid materials are numerous and these are categorized into pyrometallurgical, hydrometallurgical, or biometallurgical, without regard to the source of PGM. The use of the correct metallurgical method largely depends on the sort of metal and the energy cost needed to process the waste. The availability and quantity of the corresponding metal in nature is also another factor to be considered.

This thesis aims at extracting and separating Pd from the spent catalyst, which, is comprising Pd/Al_2O_3 as active materials, by using a simple and clear approach. For use in experimental studies, a commercially available spent catalyst containing Pd was procured. Respective catalyst used to be mounted and utilized orginally in a passenger car and its porous Al_2O_3 structure was coated by a Pd layer. To ensure the optimum recovery of Pd, a solution of distilled hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) were studied. Finally, addition of formic acid (HCOOH) was applied for separating Pd from the solution.

Consequently, Pd dissolution was accomplished by the leaching liqueur consisting of 6.3% HCl and 4.75% H_2O_2. The efficiency of the leaching was reported as 97% in response to the heat treatment at 80°C for 1.5 hours along with solid/liquid ratio of 1/9.5. Pd was reduced then effectively with the same volumetric raitos of leach liquor and HCOOH. Additional thermal process at 100°C for 1 hour was adequate to obtain efficiency of 95% for Pd recovery. Herewith a simplex and eco-friendly method was suggested in order to recover Pd from the spent catalyst on the basis of Al_2O_3 carrier.

KATALİTİK KONVERTÖRLERDE KULLANILAN NANO-MATERYALLERİN GERİ KAZANIMI VE OPTİMİZASYONU

ÖZET

Platin grubu içerisinde bulunanan metallerin (PGM) önemli bir miktarının otomotiv katalizatörleri olarak adlandırılan katalitik konvertörler üretmek için kullanılması son yıllarda dünyada bu tür metallere olan talebi arttırmıştır. İlk olarak 70'lerde, Amerika Birleşik Devletleri'ndeki otomobil üreticileri, otomotiv egzoz emisyonlarını azaltmak için değerli metalleri içeren katalitik konvertörlerin kullanılmasını önermişken, Batı Avrupa'da ise bu uyguluma daha sonra 80'lerde firmalar tarafından gönüllü olarak uygulanmaya başlamıştır. Yine ilerleyen yıllarda egzoz gazı emisyonlarını azaltmak amacıyla araç üreticilerinin mevcut katalitik konvertörlerin performansını modernize etmesini zorunlu kılan düzenlemeler zamanla devreye girmeye başlamıştır.

Günümüzde ise otomobillerin PGM içeren katalitik konvertör ile üretim oranı %98'e ulaşmış ve teknolojilerin gelişmesi ile birlikte değerli metallerin tüketim miktarı artmaya devam etmektedir. Platin gurbu metallere ait olan paladyum (Pd) bunlardan biri olmakla birlikte 2018 yılıyla itibariyle 304 tonluk üretim rakamlarına ulaşmıştır. İstatistiklere bakıldığında üretilen Pd miktarının yaklaşık %70'inin petrol-kimyasal madde rafinesi ve otomotiv katalizatörleri gibi katalitik konvertör endüstrisinde kullanıldığı görülmektedir. Ayrıca, Pd rezervleri Güney Afrika, Zimbabve, Rusya, Kanada ve Amerika Birleşik Devletleri gibi az sayıda ülkede yoğunlaştığı için, bu durum diğer ülke ve bölgelerin Pd arzını tehlikeye sokmaktadır. Bu nedenle, kullanılmış otomotiv katalizatörleri gibi atık veya ikincil kaynaklardan elde edilen PGM'yi geri kazanmak için etkili bir süreç geliştirmek, hem ekonomik hem de çevresel faktörler açısından önem arz etmektedir.

Araçlarda kullanılan katalitik konvertörlerin ana bileşeni seramik veya metalik taşıyıcıdan oluşmaktadır ve bu taşıyıcı başta platin, paladyum ve rodyum olmak üzere değerli metalleri içeren aktif bir tabaka ile kaplanmış durumdadır. Aktif katalitik materyalin kristal yapısının boyutu ne kadar küçükse (yüksek katalitik yüzey alanı), reaktanların etkileşime girmesi için o kadar fazla yüzey mevcut hale gelir. Kabaca, katalitik yüzey alanı ne kadar yüksek olursa kinetikler tarafından kontrol edilen bir süreç için reaksiyon oranı o kadar yüksek olur denilebilir. Bahse konu katalizörler, Al_2O_3, SiO_2, TiO_2, kristalimsi alümina-silikatlar veya zeolitler gibi yüksek yüzey alanlı bir destel malzemesine yayılır ve bu inorganik oksitler konvertörün aktivitesini, seçiciliğini ve dayanıklılığını korumada kritik bir rol oynar.

Ana yapı olarak kullanılan seramik taşıyıcıların üretimi için kordiyerit temel malzeme olarak kulanılır ve taşıyıcı üzerindeki alüminyum oksit CeO_2, NiO, BaO, CaO ve La_2O_3 ilavesiyle aktive edilir. Örnek olarak CeO_2'nin bu yapıdaki rolü, konvertörün oksijen depolama kabiliyeti arttırmak ve PGM dağılımının stabilizasyonunu sağlamaktır. Metalik taşıyıcılar ise aside dayanıklı çelikten yapılmış spiral veya haddelenmiş bir filmden oluşmaktadır. Metal yapının duvar kalınlığı, seramik eşdeğerinden %25 daha düşük olduğu için bu durum katalitik konvertör içerisindeki basınç düşümünü azaltmakta ve ısı iletkenliğini arttırmaktadır.

Diğer yandan Fe, Co ve Ni gibi baz metaller de endüstriyel uygulamalar için katalizör görevini görmektedir. Bu baz metaller Pt, Pd ve Rh'ye göre daha az katalitik aktiviteye sahip olmasına rağmen, çok daha uygun maliyetlidir ve bazı durumlarda daha seçici bir reaksiyon gösterir. Temel metallerden oluşan malzemelerin ticari uygulamalarda, özellikle katalitik konvertörlerde değerli metallerin yerine geçmesi amacıyla yapılan çalışmalar gün geçtikçe artmaktadır. Ancak, düşük katalitik etkinlik seviyeleri, zehirli bileşenlerle birlikte devre dışı kalmaları ve otomobil egzosunun yüksek ısılı ortamında hidrotermal stabilite sağlayamamaları sebebiyle henüz olgun bir ticari ürün ortaya çıkmamıştır.

Fonksiyonel anlamda ise katalitik konvertörler, egzoz gazlarının %90'ından fazlasını nötralize eder. Böylece NO_X gazının indirgenmesi, hidrokarbonlar ile karbon monoksitin %80'e kadar oksidasyonu sağlanmış olur ve nihai olarak N_2, CO_2 ve H_2O ürünleri ortaya çıkar. Komponentin bu yolla sağladığı katkıyı özetlemek gerekirse, 1960 yılında satılan bir otomobilin, 2014 yılında PGM içeren katalitik konvertörlerle üretilen yüz otomobilden daha fazla egzoz gazı ürettiğinden bahsedilebilir. Sonuç olarak içten yanmalı motor ile çalışan araç üretimi devam ettikçe değerli metallere olan talep artmakta ve bahse konu nano-yapıların kullanılmış katalizatörlerden geri kazanımı önem kazanmaktadır.

Katı malzemelerden metal geri kazanımı elde etmek için normal şartlarda birçok farklı teknik bulunmaktadır. Kaynağından bağımsız olarak, PGM'nin geri kazanım teknikleri, pirometalurjik, hidrometalurjik ve biyometalurjik olarak üçe ayrılabilir. Uygun metalurjik tekniğin seçilmesi, öncelikle metalin türüne ve atıkları işlemek için gereken enerjinin maliyetine bağlıdır. Göz önünde bulundurulması gereken diğer bir parametre ise ilgili metalin yer altı kaynaklarının yeterli olup olmadığı konusudur.

Bu tezin amacı, doğada az bulunan saf paladyumu halihazırda kullanılmış bir katalitik konvertörden temiz ve basit bir teknik kullanarak ayırmak ve geri dönüşümünü sağlamaktır. Bu sebeple deneysel çalışmalarda kullanılmak üzere yapısında paladyum içeren kullanılmış bir katalizatör tedarik edilmiştir.

Deney çalışmaları için alınan katalizatör daha önce bir binek araçta kullanılmış ve ince bir palladyum tabakası ile kaplanmış alümina gözenekli bir yapıya sahipti. Deneyler sonunda Pd'nin optimum miktarda geri kazanımını sağlamak için bir seyreltik hidroklorik asit (HCl) ve hidrojen peroksit (H_2O_2) karışımı üzerine çalışıldı. Sonraki adım için ise formik asit (HCOOH) ile Pd'yi liç liköründen ayırma işlemi öngörüldü. Kullanılan tüm kimyasallar laboratuvar kullanımı için uygun ürünlerden seçildi ve seyreltmeler için saflaştırılmış su kullanıldı. Çalışmanın sonunda ise gerekli nicel analizler farklı spektrometre cihazları kullanılarak yapılmıştır.

Deney adımlarını kısaca özetlemek gerekirse şu işlemlerden bahsedilebilir: Piyasadan alınan kullanılmış katalitik konvertörün bir örneği havan ile ezildi, öğütüldü ve liç adımlarında kullanılmak üzere bir elek içinden geçirildi. Daha sonra XRF analiz cihazı ile Pd'nin kullanılmış katalizatör tozundaki karakterizasyonu tespit edildi. Ardından gerekli miktarda katalizatör tozu, kullanım sırasında yüzeye bağlanan karbon bileşikleri yakmak amacıyla ısıl işleme tabi tutuldu. Katı madde içerisinde bulunan mevcut Pd'yi çözmek adına beherlerde farklı kombinasyonlarda liç çözeltileri hazırlandı ve karışım manyetik bir karıştırıcı ile karıştırıldı. Her deney aralığının sonunda, çözelti süzüldü ve Pd'nin çözünme miktarının hesaplandığı atomik absorpsiyon spektrofotometresi (AAS) ile Pd konsantrasyonu analiz edilmiş oldu.

Tüm deney adımlarının sonunda ortaya çıkan en iyi liç koşullarında, Pd içeren bir stok çözelti hazırlandı ve bu çözelti HCOOH ile Pd ayırma deneyleri için kullanıldı. Bu yöntemin kullanılma sebebi paladyumun formik asitle indirgenerek ayrılması noktasında birçok avantaja sahip olması idi. Formik asit, paladyumu metalik forma indirger ve çözeltiyi kirletmeyen ya da bir kirlilik sorunu oluşturmayan karbondioksite ayrıştırır. Diğer çökelme tekniklerinden farklı olarak, formik asitle indirgeme işleminin paladyumu yüksek geri kazanımla verimli bir şekilde ayırdığı bilinmektedir. Bu nedenle, formik asit paladyumun harcanan katalizatörün liç liköründen indirgenmesi için kullanılmış ve bu işlemi etkileyen farklı parametreler deneylerde incelenmiştir. Bu amaçla, liç çözeltisi numuneleri, balon jojelerde farklı hacimlerde konsantre formik asit ile karıştırıldı ve hazırlanan son çözelti uygun koşullarda ısıl işleme tabi tutuldu. Son olarak, çözelti süzüldü ve çözelti içinde kalan eser miktardaki Pd, indirgeme veriminin hesaplanması için endüktif olarak eşleşmiş plazma-kütle spektrometresi (ICP-MS) ile analiz edildi.

Nano-materyallerin kullanılmış katalitik konvertörlerden geri dönüşümünü yapmak bugünlerde önemli ve kapsamlı bir şekilde incelenen bir konu haline gelmiştir. İlgili değerli metallerin geri dönüşüm için işlenmesi atıkları ve gün geçtikçe azalan yer altı kaynaklarının kullanımını azaltır. Ancak bu süreçler geri kazanım maliyetlerinin firma satışlarından elde edilen meblağdan önemli ölçüde düşük olması halinde anlamlı olmaktadır. Bu nedenle çalışmalarda düşük maliyetli çözüm bulunmasına özellikle önem verilmiştir.

Deneysel çalışmaların sonucunda paladyumun çözünmesi %6.3 HCI ve %4.75 H_2O_2 asit konsantrasyonunda 9.5/1 sıvı katı oranı ile 80°C'de 1.5 saat boyunca ısıl işleme tabi tutularak sağlandı ve %97 oranda çözünme verimi ile gerçekleşti. Çökeltme adımlarında ise eşit hacimsel oranlarda Pd çözeltisi ve formik asit 100°C'de 1 saatlik ışıl işleme tabi tutuldu ve netice olarak %95'lik Pd geri kazanım verimi elde edildi. İşbu tez ile birlikte kullanılmış bir katalitik konvertörden paladyumun geri kazanılması için basit ve çevre dostu bir çözüm geliştirilmiştir.

1. INTRODUCTION

Nowadays, air contamination is a danger for the humankind, since perilous or extreme amounts of substances including gases, particulates and natural particles are emitted intensely into the Earth's atmosphere. For people it might cause sicknesses, hypersensitivities and even demise, on the other hand it might likewise make hurt other living beings, for example, animals and crops by damaging their habitats. Thus, the contamination created from mobile sources is likewise an issue of general intrigue.

According to latest researches, vehicle armada on the planet has expanded from around 40 million vehicles to more than 1.3 billion over the most recent 70 years [1]. This issue has already started to threaten the environment, since most of the engines utilize the fuel combustion. Such fuels come from plants and animals that had existed in the past and the raw petroleum products can be additionally produced by mechanical procedures from other non-renewable energy sources. Even though petroleum products fulfill the greater part of the energy necessities for a considerable length of time, non-renewable energy sources are carbon-based and their combustion brings about the release of carbon into the air. It is assessed that generally 80% of all artificial CO_2 and green-house emissions arise from the combustion of petroleum products [2].

1.1 Emission of Pollutants

Gasolene, comprising a blend of paraffins and aromatic HCs, was expected to generate the power by combustion to drive the vehicle after the development of the four-stroke-cycle petrol engine. According to the design, gasolene was combusted with variable quantitiy of air, which is releasing completed CO_2 and H_2O outputs as well as some uncompleted ones such as CO and unburned HCs.

On the other hand, temperatures become exceptionally high during the combustion process owing to the diffusion burning of the gasoline beads and that brings about thermal fixation of the N so as to shape NO_X, which is a combination of NO, NO_2, and N_2O [3]. The amount of contamination differs with a considerable lot of the operating states of the engine; however, it is affected transcendently by air/fuel proportion in the combustion chamber.

The theoretical air/fuel (A/F) proportion for a complete combustion, is called stoichiometric air/fuel ratio, which is about 14.7/1 for a petrol engine [4]. This refers that, 14.7 kg of air is needed to combust 1 kg of gasolene completely. In non-ideal conditions, combustion of the fuel is also possible at $(A/F)_{min}$: 6/1 or at $(A/F)_{max}$: 20/1. If the air/fuel proportion is greater than the stoichiometric value, then the air/fuel compound is defined lean (e.g. A/F: 17/1) and if the air/fuel proportion is lower than the stoichiometric value, then the air/fuel compound is defined as rich (e.g. A/F: 12/1). The proportion among the $(A/F)_{actual}$ and the $(A/F)_{stoichiometric}$ is described as lambda (λ).

$$\lambda = (A/F)_{actual} / (A/F)_{stoichiometric}$$

As a response to the the lambda value, the engine operates under lean, stoichiometric or rich circumstances as shown in Figure 1.1.

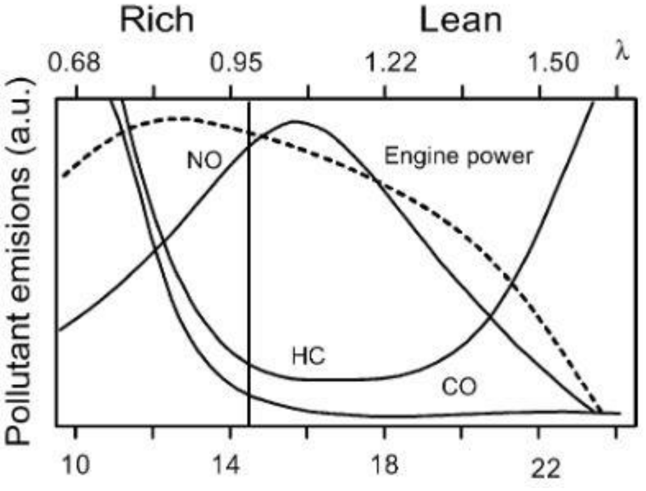


Figure 1.1: Air/fuel ratio by weight [5].

CO and HC emissions reach the maximum values, if the engine runs rich while NO_X emissions are depressed. This is on the grounds that total combustion of the gasolene is forestalled by the inadequacy in O_2. Since the adiabatic flame temperature is reduced, level of NO_X is also decreased. Because almost complete combustion dominates, CO and HC are reduced on the lean side of stoichiometric value. Once more, the amount of NO_X is lowered in light of the fact that the operating temperature is decreased. At stoichiometric value, the adiabatic flame temperature is brought down somewhat due to the heat of vaporization of the liquid fuel gasoline. “Lean” and “rich” flame stability determines the actual operating region of combustion for the spark-ignited engine, beyond which the combustion is unstable [6].

A considerable quantity of CO, HC, and NOx is transmitted to the environment inside the operation region of the petrol engine. Briefly, it very well may be expressed that, CO is an immediate toxin to people, though HC and NO_X undergo photochemical reactions producing smog and ozone in the daylight.

1.2 Conversion of Pollutants via Three Way Catalytic Converters

The essential conversion of the toxins is achived with the percentages greater than 95%, if the required values of the A/F is achieved in a limited working range. For this purpose, a sophisticated system is utilized to control the exhaust emission values, planned for keeping up the A/F proportion as near as possible to the stoichiometry (See Figure 1.2). A control unit connected with an oxygen sensor (λ) situated at the inlet of the three way catalytic converter (TWC) measures the quantity of air and injected fuel to ensure a proficient control of the A/F proportion.

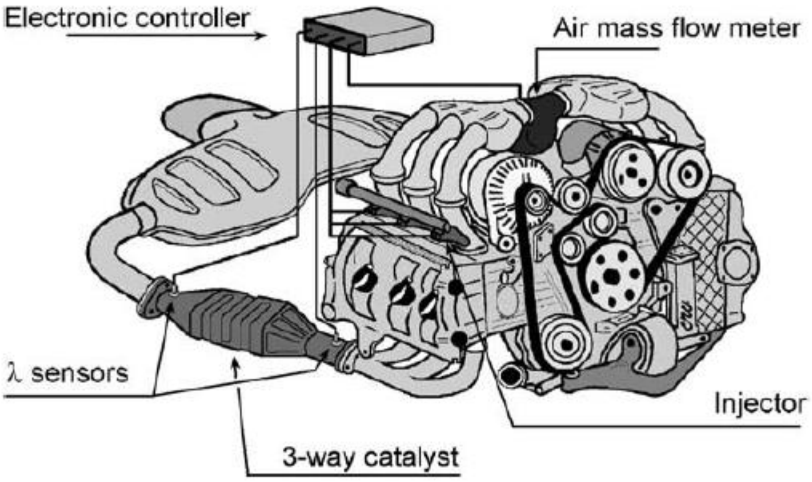


Figure 1.2: Control mechanism of the exhaust emission [4].

The signal sent from the λ sensor is utilized as an input for the control system injecting fuel and air. An additional λ sensor is mounted in the output of the catalyst. Herewith (A/F) fluctuations are determined by the comparison of the O_2 concentrations before and after the catalyst and the wide fluctuations of (A/F) are detected by the signal system. This setup underlie the on-board diagnostics (OBD) for the engine and it assumes certainly that a narrow working range of air/fuel proportion at the stoichiometric point is the unique mark of an efficient converter system.

Recently declared US and European regulations for the emission of the vehicles require the use of the converters and OBD techniques so as to satisfy the emission standards. In case it is viewed as that TWCs are improved for a considerable length of time, an inquiry is arrising why the advancement stage has not yet reached the end. The explanation is the following: As the performance of catalytic converters improved, increasingly elevated goals are being put forward by policymakers, such as reducing emissions and increasing longevity. Further innovations for the de-contamination is also required. This is the one of the fundamental motivations behind why catalytic converters are selected as the subject of the thesis.

1.3 Recovery of Precious Metals Used in Catalytic Converters

Practically all catalysts consist of costly platinum might be used again after the degradation of catalyst group metals (PGM), which. Palladium (Pd) is one of those significant precious metals that plays a critical role in modern industry, particularly in the catalyst field. As indicated by a survey in USA, the worldwide consumption of Pd came to 304 tons in 2018 and continues expanding alongside the advancement of the related technics. Approximately 70% of Pd is used in the catalytic industry, including chemical refining and automotive catalysts [7].

However, as as demonstrated in Figure 1.3, Pd's reserve in South Africa, Zimbabwe, Russia, Canada, and the United States is so limited and highly concentrated that it endangers the supply to other regions [9]. Moreover, 1 kg of Pd extraction from spent catalysts can save about 45% of energy costs and decrease water consumption of 400m^3 in comparison to mining process [10]. Therefore, recovering Pd from spent catalysts has become recently crucial.

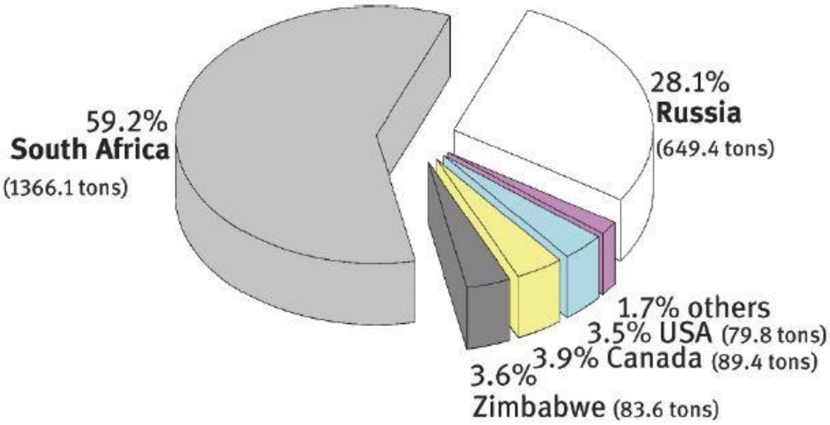


Figure 1.3: Distribution of PGM mine production [8].

Within this thesis, an eco-friendly process is developed to recycle Pd from spent catalysts to eliminate the potential environmental risks associated with recovery from Pd, using H_2O_2 as oxidizing agent in diluted HCl media to leach Pd and to separate Pd from the leaching solution by reducing with HCOOH. This procedure may improve the recovery eficiency of Pd and bring down the level of contamination. This study may likewise provide an additional method for the recovery of Pd from other auxiliary resources.

2. OVERVIEW OF THE CATALYTIC CONVERTERS

2.1 Catalytic Converters Used in Automative Industry

At the outset, automotive manufacturers assumed that catalytic converters would provide only temporary measure because the technology of the engines equipped with electronic control units was evolving at a rapid pace. However, they keep utilizing specific catalysts even after 30 years in combination with innovative engine control technologies and on-board diagnostics. Catalytic converters are still at the core of the emission control today.

2.1.1 Working method of a catalytic converter

When a driver starts the vehicle, engine and the catalytic converter are initially cold and they come a temperature that is sufficiently high to trigger catalytic reactions as the exhaust gases slowly warm up. This phenomenon is called the light-off temperature. The rate of reaction is kinetically controlled and it relies upon the chemistry of the catalyst because of the rapid transport reactions represented in Figure 2.1. Usually CO reaction starts first, accompanied by the reactions of HC and NO_X and the respective chemical reaction rates are fast, once the vehicle exhaust is hot.

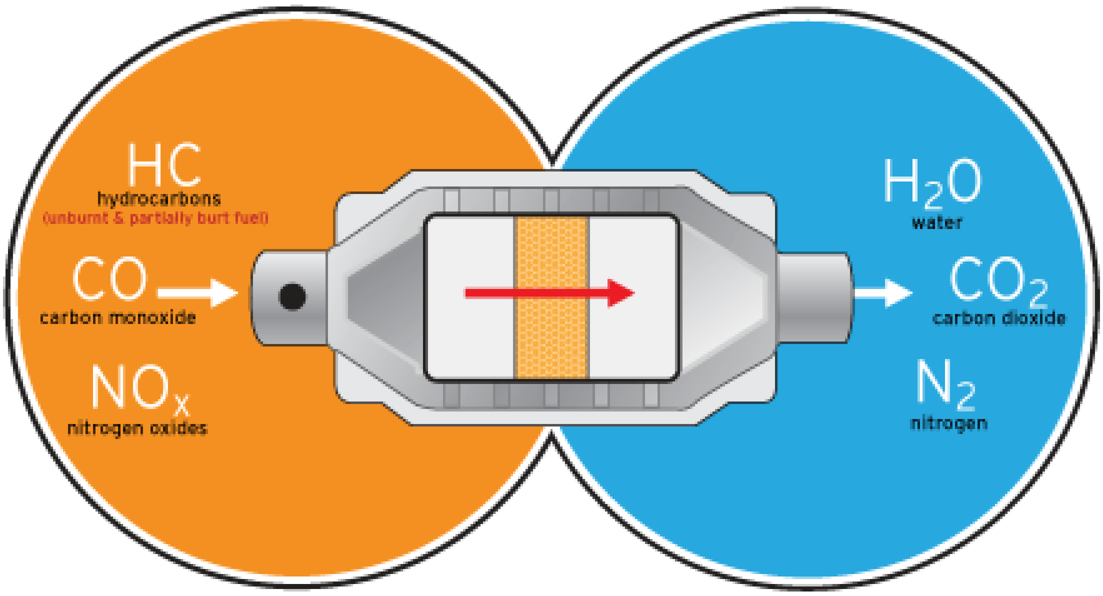


Figure 2.1: Catalytic converter is the agent, which catalyzes reactions above [11].

Diffusion of pore and move of the bulk mass have also an effect on general conversion of the exhausted pollutant.

The essential role of the catalyst in the exhaust system of an automobile is performing the reactions indicated in Table 2.1.

Table 2.1: Simultaneous tasks of the three way catalytic converter

Definition	Reaction
1) Reduction: $NO_X \rightarrow N_2$	$(2+n/2)NO_X + C_yH_n \rightarrow (1+n/4)N_2 + yCO_2 + n/2H_2O$ $2\ H_2 + 2\ NO_X \rightarrow 2\ H_2O + N_2$ $2\ CO + 2\ NO_X \rightarrow 2\ CO_2 + N_2$
2) Oxidation: $CO \rightarrow CO_2$	$2\ CO + O_2 \rightarrow 2\ CO_2$
3) Oxidation: unburnt HCs $\rightarrow CO_2$ and H_2O	$C_yH_n + (1+n/4)O_2 \rightarrow yCO_2 + n/2H_2O$

2.1.2 Structure of the catalytic converter

From the advent of automotive emission controls on, Al_2O_3 beaded and washcoated monolithic converters were preffered for the production of passenger cars. GM, for instance, was the major company in the USA utilizing spherical beads as a carrier for catalytic converters, while Ford and others used washcoated monoliths from Al_2O_3 [21]. Currently, the monolith design is used primarily in automotive exhaust emission control.

At the early stage many engineering issues such as screening, deactivation, and durability had to be discussed in tandem with all the studies related to catalyst. How much backpressure should be crated due to the existence of a catalytic converter in the exhaust manifold? Should the catalyst in the extreme temperature and corrosive environment of the exhaust be able to maintain its physical integrity and shape? How much weight should be applied to the vehicle, and what impact should it have on the fuel consumption? Where should the catalytic converter be positioned? How should the monolith fit in a proper housing? Should the energy from the reactions in the monolith impact the vehicle's thermal balance? Compared to the regular catalyst operation another complicated issue was that, the exhaust catalyst function was in a constantly transient state, since temperature varies in short time. As the customers required a profoundly solid, economical, trouble-free vehicle with promptly delivered performance, respective problems were studied in a businesslike manner.

2.1.2.1 Pellet type catalyst

How to locate the catalyst in the exhaust was an important question that the automotive manufacturers had to answer. Use of spherical particles from Al_2O_3, anywhere from a diameter of 0.3 to 0.6 cm, was the conventional way, in which the stabilizers and active catalytic elements such as precious metals would be added. Such "beads" was placed just before the muffler, in a spring-loaded converter platform as demonstrated in Figure 2.2. An air compressor was used to add air into the exhaust, because the exhaust gas of the engine was lacking in oxygen. The reason for this was as follows: For many years in the oil, petrochemical and chemical industry catalysts had been produced on these forms of carriers and known converter designs and flow models had been built which would allow simple and efficient structure. One of the main concerns was the Al_2O_3 particles' wear tolerance, as they would undergo multiple mechanical stresses during the converter's lifespan.

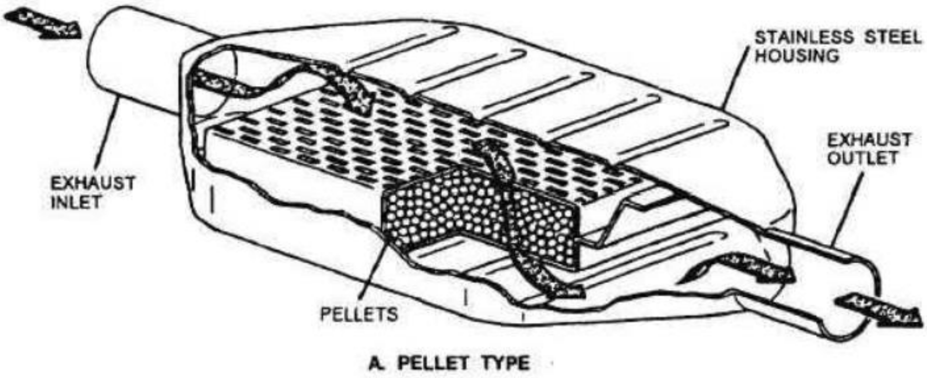


Figure 2.2: Overview of a pellet type converter [12].

The beads are formed by inserting the stabilizers into the design. Required metal salts are permeated into the bead and set in specific locations using proprietary methods to provide 80,000 km of durability and adequate performance. In the next step, beads are dried at regularly 120°C and calcined around 500°C to the completed phase. Approximately 0.05% of the finished form of catalyst was PGM with Pt/Pd weight proportion of 2.5/1. The need for NO_X reduction subsequently required the introduction of small quantities of Rh into the catalysts of the second generation. Several experiments had been carried out to modify the position of the active catalysts within the bead framework in order to control the deactivation rate and efficiency of the bead catalysts [13]. Initially, the bead catalyst worked and gave excellent efficiency in removing CO, HC and NO_X pollutants. Related issue here was the beads' own durability as the vehicle's vibrations eventually ground the beads into a smaller size causing the reactor catalyst bed to settle and the reactants to bypass resulting in poor performance.

2.1.2.2 Washcoated monolith catalyst with porous structure

A ceramic honeycomb monolith with open channels in parallel was an alternative approach to support catalytic components and for the first time, monolithic structures were used to reduce emissions from forklifts, mining trucks, stationary engines and etc [14]. The basis for washcoating technology for automotive applications was the catalyst preparation studies on these monolithic catalytic exhaust purifiers, which had an operational life of 10,000 hours. The effects on catalyst durability of operating temperature and feed impurities were also determined. Hereby gained experience showed that for automotive applications the monolithic support was a feasible product. Precious metals were accumulated in the Al_2O_3, which was washcoated and deposited on the walls of the honeycomb channels as depicted in Figure 2.3.

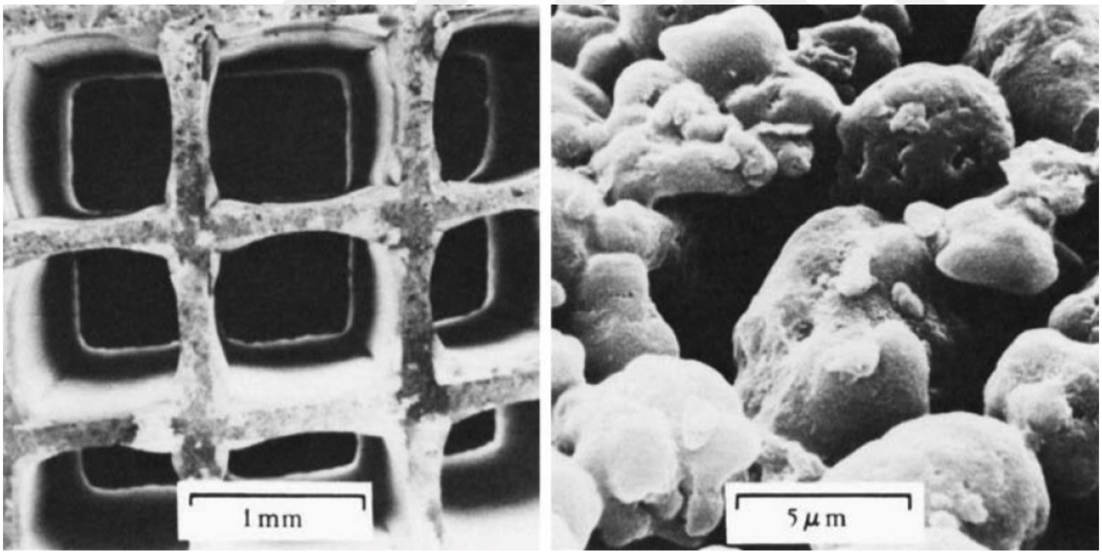


Figure 2.3: Porous structure of the washcoat [15].

Because the honeycomb design had a very high open frontal area, which was around 70%, and parallel streams, one major advantage would be low-pressure fall. Besides, they could be shaped in several directions to work in the exhaust manifold owing to their monolithic construction. In spite of the offered potential flexibility, the materials and geometries had to be optimised and redesigned subsequently for this modern and very challenging use.

The honeycomb-structured catalyst is built in the steel canister wrapped around it with a flexible matting stuff to ensure protection from friction and vibration (Figure 2.4). Because of the size and weight advantages, a positive experience with honeycomb systems has led to increased use of these structures over that of the beads. Despite the early honeycombs being ceramic, metal substrates have been finding use in recent years, as they could be built with thinner walls and have almost 90 percent open front face, permitting a smaller decrease of the pressure. It is feasible to use cell densities lower than 400cpsi, which allows for smaller volumes of catalysts when using higher cell densities. In order to coat the metallic monoliths, the surface must be heat treated to form an Al_2O_3 phase on the surface so that the washcoat can adhere. The washcoat's actual deposit is essentially the same as the ceramic counterpart. These metal catalysts are not preferred because of expenses and possible temperature limitations. Nonetheless, due to their low-pressure-drop features, low heat capacity for fast warm-up, and rapid responses to transient temperature operations, they are finding some niche markets [17].

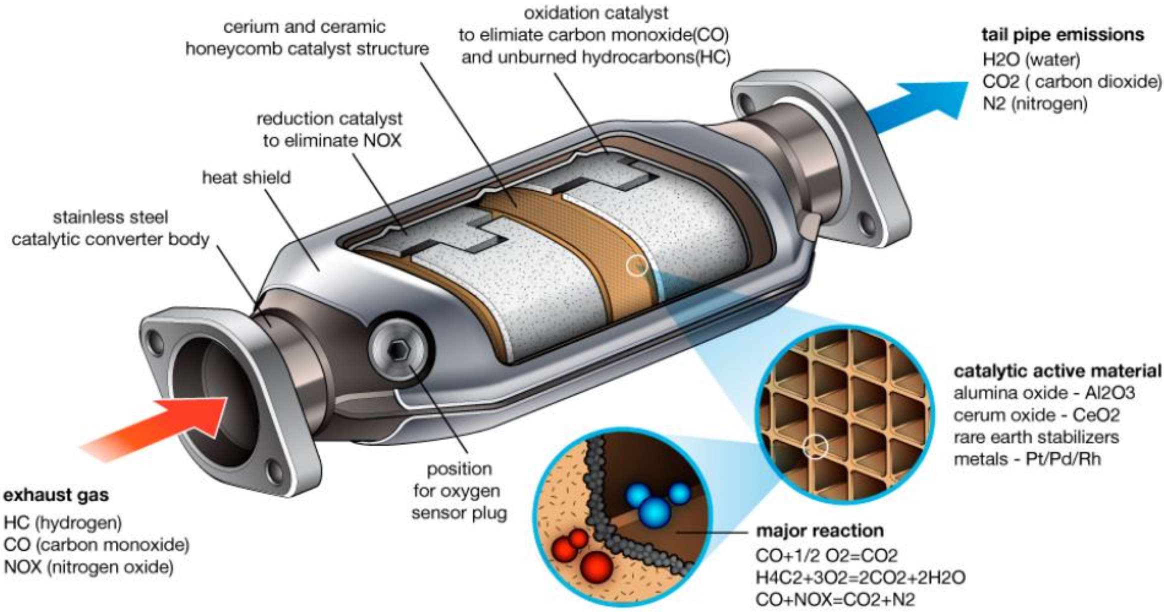


Figure 2.4: Basic components of a catalytic converter [16].

Technological developments were driven by the quest to use the petrol engine as the power train for a zero emission vehicle. The automotive engineers developed therefore novel technologies for engines, control units and sensors along with the catalytic converters. The dream of the zero emission with combustion engine has not yet come true but this concern has resulted in the full integration of the catalyst into the emission control system. Herewith catalysts have been fully integrated into the emission control system.

2.1.3 Catalyst technologies with low-emission

In the 90s, several approaches were investigated to fulfill the low emission values determined in the legal obligations, which focused on reducing HC release within the combustion. It was reported that the vast majority of the HC emissions are produced in the vehicle's cold-start phase, as an instance during the first 2 minutes of operation. Mentioned HCs consist of the compounds listed in Table 2.2.

Table 2.2: A typical hydrocarbon composition at cold start [18].

Hydrocarbon Type	Approximate HC composition (%)	
	Sampling - 3s	Sampling - 30s
Paraffins	20	35
Olefins	45	20
Aromatics, C_6, C_7	20	20
Aromatics, $>C_8$	15	25

Existing methods for controlling HCs, which emitted with cold-start, contain multi-composition under-floor catalysts. Thereby it has become obvious that the leading technology should comprise closecoupled catalysts operating at high temperature. The followings are described as the different technologies, which were developed in this direction.

2.1.3.1 Closecoupled catalysts

The idea of using the catalyst close to the engine's exhaust ports or the firewall was put forward to decrease the warm-up time. Despite that, respective operations were at quite low temperature and the maximum heat was heavily restricted anyhow. For instance, applications like overfueling and acceleration enrichment had resulted in high emission of HCs and CO. Increment of drivers driving at high speed boosted also discharging temperatures of engine manifold to about 1,050°C, which was shifting the operating window of the closecoupled catalyst negatively in high-volume engines [19]. It is noteworthy that a cost analysis found that the closely coupled method was the least expensive solution; nevertheless, there was no appropriate technology for the reliability criteria of more than 160,000 km and therefore the electrically heated catalysts could be the prevailing design [20].

Required technological change for the closecoupled catalysts took place once a closecoupled catalyst was produced with a constant efficiency after aging under 1,050°C and it demonstrated good performance in conjunction with an under-floor catalyst as shown by Figure 2.5. Closecoupled catalysts were primarily developed to remove HC, even as remaining CO and NO_X pollutants were eliminated by the under-floor catalyst. The intention here was to have less CO oxidation for the closecoupled catalysts so that extreme temperatures could be reduced whenever great concentrations of CO arise during rich transient driving loop [22].

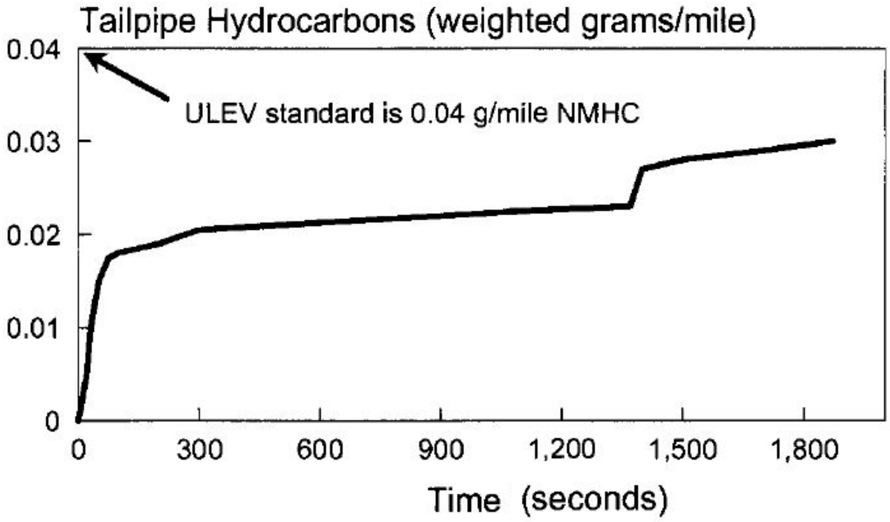


Figure 2.5: Closecoupled catalysts satisfying low emission criteria [21]

2.1.3.2 Trap for hydrocarbons in catalytic conversion

An additional solution for emission was the HC adsorption trap that adsorbs cold-start HCs until the catalyst exceeds light-off temperature. HC trap components that have been taken into consideration to date were mainly different types of zeolites with components based on carbons. Researches were carried out to quantitate the species of HCs during the drive cycle of the engine [23]. HCs must be elucidated from the trap right at the moment that under-floor catalysts reach the temperature of reaction, which is greater than 250°C, in order inline HC trap to function. HCs are then released and oxidised in a standard TWC catalyst. Since HC trap components were not able to retain HCs at this temperature, HCs were transferred then non-reacted through the under-floor catalyst and the tailpipe (Figure 2.6).

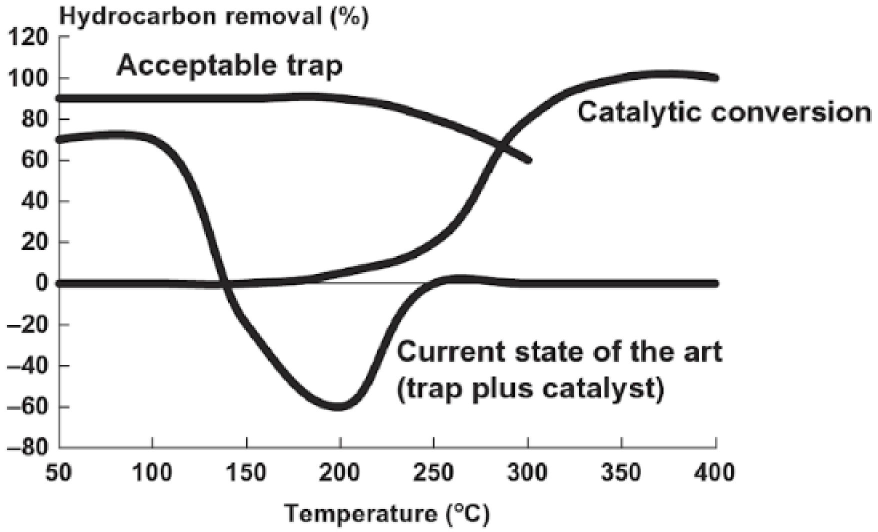


Figure 2.6: Hydrocarbon trap is not functioning as intended [24].

Some unique designs for this system have been proposed, though. During the testing process, a device for crossflow heat exchanger trap exhibited a 70% decrease of HCs at cold start [25]. An alternative trap was studied as well, using cylinder with a central-hole for allowing exhaust gas to pass through. Such designs included HC traps, light-off and downstream catalysts. During the cold-start, air was injected into the hole to redirect most of the exhaust to the cylinder trap and the limited volume evaded with the hole preheated the downstream catalyst. If the light-off catalyst was working and the downstream catalyst reached the required temperature, the air flow would be disabled and the trap would desorb the HCs. Such methods were intriguing but not marketed back then, only some products in combination with closecoupled or electrically-heated catalysts were planned to be used [26]. The trap would, however, be built for only a small portion of the cold start (in the first 10s), and not the complete cold-start as planned by these first studies.

2.1.3.3 Electrically-heated catalysts

An auxiliary solution to resolve the cold-start was to heat the exhaust using voltage supply. In the beginning, studies began to develop an electrically-heated monolithic structure, which was able to supply on-site heat to the cold exhaust. Surface of the catalyst was pre-heat treated, if the electrically-heated monolith was catalyzed. The catalyst provided hereby an effective cold-start reaction, since it was located in front of a small light-off catalyst receiving the heated gas. Another larger volume under-floor catalyst provided the reaction efficiency after the cold-start within the rest of drive cycle.

There were two ways to design electrically-heated monolithic catalysts. First method asserted making metal foil to shape an electrical resistor, in which the washcoat was deposited on the metal. The resistor was mounted on the electrical connections and could be rapidly brought to the catalyst's light-off temperature (Figure 2.7).

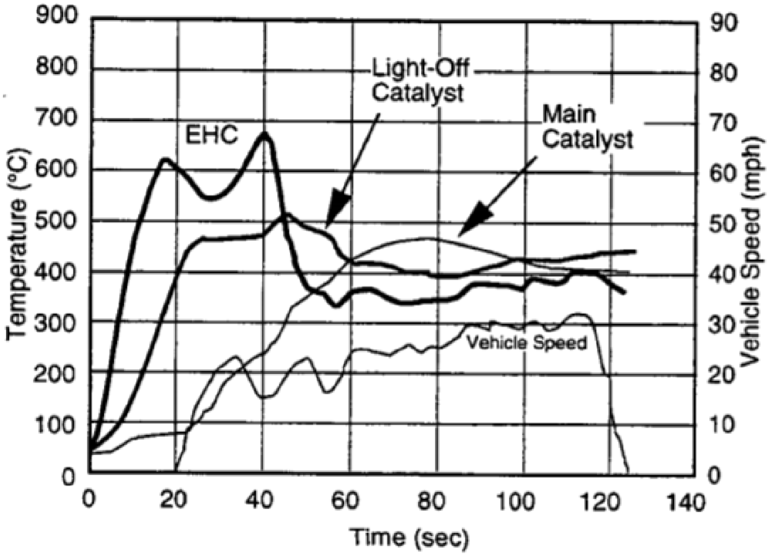


Figure 2.7: Electrically heated system's temperature profile [27].

Other method was designing a monolith of sintered metal and then depositing of the washcoat of catalyst. The core component was ferritic steel with variable quantities of rare earth containing Cr/Al/Fe. Significant progress has been made with decresing the required power for this type of catalysts and eliminating the need for further batteries, since electrically-heated catalyst could be herewith powered by alternator [28]. Regulations had been shown to be achieved by electrically-heated catalysts in short distances; but the endurance after 150,000 km remained as an open point. The system was tested on heavy-duty vehicles, but in particular, this method was not commonly utilized [29].

2.1.3.4 Non-catalytic methods

Futher approaches for reducing cold-start emissions had been studied in combination with catalysts. In one of them, a pre-heat burner, which was using the gasoline as fuel, was positioned ahead of the catalyst. During the cold-start, the burner was switched on and the warmed up the catalyst so that the catalyst could be hot enough when the cold exhaust gas reached the catalyst [30]. Two different components were used and it was observed that the total output of the burner could not be more than 96%, if the quantity of exhaust gas was considered during the cold-start (Figure 2.8).

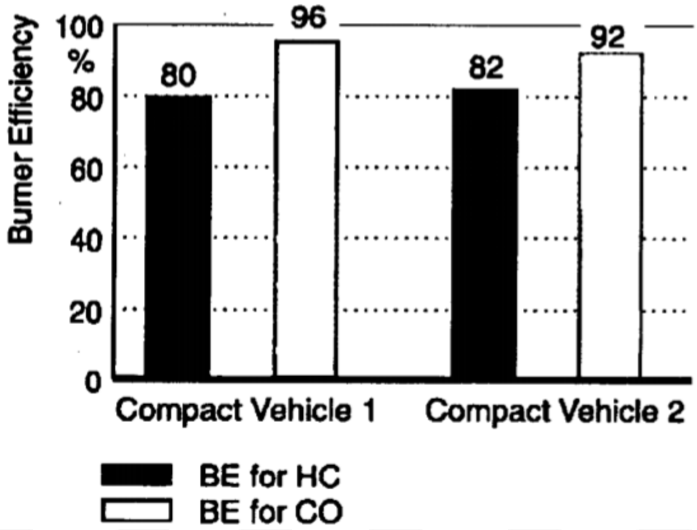


Figure 2.8: The burner's efficiency during the cold start [30].

An exhaust gas igniter, which was placed between the catalysts, was also suggested. When engine operated rich during the cold-start, it injected a few air to make the mixture ignitable and afterwards catalyst was heated [20]. In another method, catalyst was heated chemically using the vehicle's extremely reactive species, generally H_2. Because it occured above the catalyst at the room temperature, the reaction warmed the catalyst within the cold-start [31].

Each method heated the catalyst quickly during cold-start that resulted in low emission. Still, process reliability was not clear and the methods seemed to be complicated and expensive. In the new low-emission technologies, none of the respective methods are actually being used.

2.1.4 Additional studies on catalyst design

Efficiency of the system design solution which merged catalyst technology with the engine technology was realised long after the invention of converters. First designs only addressed four cylinder engines because they had low emissions from the engine and the tailpipe emissions could be met afterwards. Still, as the pollution standards were extended for high-volumed engines, owing to the resulting more engine emissions, the target became more overwhelming. As in the four cylinder engines, the first challenge was to minimize fuel pollution by enhancing engine design and achieve greater combustion performance and advanced exhaust gas recirculation (EGR) techniques, which could be executed outside or inside the engine, to limit NO_X production. Afterwards, the cold-start strategies were refined for catalyst light-off to reach higher temperatures within 10 seconds in the testing and lean starting strategies were implemented to provide the essential oxidation reactions. Eventually, to diminish emitted NO_X and HC, closedloop control was realized in a quick way and rapid reaction during vehicle accelerations was achieved in the testing process. As vehicle emission control strategies continued to be refined by engine manufacturers, they realised that the catalyst technology could be changed. In particular, for both closecoupled and under-floor applications, the noble metals could be lowered in the catalysts. That could be achieved by reducing the metal load or using a zone-coating system, so that the front of the monolith had higher loads and lower loads were present in the back part. Naturally, it was not possible to compromise the performance and durability of the main catalyst.

Studies aimed at optimizing the catalyst configuration of closecoupled and under-floor catalysts considering many variables, including the type of precious metal, loading location, cell density, Ce/Zr package, volume, location, etc. The tools included therefore the experimentation as well as extensive modeling based on previous accumulated databases over the past 20 years. Such a study not only considered these variables, but also examined the interaction between the catalyst's upstream oxygen sensor and downstream oxygen sensor as well as the catalyst's oxygen storage capacity. That study showed that a small volume, closecoupled catalyst was sufficient for light-off and that precious metal could be reduced in the under-floor catalyst. An optimal design of washcoat for using in under-floor solutions was improved premised on the experiments and modelling of the dynamic operation of the catalyst. Over half of the noble metal loading was reduced without any lost of catalytic activity was succeeded in comparison to the industrial catalysts [32]. Therefore, using the structure of the catalyst and the control technique for the catalyst, a total system methodology was implemented. The influence of monolith diameter and cell density was analyzed as a supplement to this type of study for both closecoupled and under-floor catalysts as well as for Pd and Rh loading. Increased density of cells in the closecoupled position made it work fine and could lead to a reduction of precious metals. Thus, in a catalyst system design, the relationship between monolith cell size and oxygen concentration portrayed in Figure 2.9 should be taken into account.

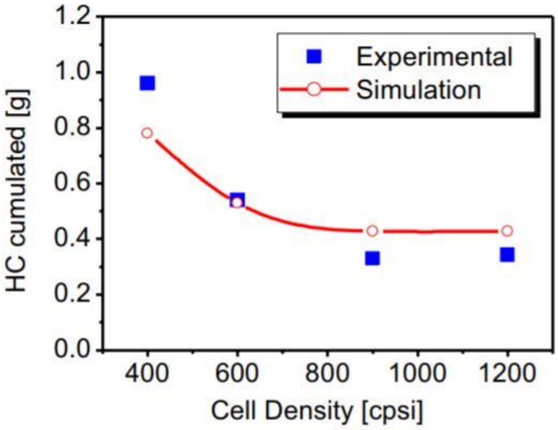


Figure 2.9: Together with cell density, HC emission was graphed [32].

In combination with the base metal formulations, advancements in the durability of Ce/Zr were reached after the structural optimizations. Latest compositions displayed remarkable durability up to 1100°C with compounds from Ce_{rich} to Zr_{rich}. Another paper showed that catalytic efficiency was linked to the sort of interacting between noble metal and the support. For example, for catalysts comprising Pt metal, Ce_{rich} oxides exhibited better light-off activity, whereas catalysts including Pd achieved the same with Zr_{rich} oxide with 20% ceria. Finally, the finest catalytic conversions were acheived for components supported by Rh including 40%, 60% Ce, respectively [33].

The position of the noble metals within the layer to stabilise the materials thermally is still an area to be explored. A washcoat, in which a study looked at the application of Pt and Rh, was another instance of the so-called segregated washcoat (Figure 2.10).

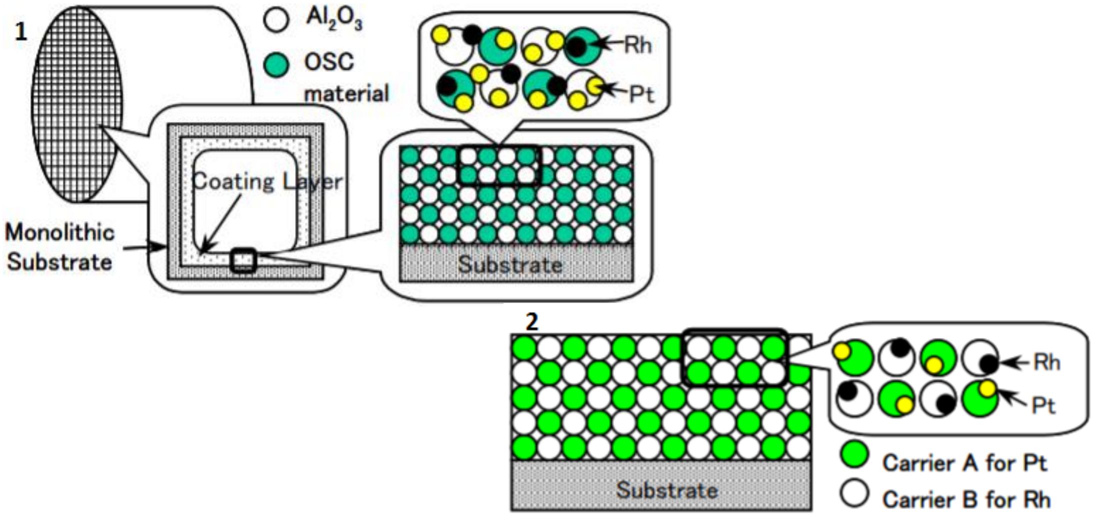


Figure 2.10: A typical catalyst's structure (1), fresh developed catalyst (2) [34].

For the Pt and Rh, the interaction between different carriers with the Ce/Zr storage material for oxygen and the effect of aging in the atmosphere was studied. The development of an optimised formulation of a CeO2-ZrO2 and a ZrO2 material has resulted in excellent durability, improved oxygen storage capacity, and increased interaction between precious metals and supporting materials, as well as increased thermal stability [34].

2.2 Preparation of Catalytic Components

PGMs are widely applied catalysts in industry, which are spread over the surface area of supports such as Al_2O_3, SiO_2, TiO_2, Al_2SiO_5 and zeolite. These are generally mounted on the wall of monolith structures once they are catalyzed.

A commercial catalyst is generally produced, set active and shaped by common methods; however some important points are kept as trade secrets to ensure the property of the good, which belongs to the suppliers. While suppliers hold many patents for different methods, it is not guaranteed if it will really be implemented or not. For each manufacturer, it is crucial to hold a particular benefit of their brand in comparison with the technologies of the rival. Subsequently, what is portrayed below are widely utilized methods.

2.2.1 Supports

Supports are normally inorganic high-surface components that contain complicated porous structures, in which catalyticly active components are deposited. Once it was considered that, the surface was provided to spread the catalytic material in order to maximise the catalyticly active areas. However, that is now clear, that it takes part significantly for preserving the finished catalyst's operation, selectivity, and longevity. The high-surface inorganic oxides listed below are the majority of supports.

2.2.1.1 Al_2O_3

For industrial projects, Al_2O_3 is the usually selected support and its sources have different surface areas, proportions of pore size, acidic surface properties, trace element compositions, and crystal structures [35]. The characteristics depend on its background of processing and pureness. Different crystal $Al(OH)_3$ are obtained from acidic or basic solution by precipitation, such as amphoteric oxides soluble at pH levels

>12 and <6 and some crystal hydrates are shaped in this wide pH scope. To illustrate, trihydrate species ($Al_2O_3 \cdot 3H_2O$) are shaped at pH 11, while, pseudo-boehmites ($Al_2O_3 \cdot H_2O$) are formed at pH 9. The precipitation is lacking a certain long ranged crystalline form on acidic side, like pH 6, and is defined as "amorphous". The high-surface areas are created by thermal treatment at around 500°C and calcination in the air, where Al_2O_3 particles bind together forming polymer-type chains. It can be observed that the structure is made up of primary agglomerated Al_2O_3 particles, which shape extremely porous networks as revealed in Figure 2.11.

It is completely washed to expel contaminants from precursor-salts after the precipitation and when NaOH neutralises an acidic solution of Al^{+3}, the Na^+ must be extracted by a wash as well. Desiccation is usually carried out at approximately 110°C to extract excess H_2O and salts that contain volatile species such as NH_3. The ultimate crystalline form, which defines the characteristics chemically and physically, is determined by calcinations at different temperatures.

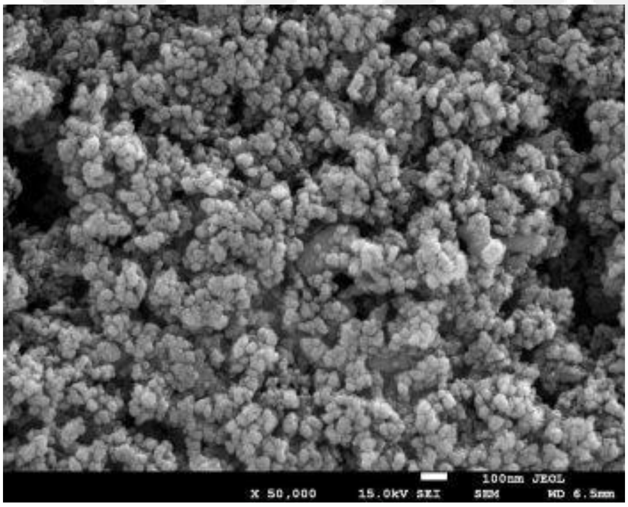


Figure 2.11: Nanoparticles of aluminum [36].

Also some materials may behave as "negative catalysts" and decrease the rate of sintering of the Al_2O_3. Existence of small percentage of stabilizers like La_2O_3 can significantly delay the sintering and this has been of significance for the production of high temperature, robust automotive converters. Several experiments have provided explanations that clarify the consequences of stabilization of CeO_2, La_2O_3, SiO_2 and BaO [37]. Such thing is commonly acknowledged that solid stabilizing ion solutions in the Al_2O_3 structure decline the Al and O ions' mobility, bringing about the decrease in pace of sintering or phase-transition.

2.2.1.2 SiO_2

SiO_2's inertness to react in exhaust streams with sulfur oxide (SO_X) compounds makes it an appropriate catalyst carrier. Al_2O_3, on the other hand, is highly reactive to SO_3 and shape forms that vary the carrier's internal surface, which gives rise to deactivated catalyst. An alkaline silicate solution (pH > 12) can be neutralised by acidic media, leading to silicate acid formation. That may then polymerise, shaping a network of high surface areas with different pore sizes interconnected:

$$SiO_4^{-2} \rightarrow [Si(OH)_4]_X \rightarrow SiO_2 \,.\, H_2O \tag{2.1}$$

That is then washed, desiccated, and calcinated, similar to Al_2O_3. Materials of high surface SiO_2 may be 300~400 m^2/g.

2.2.1.3 Zeolites

Natural Al_2SiO_5 products that exist or are artificial with well defined crystal forms and pore sizes are termed zeolites. Al_2O_3 and SiO_2 are bound to four oxygen anions in a tetrahedral form with Al and Si cations. As can be seen in Figure 2.12, each O^{-2} is attached in an arrangement to either a Si^{+4} or Al^{+3}.

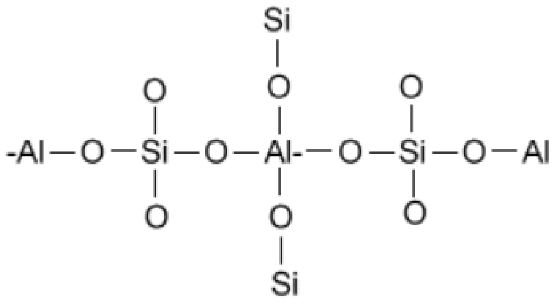


Figure 2.12: Basic zeolite structure [38].

Thanks to well defined crystal forms and surface characteristics, zeolites are of great importance. Amendments for the preparing change SiO_2/Al_2O_3 rate, eventually has an impact on the amount of acids on the surface and interchangeable cation sites. As the proportion of SiO_2/Al_2O_3 decreases, the system contains less Al cations and therefore less H^+. One may be inclined for rising zeolite Al content to maximize the active sites; but, as the SiO_2/Al_2O_3 rises, thermal stability decreases. As a consequence, zeolites provides different characteristics as supports of numerous metal ions on the basis of reactions and different circumstances, under which it should work [39].

2.2.1.4 CeO_2

Ceria (CeO_2) with high surface became a significant O_2 storage material in catalysts together with different metal oxides suchlike ZrO_2. Its ability to store and release O_2 quickly and reversibly, makes it possible to adjust the conversion in the three-way catalytic converter when the engines run close to the stoichiometric air/fuel point. It also contributes during fuel-rich operation for the steam-reforming reaction. Eventually, it acts as the support for several catalytic elements, which facilitates the activity for a number of reactions.

2.2.2 Preparing of catalysts

2.2.2.1 Impregnation

Impregnating an aqueous solution comprising a salt of the catalytic component is the general industiral method to disperse the catalytic species via the support [40]. The majority of the techniques involve soaking the support within the solution and then capillary and electrostatic forces distribute the salt over the porous structure's surface. The salt that produces the cations or anions including the catalytic component is selected to comply with the carrier's surface load to ensure effective adsorption and/or ion exchange. As an instance, on the surfaces of $A1_2O_3$, which contains OH^-, $Pt(NH_3)_2^{+2}$ salts can exchange ions with the H^+ and anions like $PtCl_4^{-2}$ would be electrostatically attracted to the H^+ sites. The support's isoelectric point, which is pH-dependent, is useful to determine about salts and pH conditions of the preparation.

2.2.2.2 Fixation of catalytic elements

In general fixing the catalytic elements after impregnation is necessary so that next steps such as washing, desiccation and calcination at high temperatures do not cause an important move or assemblage of the catalytic species, which dispersed as intended. The solution's pH is adjusted for precipitating the catalytic elements into the honeycomb. To illustrate, applying an acidic Pd salt such as $Pd(NO_3)_2$ can precipitate hydrated PdO in the pores, if the support, $A1_2O_3$ is pre-soaked in an NH_4OH solution.

H_2S may be also used as a precipitating agent and the catalyst is processed at high temperature to decompose and burn off the sulfur in the wake of preparation process. This procedure was used in vehicle catalysts to fix Rh to $A1_2O_3$ support:

$$Rh_2O_3 + H_2S \rightarrow Rh_2S_3 + H^+ \tag{2.2}$$

$$Rh_2S_3 + O_2 \rightarrow Rh + SO_2 \tag{2.3}$$

An alternative approach is to add reduction agents for precipitating catalytic elements as metals. This technique is especially effective for the PGMs as they are simply reduced to the metallic state. The benefit of the above-mentioned reduction agents is that they do not leave any residue after an additional heat treatment:

$$HCOOH + Pd^{+2} \rightarrow Pd + 2H^{+1} + CO_2 \tag{2.4}$$

Drying and calcinating of the catalyst are the final steps of the preparation process.

2.3 Monolithic Structures as Catalyst Substrates

Offering many benefits over conventional pellet shaped catalysts; monolithic products are preffered for the most of the eco-friendly applications. Its single-piece structure comprises inorganic oxides and metals in a honeycomb structure of same sized and parallel channels that can be rectangular, sinusoidal circular, etc. Today monolithic systems are accessible as ceramic or metal with different channel sizes and shapes.

Industrial ceramic monoliths demonstrated in Figure 2.13 have large pores and small surface areas such as $0.3m^2/g$. Therefore, the high-surface support comprising the catalytic elements has to be dispersed on the channel walls. The catalyzed washcoat consists of a high-surface support impregnated with catalytic components such as $A1_2O_3$.

The washcoat is deposited across the whole wall, but it is concentrated at the corners of ceramic monolith. The "fillet" thickness depends initially on the channel geometry and the coating technique. The toxic gases pass the channels regularly and spread through the porous structure in which they are converted catalytically. The number and diameter of the channels determines the size of surface area on which the washcoat is deposited.

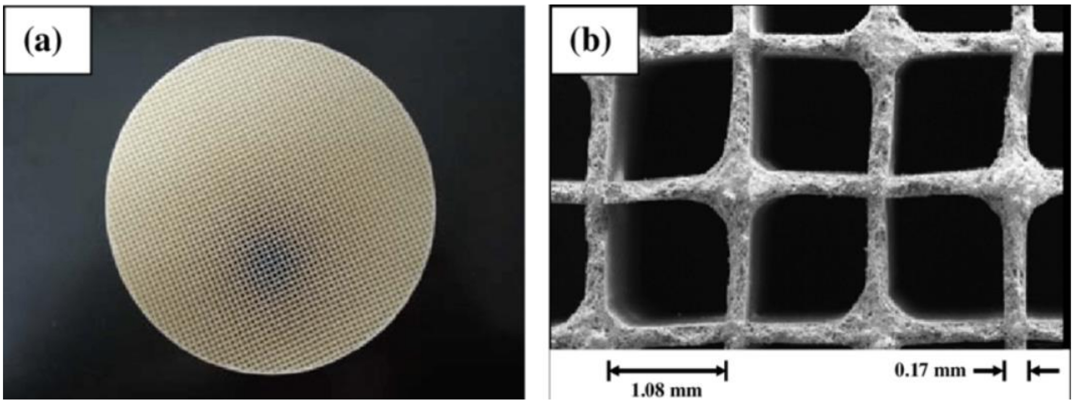


Figure 2.13: Ceramic monolith substrate (a), enlarged image of the cells (b) [41].

Monolithic structures are used widely since they render possible some benefits for the design e.g., the low pressure-drop at high flow rates. Monoliths have large front surfaces and straight parallel streams providing fewer resistances to flow in comparison with pellet type catalysts. Low pressure-drop means lower compressor cost for a stationary application and higher power saving for a mobile usage. Other benefits include the resistance to wear and tear, good mechanical and thermal shock absorbing capacity and so on [42].

2.3.1 Ceramic monoliths

The frequently preferred ceramic for the monolithic catalyst carrier application is synthetic cordierite ($2MgO\cdot 2A1_2O_3\cdot 5SiO_2$). The raw materials such as kaolin, talc, Al_2O_3, $Al(OH)_3$, and SiO_2 are merged, extruded, and calcined. Cell densities in the range of 9-1200cpsi might be built for the sizes up to 27cm in diameter and 17cm in length. While planning the monolith scale, the required converting, the physical space necessary for the reactor and technological limitations such as the drop in pressure are taken into account [43].

When cycled over a broad temperature range, cordierite is subjected to a little dimensional change owing to its low thermal expansion coefficient, which is $10x10^{-7}$/°C and therefore it endures thermal stress cracking. Others suchlike mullite, zirconyl mullite, and α-Al_2O_3 have greater melting point, but their thermal shock resistence is quite low since their thermal expansion coefficients are 5-10 times higher. This is a crucial variable for automobile catalysts where large gradients of axial temperature are generated within the porous structure during the operation.

2.3.2 Metal monoliths

Monoliths embodied from aluminum containing steels, which are resistant to high temperature, became trendy as supports for catalysts, since they could be built with thinner walls than its ceramic counterparts' walls (Figure 2.14). It renders possible greater cell densities with lower pressure-drop with the wall thickness of a 400-cpsi metal substratum, which is 25% lower than ceramic. With the same cell density, the open frontal area of the metal is greater (90% vs. 70%) and its thermal conductivity is 15-20 times higher than the ceramic, which enables the catalyst to heat up quicker [44]. This is especially significant during the cold-start to oxidise HCs and to lower the emission of CO. Metal components provide also many incentives for the converter's assembly so that they might be welded directly to the exhaust system.

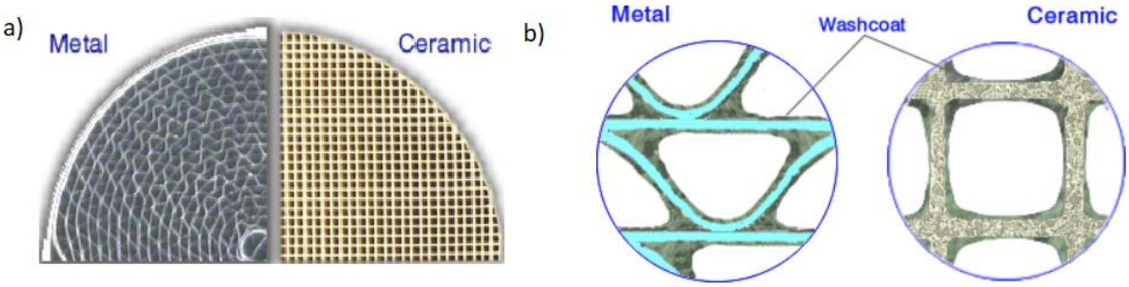
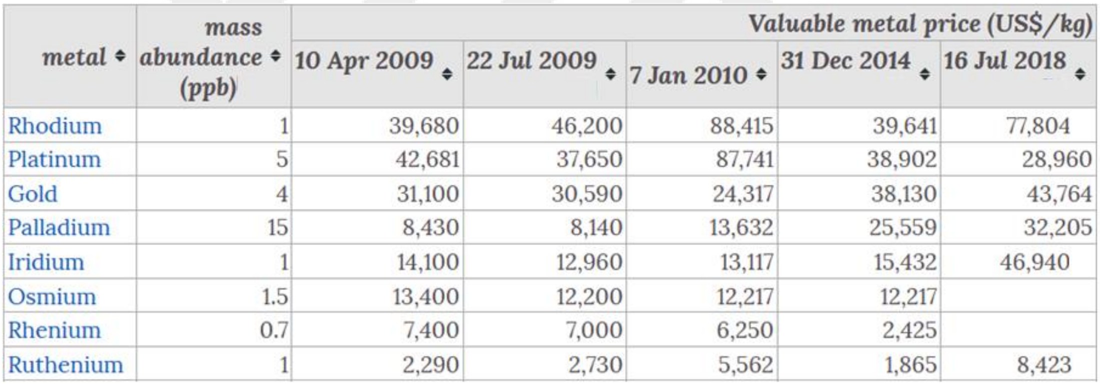


Figure 2.14: Different monolithic catalyst substrates (a), catalyst washcoats (b) [44].

Usage area of the metal monoliths are low temperature applications for NO_X in power plants, O_3 reduction in planes, and the declining of emission values emitted by restaurants, which is based on oil. They found use also in electrically-heated catalysts thanks to being electrically conductive to convert emissons rapidly at the start-up. In vehicles with high performance, they are used widely where response time is crucial during the acceleration. Consequently, metal monolith's lower pressure-drop is its most attractive asset and generally, they are more costly than their ceramics equivalent.

3. PLATINUM GROUP METALS

The demand for the PGMs is growing over recent years in spite of the insufficient natural resources, which contain limited quantities of PGM around 10 g/tn. Extraction of PGMs requires therefore extreme energy consumption, apart from being non-environmental. For instance, extracting 1 kg of Pt involves the mining of approximately 150 tons of material by deep excavation. Compared to the mining process, amount of noble metals in secondary resources is high, since around 1 kg of Pt could be acquired from two tons of spent catalysts [45]. On the other hand, costs of the noble metals have been rising in recent years as illustrated in Figure 3.1, especially for Pd and Rh metals.



metal	mass abundance (ppb)	Valuable metal price (US$/kg)				
		10 Apr 2009	22 Jul 2009	7 Jan 2010	31 Dec 2014	16 Jul 2018
Rhodium	1	39,680	46,200	88,415	39,641	77,804
Platinum	5	42,681	37,650	87,741	38,902	28,960
Gold	4	31,100	30,590	24,317	38,130	43,764
Palladium	15	8,430	8,140	13,632	25,559	32,205
Iridium	1	14,100	12,960	13,117	15,432	46,940
Osmium	1.5	13,400	12,200	12,217	12,217	
Rhenium	0.7	7,400	7,000	6,250	2,425	
Ruthenium	1	2,290	2,730	5,562	1,865	8,423

Figure 3.1: Cost of precious metals [46].

3.1 Usage Area of Platinum Group Metals

Platinum group metals are very significant for most of the industries owing to their particular characteristics, suchlike low reactivity or thermal resistance in comparison to non-precious metals. Approximately 60 percent of the world's total PGM supply, was utilized to manufacture catalysts for automobiles and 98 percent of currently produced cars have catalytic converters containing PGMs [47]. These are additionally used in different areas such as the chemistry, development of fuel cells, and the jewellery. Besides, they are preferred for the noble metal investments, production of the electronic components and dental restorations [48]. Critical issues to be addressed are the extraction of precious metals from wasted products as well as the preconcentration methods to promote the determination at low rates.

3.1.1 Platinum group metals used in catalytic converters

Initially, it was suggested in the US auto industry to use the catalytic converters including PGMs to diminish car exhaust emission. Converters were actively used in Western Europe later after 80s [50]. Subsequently, stringent obligations on exhaust emissions pressured carmakers to develope the performance of the current catalysts. The global demand for PGMs for the catalytic converters has been growing swiftly since then.

In particular, the automotive catalysts neutralise the toxic gases with the percentage above 90%. They catalyse the reduction of NO_X, oxidation of HCs and CO to N_2, CO_2 and H_2O. As an instance, a vehicle sold in 1960 had higher emission values in contrast to 100 vehicles manufactured in 2014, which include PGM containing catalysts. While vehicle production continues to rise, the demand for PGMs is growing and the recovery from spent catalysts (Figure 3.2) of these nanomaterials is gaining importance [51].

Figure 3.2: Spent catalyst before and after grinding.

The automotive catalyst has a ceramic support with porous structure made from cordierite, whereas the metal support is formed as helical film made from the steel, which is resistant to acid. Cordierite is a mineral comprising MgO, Al_2O_3, SiO_2 and Fe_2O_3 and it might consist of minor amount of Na_2O, CaO. Cordierite is therefore a primary component used for the manufacturing of ceramic supports for the catalyst. Al_2O_3 on the support becomes activated by appending CeO_2, NiO, BaO, CaO and

La_2O_3. For example, the function of CeO_2 is to increase the converter's oxygen storing capacity and to stabilise PGMs scattering [49].

3.2 Recovery Process of PGMs from Spent Automotive Catalysts

Because of the strong demand for PGMs, an efficient way to recycle noble metals from spent catalysts became significant research topic. Waste catalyst reprocessing is only meaningful, only if the recycling costs are considerably less than the earnings from the recovery. Therefore, the feasibility depends also on the intricacy of the processing to acquire a tradable good. Used catalysts are known as recyclable materials in terms of PGMs, but they also include many base metals. Table 3.1 illustrates different formulations of spent catalytic converters comprising PGMs. The structure of different vehicle catalysts varies significantly and depends on the active component type, sort of carrier, availability of promoters, and catalyst usage. Automotive catalysts contain in general 300-1,000µg/g Pt, 200-800µm/g Pd, and 50-100mg/kg Rh [52].

Table 3.1: The content of PGMs in several converters [53].

Catalytic converter	Structure
1	0.035% Pt, 0.013% Pd, 0.008% Rh, 44.3% Al, 38.3% Si, 14.8% Mg, 1.6% Fe, 0.56% Ce, 0.51% Ni
2	20.3% Al, 5.9% Mg, 1.2% Ba, 1.5% Zr, 6.2% Ce, 2300ppm Pt, 530ppm Rh
3	13.70% Pt, 1.30% Rh, 16.90% Fe, 2.46% Ni, 1.15% Ca, 1.35% Mg, 0.15% Cu, 0.17% Zn, 0.17% Pb,0.62% As,0.84% Re, 8.25% Si
4	1.1% Cr, 3.5% Fe, 0.4% Pt, 65.4% O, 29.3% Al, 0.3% Si
5	20% Al, 1,3% Ce, 0.03% Zr, 0.12% Pt, 0.02% Pd, 0.01% Rh
6	3.68% MgO, 0.43% CaO, 13.94% Al_2O_3, 12.54% SiO_2, 20.0% Fe, 0.01% Cu, 0.04% Ni, 0.16% Pt, 0.12% Pd, 0.042% Rh

Methods for noble metal recovery from solid materials are various and thereby separated as pyro-, hydro-, and biometallurgical. Choosing an appropriate method relies on mainly the metal type, its chemical structure and the components wasted.

Other factors to consider may be the available volume of the metal in nature and energy costs spent to extract the material.

3.2.1 Pyrometallurgy

A method named as "Rose Process" was utilized to recover PGMs from the used catalytic converters [54]. The catalyst was merged with the additives; CuO, coke, lime, SiO_2 and Fe_2O_3 and melt in the electrical stove. These noble metals were extracted with a solvent, namely melted Cu and the ceramic support was smelted with the flux elements in order to shape the slag as shown in Figure 3.3. The Cu bearing metals were sent to the furnace, in which the Cu was oxidised and the PGMs were removed. Product concentration was hereby rose to 75%Pt, which was recovered afterwards. Oxidised Cu was reduced by coke in the stove and reused.

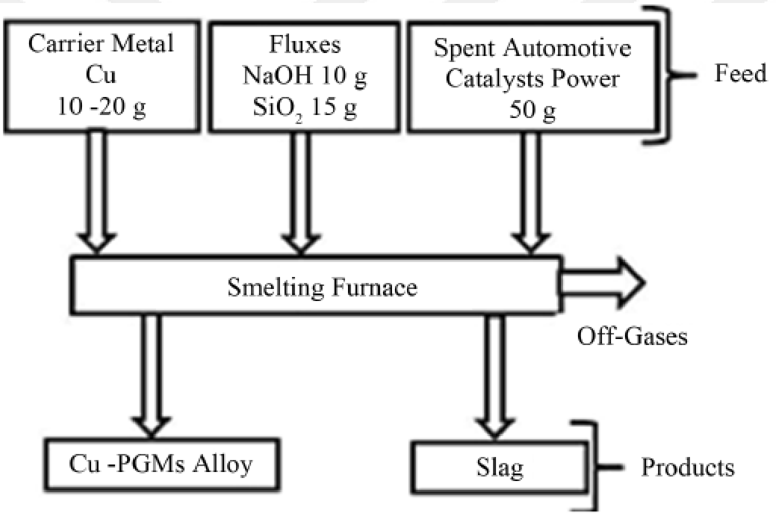


Figure 3.3: Simplified flowsheet of the pyrometallurgical process [55].

3.2.2 Hydrometallurgy

In a conferance (USA, 90s), issues related to the reuse of PGMs acquired from used catalytic converters were addressed for the first time [56]. Various methods of the recovery from spent catalysts including PGMs were studied in one report. Eventually, leaching process using condensed HCl was suggested as the best and efficient method for the spent catalyst. Since a spent automotive catalyst contains also metals like Cu, Fe, Mg and Al, they need to be dissolved and only the noble metals should be separated from others in the leach liquor [57]. Typically, the metal ions are leached from the spent catalysts using HCl but also with H_2SO_4 and recovered by several techniques as exemplified in Figure 3.4. Noble metals are commonly resisting in acid media comprising HCl and for the dissolution an oxidant is required to extract PGMs in Cl^- solutions. "Cl^- leaching" by HCl requires therefore adding Cl- precursors such as $AlCl_3$ and $CuCl_2$ or oxidizing agents like HNO_3 and H_2O_2, to extract resisting PGMs [58].

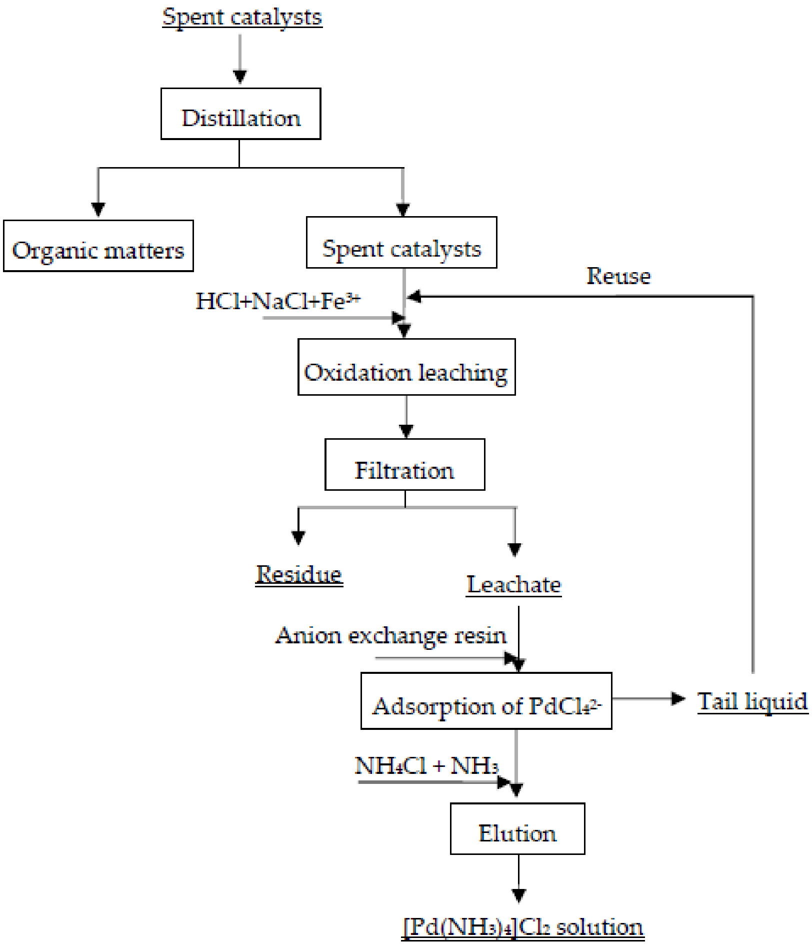


Figure 3.4: An example: Flowsheet for the leaching Pd from catalysts [59].

Because acids dissolve simply Al_2O_3 washcoat, most methods for the recovery of noble metals aim to reduce Al_2O_3 catalyst-support dissolution. PGMs shall be ideally dissolved from the catalyst while Al_2O_3 are left unattacked. However, Al_2O_3 is dissolved in reality with HCl in oxidizing circumstances and it has a negative effect on the feasibility of the recovery process because of the consumed acid volume. Pre-heating the catalysts at 1,200°C was proposed for the conversion of γ-alumina to α-alumina, which becomes barely soluble compound, in order to minimise the dissolution considerably [60].

The principle of reducing Al dissolution was implemeted as well by a leachate including HCl, $AlCl_3$ and HNO_3 to recover PGMs effectively and not to dissolve complete Al_2O_3 washcoat. Because dissolution of Rh is all the time lower than Pt, a treatment at the temperatures of 80-90°C and appropriate $AlCl_3$-HCl proportion is significant in order to improve Rh extraction. In addition, the solid was treated with $AlCl_3$ and H_2SO_4 in the wake of the leaching and washed by water for the remaining unleached PGMs.

Subsequently, adsorbtion with “Emberen 345 resin” was performed for separating PGM from the solution and noble metals were precipitated by cementing with aluminium powder. The percentage of recovered Pt and Pd exceeded hereby 97-98% [61]. Unlike pyrometalurgical methods, more PGMs could be recovered while the process operated at low temperature and did not bring out the waste slag.

3.2.3 Biometallurgy

For recycling metals from a low grade material, biometallurgy is used as an alternative to other metallurgy techniques. Biometallurgy was considered as an environmentally friendly method that saves costs and energy and it was performed at ambient temperature and pressure, without complex equipments. Biometallurgy was also used for S_2^- or another form of S_2^- to provide H_2SO_4, which present the microbes an acidic living condition.

As illustrated in Figure 3.5, bio-leaching uses the leaching capability of different microorganisms such as bacteria and fungi to bring several metals in a dissoluable shape [62]. Leaching comes to mean that the cells of the microorganism are contacting by adhesion the material surface for oxidising. The electrons are obtained straight from the reducing products and furthermore, some specific enzymes, amino-acids and organic acids are generated by the bacteria, which facilitate the leaching process.

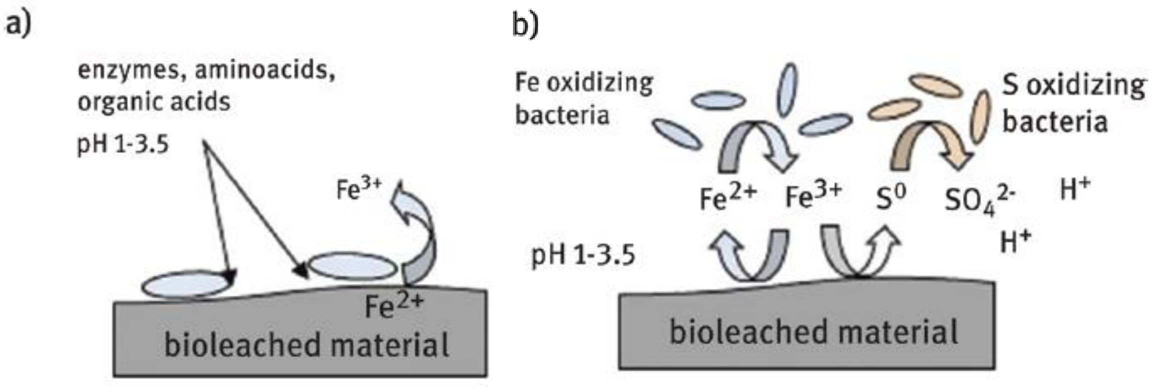


Figure 3.5: Direct (a) and indirect (b) bioleaching.

On the other hand, oxidising agent is regenerated by Fe oxidising bacteria, whereas sulfur oxidising bacteria create H_2SO_4.

Since PGM requires heavily oxidising circumstances as a soluble, bio-leaching with microorganisms seems not feasible. Therefore, a counter method to metal bio-leaching from catalysts suggests that “Acidithiobacillus” strain was used to leach non-precious metals from the carrier, keeping PGMs unleached and thereby distinguishing them from base metals [63]. In the wake of the connection with bacteria for 14 days, it was observed that the leach process for Fe and Cr progressed as biological oxidising while aluminum was leached not by micro-organisms, but oxidized chemically.

In summery, bio-leaching with “Acidithiobacillus” bacteria did not result in the noble metal recovery from catalysts, because the respective metals require highly acidic or oxidising circumstances. “Desulfovibrio” strain was the most commonly used for the treatment of PGMs, but they acted not for leaching, but for biosorption.

3.3 Analysis Methods Used in PGM Recovery

3.3.1 X-ray fluorescence spectrometers

X-ray fluorescence (XRF) is an experimental technique determining the surface structure. XRF analyzers evaluate a sample's composition as described below.

A solid or liquid specimen is irradiated by highly energized X-rays from a regulated X-ray tube. Once an atom of the specimen is struck by an X-ray including required energy, an electron is dislodged from the inner orbital shell of the atom as depicted in Figure 3.6. However, the atom regains equilibrium, replacing this electron by the one from the higher orbital shell and filling the hole left in the internal orbital layer. Which means, the electron falls to the lowest energy by emitting a fluorescent X-ray. X-ray's energy equals to the particular energy difference between its quantum states and hereby characterization of the elements specimien is completed. Described energy measurement is the basis for XRF analysis [64].

3.3.2 Inductively coupled plasma mass spectrometer

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a sort of spectrometry using an inductively coupled plasma to ionise the specimen. It atomises the specimen, by creating atomic and small polyatomic ions, which are identified afterwards.

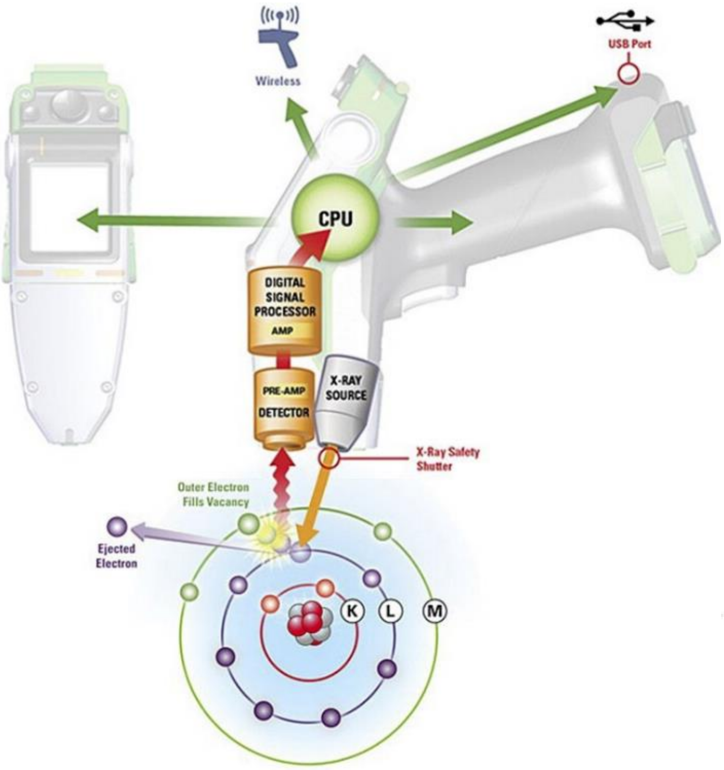


Figure 3.6: The X-ray fluorescence process [63].

Many laboratories prefer an ICP-MS including quadrupole mass spectrometer thanks to its overall performance and ecostly benefits. A quadrupole works by setting voltage and radio frequency to ensure ions within the rods of a given mass/charge proportion to stay steady and go through to the detection. Ions with various mass/charge proportions in the cell are volatile and expelled and electronics quickly change the quadrupole's conditions to allow passing of ions at various mass/charge rate for covering the full mass range [65].

In ICP-MS method, the DRC (Dynamic Reaction Cell) is a new structure containing a reaction room between lens structure for ions and the quadrupole control. As shown in Figure 3.7, a reactive gas like NH_3 is inserted into the cell and the gas reacts with the ion beam through a number of mechanisms for ion molecule reaction, turning the interfering ions into species that will not interfere with the analyte. Under the same circumstances, the analyte of interest remains stable and can continue to the detector and this method of washing is called as chemical resolution [66].

3.3.3 Atomic absorption spectrophotometer

Atomic absorption spectroscopy (AAS) is spectroanalytic method used by free atoms in the gas state to evaluate materials quantitatively by receiving optical radiation.

Required signal for the absorption is in proportion with the concentration of free atoms in the optical route.

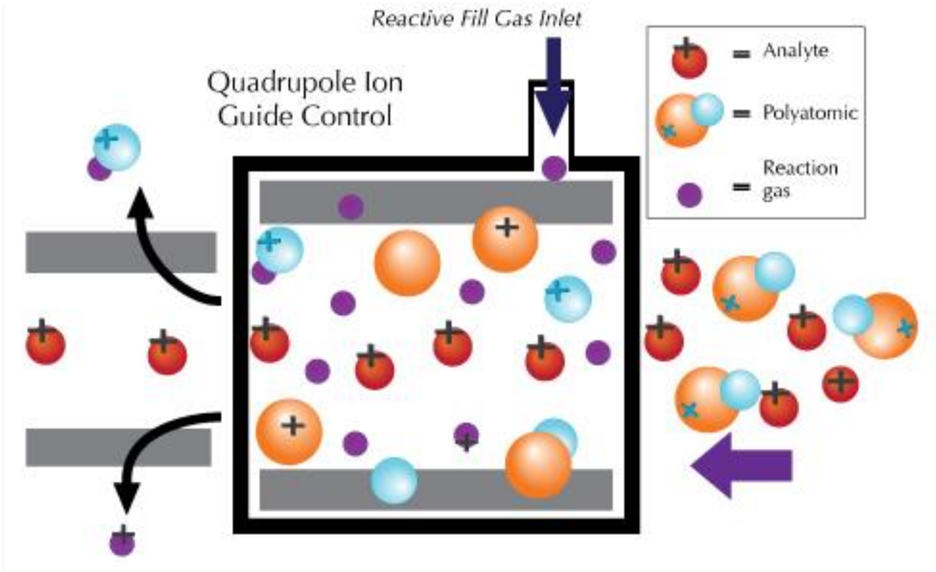


Figure 3.7: DRC scrubs interfering species chemically using reaction gas [66].

For AAS measurement, the analyte should be initially turned into atoms in the gas form, usually by applying heat to the cell named as atomiser. The sort of atomiser determines the two main AAS based analytical methods: Flame AAS, which gives analytical signal in the continuous mode and electrothermal AAS, which delivers analytical signal in the discontinuous fashion. Either way, liquid specimen is simply brought into the analyzer [67].

4. EXPERIMENTAL STUDIES

Because of its poor availability in nature, it is prevalent nowadays to extract and process Pd from various spent goods [68]. Effective and complete seperation of Pd is therefore a crucial step for the recovering. As described in the previous chapters, hydrometallurgical methods are used usually for the recovery and seperation from the catalysts, which consist of a metal coating supported by often-used Al_2O_3. These methods are categorised as dissolution of "support" and "precious metals" [49]. Within the first one, a non-oxidizing acid dissolves only the support and brings it into the form of slurry, but great deal of reagents is needed. In contrast, an oxidative agent extracts the noble metals from the support in the second method. Nevertheless, γ-Al_2O_3 is partly soluble in both of these methods and interferes with PGMs. Majority of different techniques for dissolving the noble metals are founded on aggressive reactants and leach process with high pressure that are non-environmental, costly and exceptionally destructive.

Unlike other PGMs Pd can be easily solved and therefore several leaching solvents like HCl, H_2SO_4, NaCl with oxidants such as HNO_3, Br_2 or Cl_2 were utilized as Pd leaching agents. Majority of these leachants, however, endanger the environment. Even though Pd can be dissolved smoothly by the concentrated HNO_3, this method seems not feasible due to the heavy price of the acid and the release of dangerous NO product. Furthermore, before separating Pd, HNO_3 should be completely repelled from the leachate, since highly oxidizing nature of the remaining HNO_3 would prevent Pd reduction. Hence, an additional leaching system was required for Pd recovery [69].

The objective of this thesis was recovering and separating Pd from the Pd/Al_2O_3 structured catalyst using a simplificative method. To ensure the optimal recovery of Pd, a solution of distilled HCl and H_2O_2 was studied as indicated in Figure 4.1.

4.1 Materials and Chemicals

For use in experimental studies, a spent catalyst, which used to be installed in a passenger car, was provided. It was a ceramic catalyst containing Pd, coated as a thin layer on the porous structure of Al_2O_3. The spent catalyst was then pulverized and the amount of palladium was determined by XRF (X-ray Fluorescence Spectrometers) analysis. The amount of palladium contained in spent catalyst powder was roughly 1.312%.

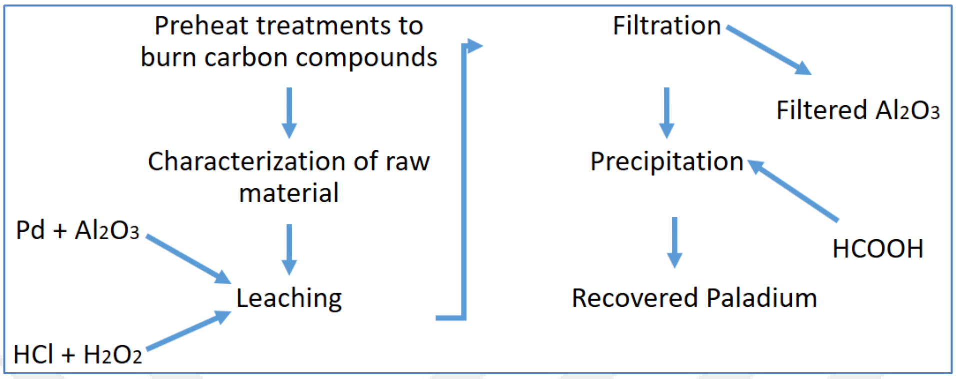


Figure 4.1: Steps of the process.

For the preparation of leaching solutions, doubly distilled water has been used to dilute the hydrochloric acid (30-32%) and hydrogen peroxide (30%), while formic acid (96%) was utilized subsequently for palladium reduction. All provided chemicals were of high quality for use in the laboratory.

Equipments used in the experimental studies were as follows: A drying oven branded as Thermo Heraues for the desiccation of the final products, glass-coated, thermometer controlled heater and magnetic stirrer branded as Heidolph MR3001K, Sartorius analytical balance for the weighing, open atmosphere furnace heating up to 1,200 ºC for the combustion of excess carbon, Thermo Scientific Niton XL2 XRF analyzer for the characterization of the raw material, ICP-MS system of PerkinElmerSCIEX named as ELAN DRC-e and AAS device branded as ContrAA 700.

Spatula, porcelain crucible, standard laboratory glassware such as test tube, beaker, flask, etc., blue band filter paper, ISOLAB sintered glass filtered gooch funnel and Vacuubrand vacuum pump for the separation of solid from the liquid were the other materials used during the experiments.

4.2 Preheat Treatments for Burning Carbon Compounds

Because spent catalysts contain carbon compounds attached to the surface during use in the automobile, 50 grams of catalyst powder samples were preheated in a muffle furnace (See Figure 4.2) for 15, 30, 60 and 120 minutes at 700°C and the reduction of the masses was observed. The decrease in percentage of solid carbon compounds in the samples were 2,791%, 3,294%, 3,677% and 3,506% respectively. According to the data obtained, optimum treatment duration for the next experimental steps was determined as 60 minutes. The color of the powder was initially dark grey and it was observed that the powder is discolored in the wake of burning process.

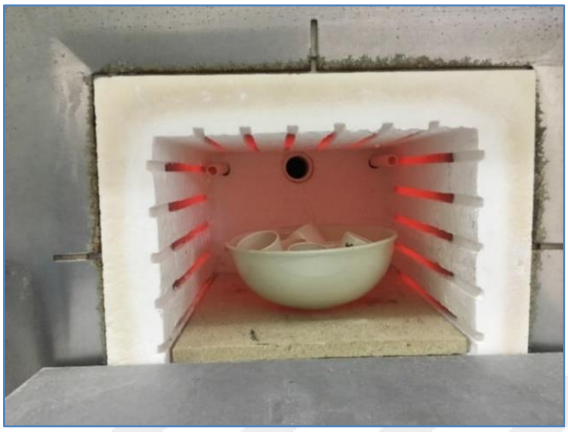


Figure 4.2: Burning process of the carbon compounds in the furnace.

4.3 Characterization of the Raw Material

Palladium characterization in spent catalyst powder was identified by XRF Analyzer in the laboratory of Borsen Pipes as shown in Figure 4.3. XRF analyzers evaluate a specimen’s composition by computing X-ray fluorescent released from the specimen when the resource of X-ray excites it. Each of the elements available in the specimen generates an array of typical X-rays fluorescent, which is special to the particular element and offers a precise and non-destructive method for measuring the purity and chemistry of all precious metals. As a consequence of the analysis, the concentration of palladium in the heat-processed sample was 1,312%.

```
# 218 General Metals
NAV Tools
Time 32.0 sec
No Match 8.1
Ele   %      ±2σ
Ni  0.071  0.061
Cu  0.106  0.060
Zn   2.21  0.10
Se  0.000  0.008
Fe  0.143  0.90
Nb  0.706  0.062
Mo   1.25  0.15
Pd   1.31  0.09
```

Figure 4.3: XRF Analyzer.

4.4 Experimental Steps

Previous studies have shown that grinding the catalyst is not a controlling parameter for Pd recovery process. The grinding, however, was necessary to homogenise the specimen. 400 g of the spent catalyst was therefore crushed, ground, passed through a 250 mm particle sized sieve and used in the leachate.

Leaching liquor including particular combinations of reagents were prepared in a 200 ml flask, which was privously washed by distilled water. Measured amount of the catalyst was then stirred by magnetic stirrer in the flask. In the wake of heat treatment, the solution was filtered off and analyzed by atomic absorption spectrophotometer (AAS) for the detection of dissolved Pd amount in the liquid. Subsequently, Pd containing solution was used in the experiments for the separation of Pd. In such a case, leach solution samples were stirred in flask with variously concentrated formic acid volumes and the final solution was thermally treated. The mixture was again filtered off and analyzed via inductively coupled plasma-mass spectrometer (ICP-MS) to illustrate remaining Pd in the solution for the calculation of Pd recovery.

4.4.1 Leaching

In order to find the optimum leaching conditions, acid concentration was the first item to be observed and various acid volumes were thereby mixed in the leaching solution. Since the solvents were made up strong acid, being environmentally friendly was another asset apart from the efficiency.

The following solvent ratios (HCl-H_2O_2) were taken into the flask by 10 grams of spent catalyst samples, which were already pre-treated for 60 minutes at 700°C: 1.87%-2.5%, 2.5%-2.5%, 3.75%-3%, 4.5%-4.5%, 6.3%-4.75%, 7.5%-5.25%, 9%-4.5%, and 9%-6%. After stirring step, solutions were heat treated in the drying oven at 95ºC for 120 minutes. Using a vacuum pump with a blue band filter paper, the solution was separated then from the leach cake and stored in a 200 ml flask as revealed in Figure 4.4. According to the analysis results of atomic absorption spectrophotometer (AAS), maximum amount of Pd dissolution was obtained by the leachate containing 6.3% HCl and 4.75% H_2O_2.

Solutions should be heat treated at the ideal temperature to achieve maximum efficiency in the leaching process. Therefore, 10 grams of spent catalyst samples, which were pre-treated at 700ºC for 60 minutes, were brought into the flask consisting

Figure 4.4: Filtering the residues with vacuum pump is required.

of the solvents of 6.3% HCl, 4.75% H_2O_2 and stirred. Respective leachates were then heated in the drying oven at the temperatures of 50°C, 60ºC, 70ºC, 80ºC, 85ºC, 90ºC and 95ºC during 120 minutes. Using a vacuum pump and a blue band filter sheet, solution was separated from the leach cake and stored in a 200 ml flask. The optimal temperature was determined as 80ºC according to the findings of atomic absorption spectrophotometer (AAS) exhibited below in Figure 4.5.

Figure 4.5: Quantitative analyse with AAS (in ppm) for Pd recovery.

The time was the other factor to determine the optimum conditions for leaching. After the pre-treatment for 60 minutes at 700ºC, 10 grams of samples were taken into the flask with solvents of 6.3% HCl, 4.75% H_2O_2. Solutions were then processed in the oven for 30, 60, 80, 100, 120 minutes at 80°C. The leachate was separated from the leach cake using a vacuum pump and blue band filter paper and stored in a 200 ml flask. In reference to the results of the analysis performed by the atomic absorption spectrophotometer (AAS), it could be stated that expected Pd dissolution rate had been reached under the appropriate conditions after 100 minutes of leaching.

The last parameter that may affect the solution was the liquid/solid (L/S) proportion. Respectively 2.5, 5, 10, 20, 40 grams of spent catalyst samples, which were pre-treated at 700ºC for 60 minutes, were taken into the vessel with the same amount of solvents (HCl, H_2O_2). Solutions were heat treated for 100 minutes in the oven at 80°C after the stirring phase as listed in Table 4.1. The solution was separated from the leach cake using a vacuum pump and blue band filter paper, stored in a 200 ml flask. According to the results of the analysis of atomic absorption spectrophotometer (AAS), maximum Pd was dissolved when liquid/solid proportion was held at 9.5/1.

Table 4.1: An example table for the analysis of liquid/solid proportion.

HCl (ml)	H_2O_2 (ml)	Distilled water (ml)	Solid (g)	Temperature (°C)
20	15	60	40	80
20	15	60	20	80
20	15	60	10	80
20	15	60	5	80
20	15	60	2.5	80

4.4.2 Separation of palladium

Two criteria had been tested for Pd seperation so that optimal precipitation could be achieved: “Effect of time” and “Effect of HCOOH volume applied to solution”. Pd solutions, formulated under optimum leaching conditions were comprising 12.61 ppm (mg L-1) of Pd.

These were merged then with particular amounts of HCOOH and heated at different temperatures in the oven. A 30-minute thermal process separated Pd into the tiny shape that could be barely seperated by filter. However, longer thermal treatment made up bigger dark Pd metal grains, which were filtered by P4 pore sized Gooch funnel. Pore size of Gooch funnel, which is classified in Table 4.2, plays here a crucial role so that separated Pd could be filtered properly. In the analysis step, all samples including HCOOH and Pd solution were analyzed by ICP-MS device in order to detect the small amount of Pd elements in the liquid and to determine the effiency of Pd seperation.

Table 4.2: Nominal pore size of a Gooch funnel. (Robu & Schott, ISO 4793)

Designation	Pore size, in microns
P0 (P250)	(250~500) µm
P0 (P250)	(160~250) µm
P1 (P160)	(100~160) µm
P2 (P100)	(40~100) µm
P3 (P40)	(16~40) µm
P4 (P16)	(10~16) µm
P5 (P1.6)	(1.0~1.6) µm

5. EXPERIMENT RESULTS

5.1 Leaching Process

A nature-friendly method was carried out in the experiments to recover Pd from the spent catalyst on the basis of Al_2O_3 carrier. Pd dissolution was achieved by leaching and it was oxidised by Cl^- as a result of the following reaction:

$$Pd + 4Cl^- \rightarrow (PdCl_4)^{2-} + 2e^- \ E^0 = 0.62V \tag{5.1}$$

Above-stated "standard reduction potential" is the inclination of chemicals to be reduced, and it is scaled in V under normal circumstances. Positive potential means that the chemical is most probably to be reduced. According to the reaction below, H_2O_2 was reduced to the water:

(Standard reduction potential of H_2O_2 at 25°C was measured as 1.763V [70].)

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \ E^0 = 1.763V \tag{5.2}$$

H_2O_2 has been considered as an appropriate oxidizing agent for palladium, as specified by the "standard reduction potentials". According to the overall reaction, Pd could be dissolved using H_2O_2 as an oxidizing agent in the acid media including HCl.

$$Pd + H_2O_2 + 4HCl \rightarrow H_2PdCl_4 + 2H_2O \ E^0 = 2.383V \tag{5.3}$$

Accordingly, palladium leaching in hydrochloric acid with hydrogen peroxide was investigated in order to optimise the variables controlling the dissolution phase.

5.1.1 Effect of heat and time

As a function of time, recovery of Pd from the catalyst was observed at temperature series from 50°C to 95°C, within 4.75% H_2O_2, 6.3% HCl acid medium and L/S proportion of 9.5/1. As it is seen in Figure 5.1, Pd extraction continuously increased in parallel to increment of the time and the temperature until the maximum dissolution of

Pd is reached. Pd recovery slowly rised over time at a low temperature range of 50-60°C, but after 2 hours did not exceed 70 percent. However, the Pd recovery increased rapidly with a higher values of the temperature in the range of 60-80°C at the first 20 minutes and then gently reached after 1.5 hours to a peak value of 97.19% recovery.

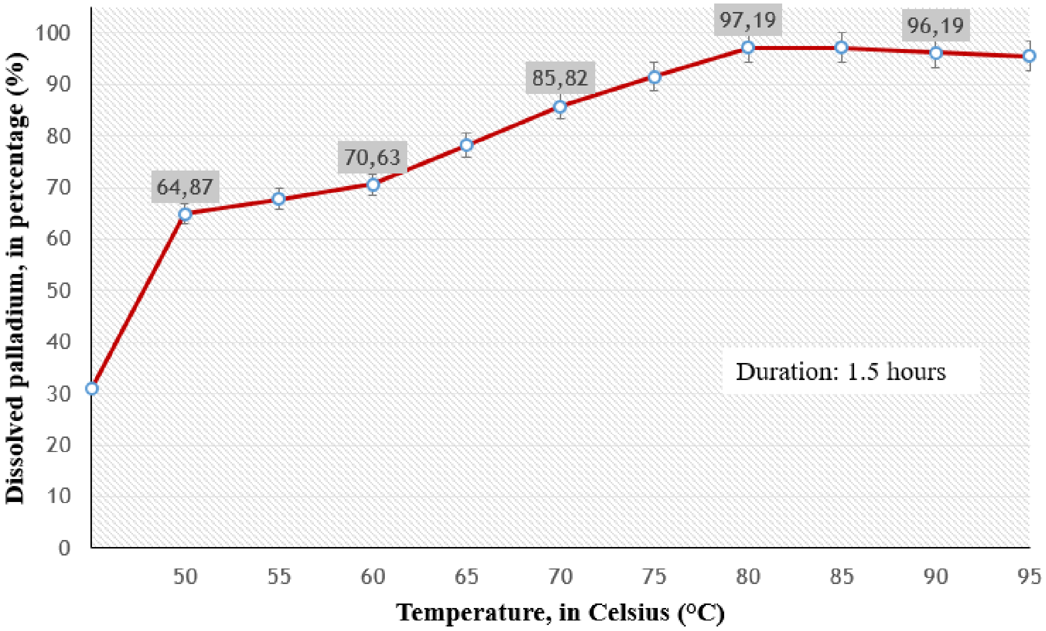


Figure 5.1: Pd Recovery in response to the temperature changes.

It is also graphed in Figure 5.2 that the increase in Pd's dissolution chart stopped at 80°C and began to fall at 85°C and higher values. The palladium recovery curve at a leaching temperature of 80°C hit the top and thus the subsequent experiments were conducted at about 1.5 hours at 80°C to obtain optimal results.

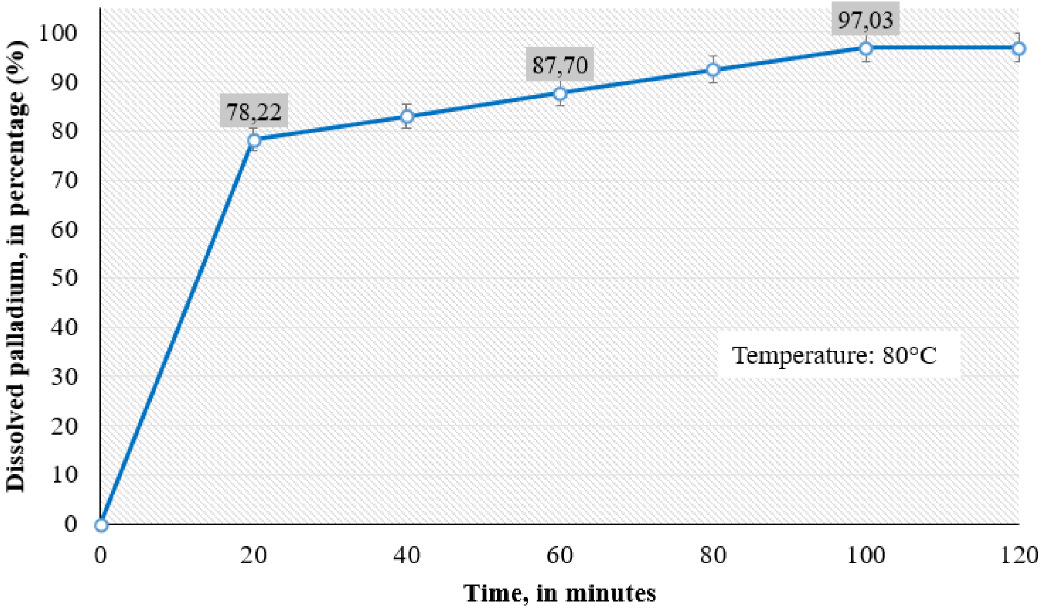


Figure 5.2: Pd Recovery in response to the time interval at optimal temperature.

5.1.2 Effect of acid concentration

Within the different concentrations of HCl and H_2O_2, Pd dissolution from the catalyst at L/S proportion of 9.5/1 was observed and the leaching process was implemented at 80°C for 1.5 hours. Without H_2O_2, the disjunction of Pd slightly grew with concentrated HCl hitting the highest point of 74% with 10% concentration of HCl. With H_2O_2, Pd dissolution increased considerably at low acid concentrations between 0.5% and 2% and then slightly rose to about 95% at 6% HCl, 4.75% H_2O_2.

Further changes such as rising HCl concentration grew the Pd recovery gently and finally the efficiency of the leaching reached 96.19% with 6.3% of HCl and 4.75% H_2O_2 as shown below in Figure 5.3.

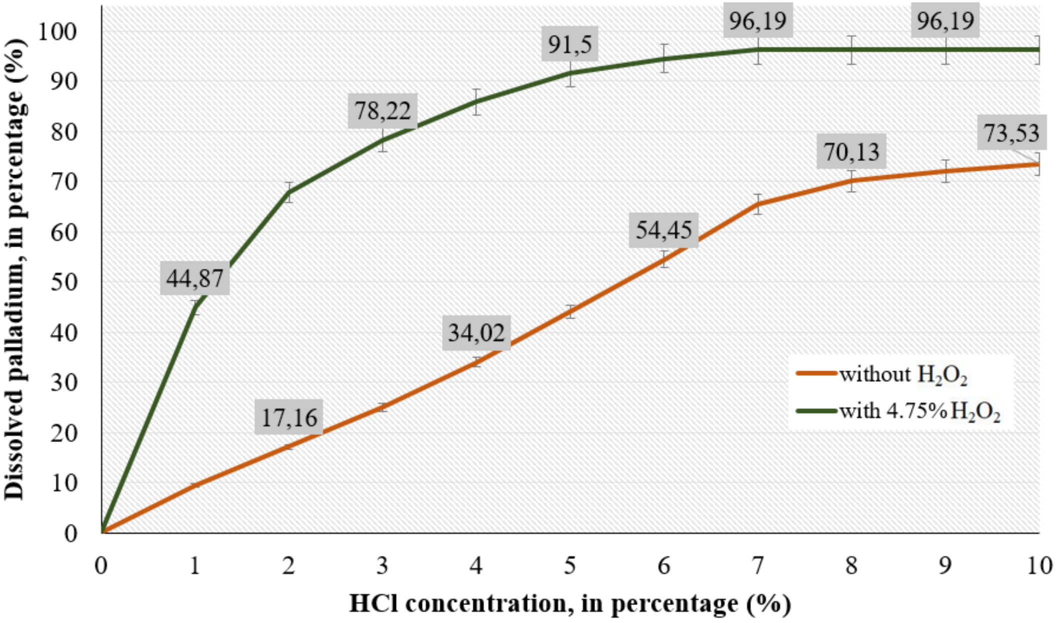


Figure 5.3: Effect of concentrated HCl on the recovery.

If a catalyst comprising Pd is kept in the atmosphere, adsorbed O covers the surface of the catalyst. Without H_2O_2, the happening dissolution of Pd in HCl is related with the oxidizing effect of O_{ads} developed on the surface of Pd:

$$Pd + O_{ads} + 4Cl^- + 2H^+ \rightarrow PdCl_4^{2-} + H_2O \qquad (5.4)$$

5.1.3 Effect of liquid/solid proportion

L/S proportion is a key economic element in the leaching process since it defines the reagent's use. Therefore, various L/S proportions in the leachate were studied to extract

Pd soluble from catalyst at 80°C in 1.5 hours using differently concentrated HCl and 4.75% H_2O_2 acid media.

It could be seen that Pd extraction expanded along with the rise of L/S proportion by all considered HCl concentrations, however it stuck at the same dissolution values with L/S ratios higher than 10/1. On the other side, Pd recovery with 2.5% HCl was only 80%, even if L/S proportion was increased to 20-25/1. This suggests that effective metal recovery cannot be achieved by rising L/S proportion to excessive values, when HCl concentration is below 5-6%. By contrast, if 6.3% HCl is used, highest amount of Pd could be extracted at L/S proportion of 9.5/1. Please see the related graph below in Figure 5.4.

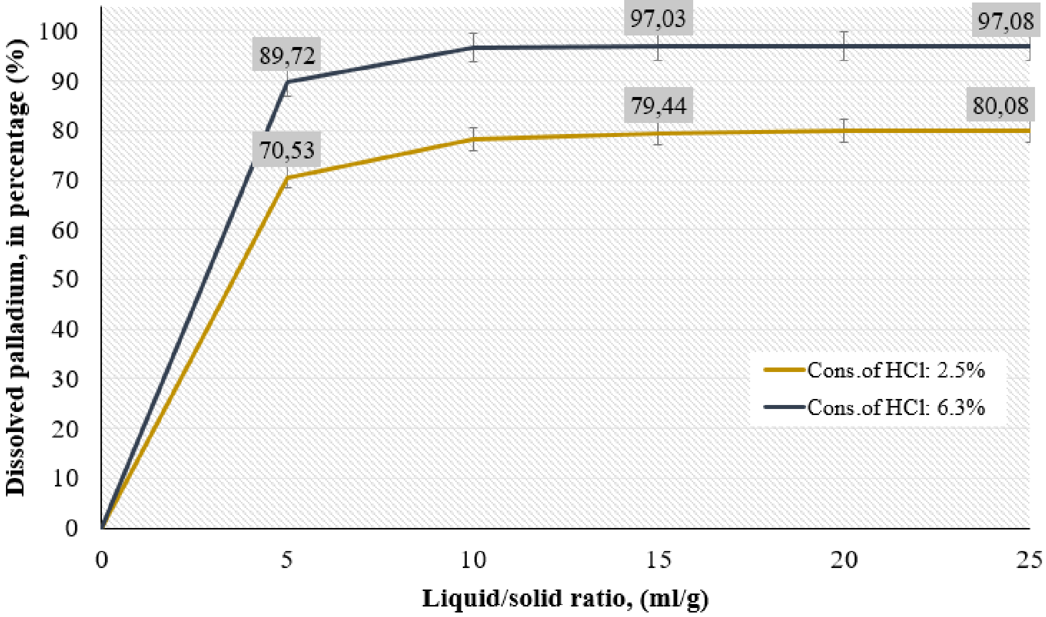


Figure 5.4: Excessive values of L/S ratio has no crucial effect on the recovery.

5.2 Separation of Palladium

As reported by the previous experimental steps, it was clear that the best possible conditions for Pd recovery were achieved by solutions consisting of 6.3% HCl and 4.75% H_2O_2, heatied up at 80°C during 1.5 hours retention time and L/S proportion of 9.5/1. In optimal leaching conditions, a leach solution was analyzed and found to contain 12.61 ppm ($mg.L^{-1}$) of Pd. The respective stock solution was then used for Pd separation experiments to reduce Pd by HCOOH, in which Pd^{2+} was reduced to Pd^0 as illustrated below (5.4). After the filtration of Pd residue from the Pd solution-HCOOH mixture, remaining amount of Pd in the liquid was found as 0,54 ppm (mg L^{-1}) according to analysis with ICP-MS device.

$$H_2PdCl_4 + HCOOH \rightarrow Pd + 4HCl + CO_2 \tag{5.4}$$

There were several benefits of separating Pd by the reducing with HCOOH. As HCOOH reduces Pd immediately to a metallic form, there is no need for further processing apart from the fast desiccation. HCOOH decomposes then to CO that does not contaminate the liquor or does not establish a pollution problem. HCOOH reduction is considered to easily seperate Pd with fast recovery unlike other methods for precipitation. For this purpose, HCOOH was used to recover Pd from the solution where the various parameters were experimented effecting the cycle.

The impact of time and heat on the separation of Pd was studied using the volumetric ratio of 1/1 for HCOOH/Pd solution. With period in the first 30 minutes, the volume of seperated Pd gradually increased at 50°C, and then stayed almost constant, reaching a value of 70% after 1 hour. Then Pd was very easily separated at 100°C and an efficiency around 95.85% was achieved in the wake of 10 minutes as can be observed in Figure 5.5. Even though Pd may be reduced with heat treatment at 100°C principally in 10 minutes, thermal process lasted for 30 minutes was favourable to filtrate precipitated form of Pd, which used to be pulverized in the beginning.

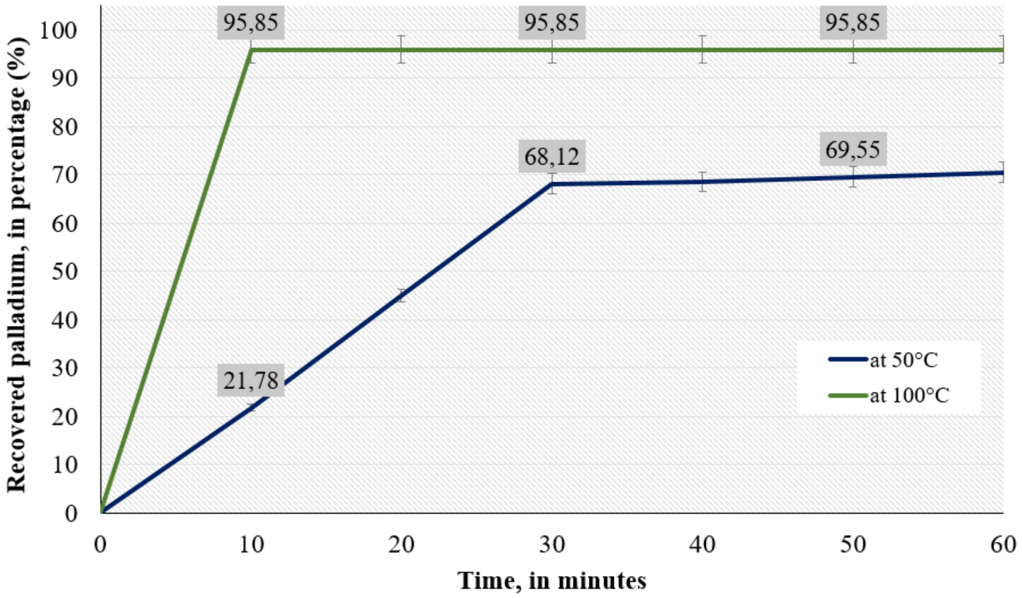


Figure 5.5: Separation of Pd is increasing over time.

Other factor affecting the seperation of Pd was the volume of HCOOH. It was added on the leachate at different temperatures and heated for 1 hour. All in all, separation of Pd rose with the increment of HCOOH at lower temperatures. As indicated in Figure 5.6, Pd separation began at 50°C with the volumetric HCOOH/Pd solution ratio, which was greater than 1/1. Pd separation rose gently with the increasing HCOOH volume at higher temperatures as 80°C. Ultimately, a peak for Pd separation was achieved at 100°C with low volumetric ratios of HCOOH and the process ended just after the reaching equal amount of the components.

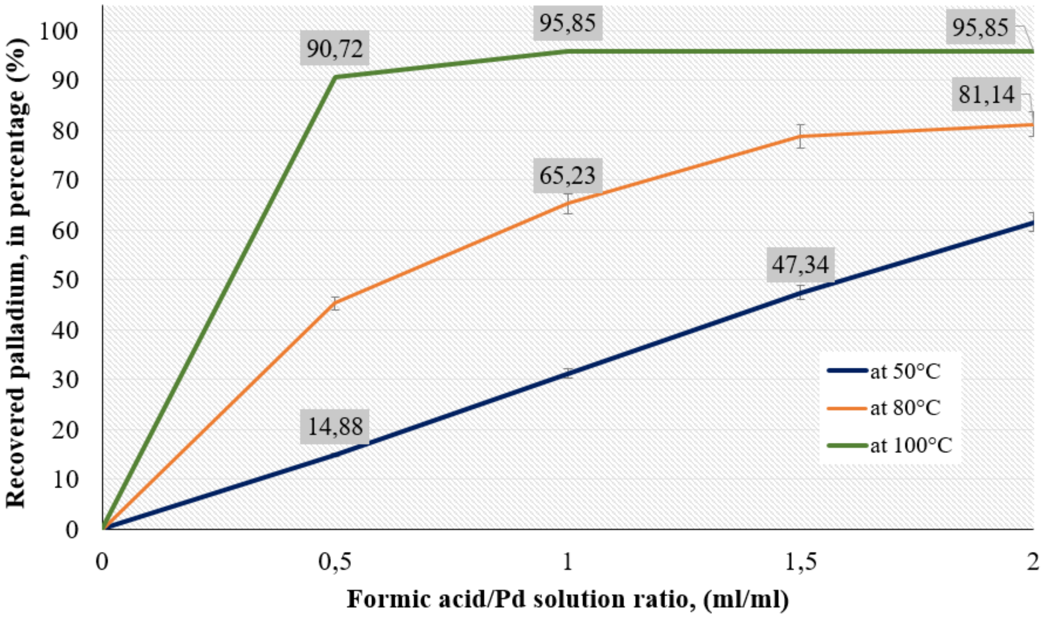


Figure 5.6: Curves for the different volumes of formic acid applied to the solution.

6. CONCLUSIONS

Within the scope of this master thesis, an environment-friendly and basic process was proposed to recycle Pd from spent catalysts to eliminate the potential risks regarding Pd recovery. This research might also provide an eventual solution for the recovery of Pd from secondary assets, since the method is cost-effective.

In studies, following experimental steps ensured to achieve maximum recovery: An off-the-shelf spent catalyst was delivered and made ready by crushing, grinding and passing through a sieve for the use in experiments with leaching. At that point the characterization of the Pd in spent catalyst powder was detected by XRF analyzer. Required catalyst quantities were heat treated to burn carbon compounds that were attached to the surface during use. Within conical flasks, solutions of various combinations of reagents were formulated and the prepared mixtures were mixed with a magnetic stirrer. In the wake of heat treatment, the solution was filtered off and analyzed by atomic absorption spectrophotometer (AAS) for the detection of dissolved Pd amount in the liquid. Subsequently, Pd containing solution was used in the experiments for the separation of Pd. In such a case, leach solution samples were stirred in flask with different concentrated formic acid volumes and thermally treated. The final mixture was filtered off and eventually analyzed via inductively coupled plasma-mass spectrometer (ICP-MS) to illustrate remaining Pd in the solution for the calculation of Pd recovery.

Consequently, the leaching of Pd was accomplished by a solution consisting of 6.3% HCl and 4.75% H_2O_2. In the wake of heat treatment with a liquid-solid ratio of 9.5/1 at 80°C for 1.5 hours, leaching efficiency of 97% was reached. Then dissolved Pd was effectively reduced by the mixture including same volumetric ratios of leach liquor and formic acid. For Pd separation, an additional thermal process at 100°C for 1 hour was sufficient to achieve 95% efficiency. Hereby it was demonstrated that recovered Pd could be used again for manufacturing fresh activated catalysts.

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