Chapter 17
Recycling of Platinum Group Metals and Alternative Catalysts for Catalytic Converters

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Abstract Platinum group metals (PGM) are used as a catalyst in the automotive catalytic converters to curb engine emissions. The modern catalytic converter (three-way) executes oxidation of CO and unburnt HC, and reduction of NO using its large active surfaces containing PGM, which are precious metals with high cost all over the world. Due to the high cost of the PGM, researchers are working on efficient methods for extracting and reusing these valuable metals from catalytic converters. Pyrometallurgy and hydrometallurgy are the most common ways for the extraction of the PGMs among other methods. Alternative to platinum, materials like titanium dioxide and other metal-based oxides can be used for carrying out redox reactions of toxic vehicular emissions. The use of such alternative catalysts can help in reducing the increasing demands and cost of PGMs. This chapter focuses on the possibilities of recycling the PGMs from catalytic converters and also of reducing the ever-increasing requirement of PGMs in the manufacturing of autocatalysts in the catalytic converters. The chapter reports the recent global trends of PGM recycling and its demand for use as autocatalysts, alternative materials ~~of~~ to PGMs in catalytic converters and alternative methods for emission reduction. Further, the engine-related challenges and research on future directions of replacing PGM's as autocatalysts has been performed; it includes some experimental results of direct decomposition of

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R. K. Upadhyay et al. (eds.), *Transportation Systems Technology and Integrated Management*, Energy, Environment, and Sustainability,
https://doi.org/10.1007/978-981-99-1517-0_17

NOx using non-noble metal catalysts such as Cu-COK12, Cu-Nb_2O_5, Cu-YZeolite, and Cu-ZSM5. The article should also provide a quicker understanding of research on development of low-cost non-noble metal-based alternative autocatalysts.

Keywords Alternative catalysts · Autocatalysts · Demand · PGM · Recycling · Supply

17.1 Introduction

The harmful gas emissions from the engine exhausts contributes to air pollution and imposes a great threat to environment [1–7]; thus, the automotive industries are much inclined to counter the engine emissions. Hence, catalytic converters are applied after the exhaust pipe to reduce the emission levels from the engine exhaust [8–10]. These catalytic converters consist of an active surface of platinum group metals (palladium, platinum, and rhodium), also sometimes denoted as PGM. PGMs are preferred due to their catalytic ability for the conversion of the exhaust gases into less harmful oxides [11]. The PGM's are called the state-of-the-art Industries' Vitamin because of its exceptional characteristics like resistance toward corrosion, catalytic activity, stability (thermal and electrical), and inertness [12–16]. By employing catalytic converters, the engine exhaust emissions are controlled to be in the permitted range set by the emission controlling body.

The automobiles are used extensively in the modern world; they have now been basic daily need of an individual. But apart from all the advantages automotives have, we are paying a huge cost in the form of environmental damage, as they emit large amount of NO_x, CO, unburnt hydrocarbons, Particulate matter emissions (also known as Soot), and other toxic gases. There are many regulatory bodies around the globe who have made laws, norms and emission regulations, standards according to the country's environmental conditions and extent of air pollution. The catalytic converter serves as leading aid to fulfill such regulations, so their demand has become obvious in today's world. With the growing demand of catalytic converters, the demand of their main ingredient's such as PGM has of course increased and they are under extensive research. Carrying the fact of increased demand of PGM in such amounts, has led to beat the supply or yield globally [17–19], and consequently making them "precious and costlier metals". Table 17.1 shows the cost increment of PGMs over consecutive years.

Table 17.1 Average costs of PGM globally (in the units of U.S. dollars per kg) for 4 consecutive years [20]

Costs in →	2018	2017	2016	2015
Platinum metal	28 935.67	30 575.36	31 797.08	33 951.18
Palladium metal	31 829.23	28 131.90	19 837.01	22 344.76
Rhodium metal	67 516.56	35 783.78	22 409.07	30 703.96

Figure 17.1 depicts the data of Platinum Group Metal’s Demand Vs Supply for 5 consecutive years for various sectors. From the above graphical representation, it can be observed that supply of PGM has been lesser as compared to its demand since these last 5 years. The following Table 17.2 presents the platinum group metals’ percentage of change among total demand and supply for 5 consecutive years.

Additionally, the demand of PGMs as autocatalysts in the automobile industries for some countries around the globe is as shown in Fig. 17.2.

Moreover, this study further reviews the difference in usual usage or demand of platinum group metals as compared to its demand in the automobile industry (as autocatalysts), is shown in Fig. 17.3.

A comparison of the total gross demand of PGMs with the demand for its use as autocatalysts is given in Fig. 17.3.

Figure 17.3 and Table 17.3 reflects that good percentages of the demand of platinum group metals in automotive industry as autocatalysts with respect to its demand in global market. The platinum metal has proved its dependence in the jewelries and ornaments, so a huge percentage of platinum goes in the global market as compared to its demand as autocatalysts.

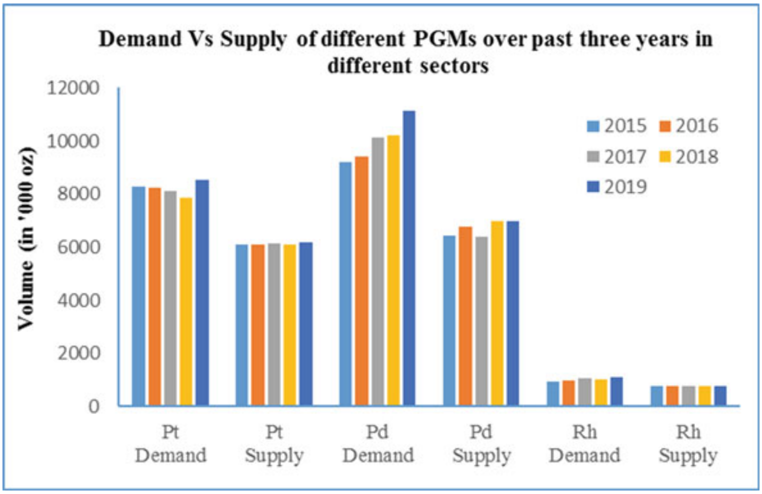

Fig. 17.1 Data of Platinum Group Metal’s Demand Vs Supply for 5 consecutive years for various sectors [21]

Table 17.2 Platinum Group Metals’ percentage of change among total demand and supply for 5 consecutive years

	2015	2016	2017	2018	2019	Average
Platinum	26	28	30	32	33	29.5
Palladium	30	33	34	37	35	33.8
Rhodium	29	23	26	28	30	27.2

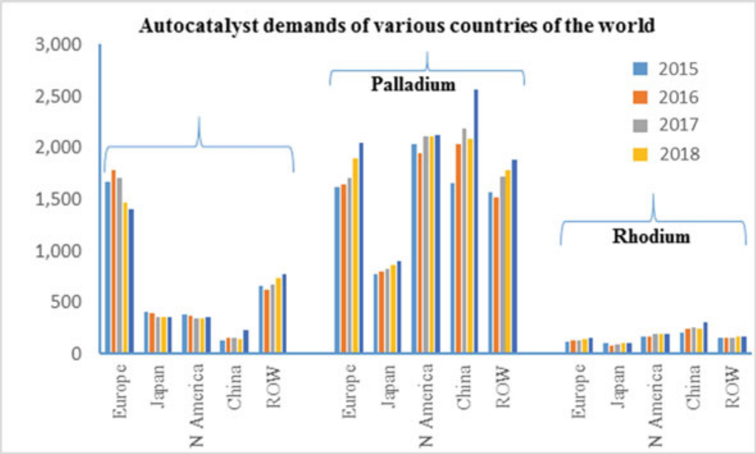

Fig. 17.2 Demand of PGMs as autocatalysts around the globe (ROW in the graph refers to the “rest of world”) [21]

The huge requirements of PGMs convey that, if by any possibility we can reduce the demand of platinum group metals in the automotive industry, the global prices will be reduced significantly. Recycling of platinum group metals has been in consideration since a long time, and it has been proved as a good practice in view of scenario of increasing cost and demand of PGMs. Researchers are investigating new materials and techniques as the alternatives to PGMs to reduce exhaust emissions in more efficient ways [22]. However, due to the superior activity and results by the PGMs, the most used metals for the catalytic conversion are platinum, palladium, and rhodium [13, 23–26].

17.1.1 History of Emission Control Research

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In 1975, after beginning of emission control research in the US, the investigations directed that palladium and platinum as most suitable oxidation catalyst. While the iridium, rubidium, and osmium showed their oxides are volatile [27]. From 1975 to the 1980s, researchers were working actively to control emissions; the other challenge was to finalize a catalyst to reduce NO_x. For the very first time, a two-bed converter came into the picture; in the primary bed, reduction of NO_x took place, and in the secondary bed, HC and CO were treated and oxidized. But the main discrepancy in this came when NH_3 formed into the primary bed went to the second one to again

Fig. 17.3 Representation of demand of PGMs in all sectors as compared to automotive sector [21]

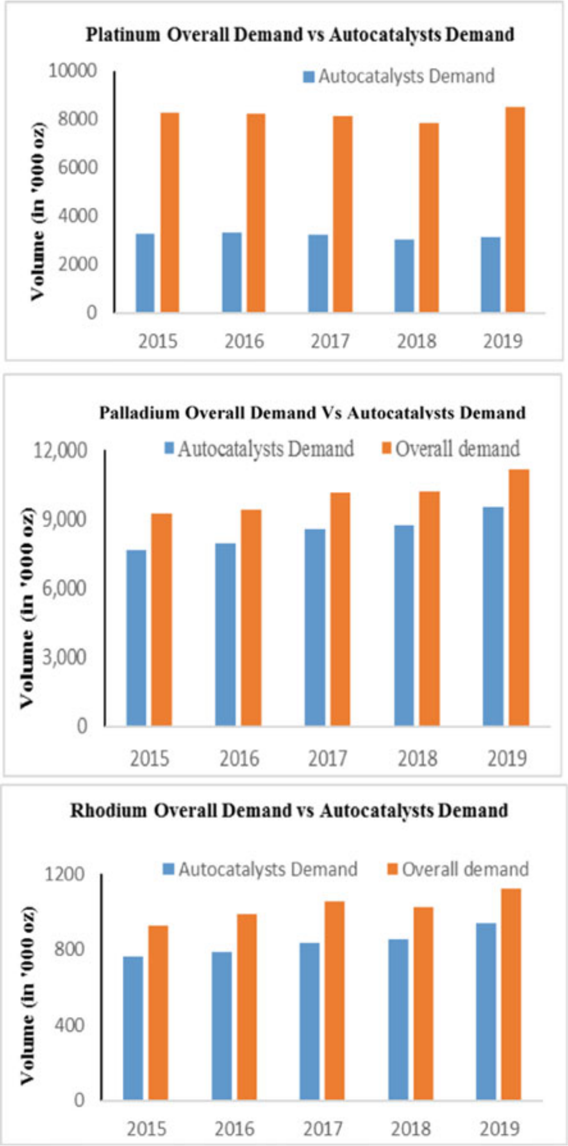


Table 17.3 Percentage of the demand of PGM in the automobile industry as autocatalysts from total demand of PGMs in the global market [21]

	2015	2016	2017	2018	2019	Average
Platinum	39	40	41	40	42	40.4
Palladium	83	81	80	82	81	81.4
Rhodium	82	81	83	84	82	82.4

form NOx into the secondary bed. Moreover, ruthenium (even while readily forming volatile oxides) was also tested and seen as a possible catalyst, and its chemical properties were tested in many different studies [28–36], but they were not preferred for further production because they did not serve the purpose as they not only proved to be an inefficient reducing agent for NO, but also showed higher selectivity toward NH_3. Additionally, rhodium was taken into consideration for reduction of NO_x, as they shown good NO_x reducing nature with lesser selectivity toward NH_3.

Eugene Houndry, a French-based mechanical engineer is the inventor of catalytic converter [37–39]. However, it was further developed by Carl D. Keith and John J. Mooney in the year 1973, where it was produced for the very first time. After 5 years of its production, the three-way catalyst was also studies for indispensable reduction of NOx [40–45]. The platinum group metals are considered as a group of highly valued and rarely available transition metals that consists of platinum, palladium, rhodium, iridium, osmium, ruthenium, (all are periodic table's d-block elements). They are all white silvery metals that are unreactive, having almost the same chemical and physical characteristics, and are also found at the same place together in mineral deposits. There is a nice history behind using Pt, Pd, and Rh as autocatalysts [46]. Due to difficulties in availability and the high costs of noble metals, in the mid-1970s the research was focused on non-noble metal-based catalysts. But after some extent of the research, it was found that non-noble metals with their oxides, for example, cobalt oxide, nickel oxides, manganese oxide, copper oxide, and chromium oxide, etc., proved to have less durability, less abatement activity toward automotive emissions [22, 27, 46–48]. So, the research was moved forward on the catalysts with noble metals due to their exceptional capabilities of higher temperature stability and lesser likeliness to react or interact with the material of support. Pardiwala et al., in their study for the USA and Japan, stated that the catalytic converter has the ability to abate the lethal emissions in forms of CO_2, H_2O, O_2, and N_2, and it has become a compulsory for every vehicle [38]. Researches also stated the same for Indian government has also made catalytic converters obligatory, and strict regulations are there for harmful emission prevention [39–41]. In 1970s, Japan and the United States of America are the countries, which made catalytic converter to be mandatory, and further, this rule was also implemented in Asia, Europe, and Australia after 10 years; additionally, later on other countries such as India, Brazil, and Mexico took 10 more years to make it mandatory for all vehicles [49].

In the same scenario for the manufacturers, platinum group metal-containing catalytic converter production became a must requirement. The position of catalytic converter as shown in Fig. 17.4, is on rear side of vehicle, inside the exhaust pipe, so that all kind of exhaust gases produced by engine combustion can pass through it and they can be dealt in the Platinum group metal-containing catalytic converter [37]. Additionally, researchers have also worked on the placement of catalysts concerning the engine and explored interesting behaviors in the reduction of emissions. For example, with the increase in distance of placement, the non-methane hydrocarbon emissions increased [50]. However, they also used another factor of palladium loading in their research and showed higher palladium loading results in lesser non-methane hydrocarbon emissions.

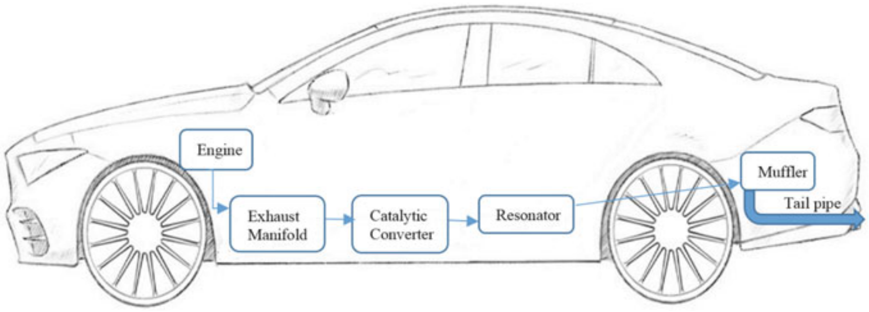


Fig. 17.4 Schematic of the placement of a catalytic converter in a car

17.1.2 Requirement of PGMs in the Catalytic Converters

PGMs are coated on the monolith substrate inside the catalytic converter so as to deal with lethal exhaust emissions; the coated surface remains active and redox reactions take place on it [5]. The catalytic converters can be further studied as two-way (where HC and CO get oxidized to H_2O and CO_2) and three-way catalytic converters (including function of converting HC and CO), it also reduces nitrogen oxides into O_2 and N_2 [2]. Researchers studied some potential candidates similar to PGMs such as Cr_2O_3, TiO_2, NiO, CeO_2, Fe_2O_3, and ZrO_2. But in 1980s, PGM was established well and found efficient in their role in the catalytic converters [2].

17.1.3 The Different Aspects of Platinum Group Metals

As discussed in the previous sections, the exhaust emissions undergo redox reactions which is the primary goal of a catalytic converter, contributing to reduce the lethal emissions [40]. The palladium metal and the platinum metal are mostly used as oxidizing agent for unburnt hydrocarbons and carbon monoxide to convert them into H_2O and CO_2, respectively, as shown in the following reactions.

$$\mathrm{CO} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$$

$$\mathrm{CxHx} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

However, rhodium is deployed to break NO into the N_2 and also steam reforming [51, 52]. Figure 17.5 shows a typical three-way catalytic converter.

The alumina washcoat which is porous in structure helps for distribution of platinum, palladium, and rhodium on the substrate's surface. The washcoat is made up of γ-Al_2O_3. It provides a greater contact area for the interaction of exhaust gases and active phases and a greater heating stability. In some cases, it may happen that

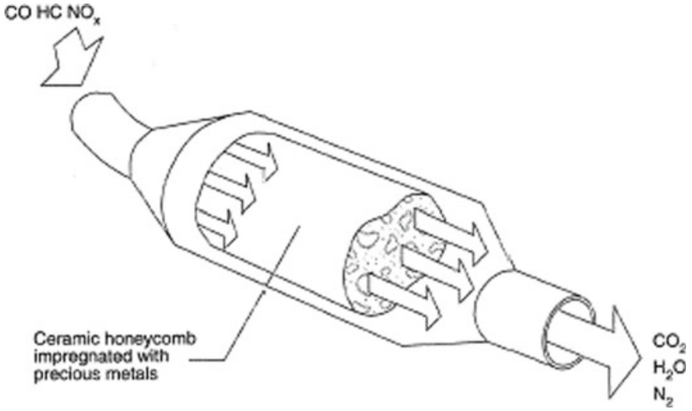


Fig. 17.5 Typical three-way catalytic converter [53]

if temperature rises, the surface area of γ-Al_2O_3 may get decreased; for this reason, metal oxides like CeO_2, La_2O_3, BaO, and ZrO_2 are used as stabilizing agents [54]. Furthermore, to assist the distribution of PGM on the substrate, a traditional additive (mixture of ZrO_2 with CeO_2) is used; this combination also helps in oxidation reactions and promotes catalytic activity [55].

17.1.4 Availability of PGMs

The maximum supply of PGM in the world market is accomplished by South Africa. Following Tables 17.4, 17.5, and 17.6 represents the supply chain of platinum, palladium, and rhodium separately from some regions around the globe.

The data in Tables 17.4, 17.5, and 17.6 clearly specifies that PGMs are immensely being used as a autocatalysts; there is a very high demand. The purpose of these tables is to give an idea that there is a need of PGM recycling and reuse and focus that recycling should be done as much as possible.

As shown in the Sect. 17.1, the current research inculcates the numbers of demand and supply of PGM metals and focuses on the need of recycling of such precious

Table 17.4 Platinum's supply available in units of '000 oz in last successive years [21]

	South Africa	North America	Russia	Others
2019	4565	385	668	956
2018	4467	372	687	959
2017	4450	370	720	953
2016	4347	369	652	153
2015	4571	318	670	149

Table 17.5 Palladium's supply available in units of '000 oz in last successive years [21]

	South Africa	North America	Russia	Others
2019	2744	983	2792	1460
2018	2543	950	2976	1458
2017	2547	960	2452	1409
2016	2571	922	2487	126
2015	2684	864	2434	142

Table 17.6 Rhodium's supply available in units of '000 oz in last successive years [21]

	South Africa	North America	Russia	Others
2019	652	52	73	67
2018	618	43	69	70
2017	611	37	78	70
2016	593	24	80	54
2015	611	23	80	50

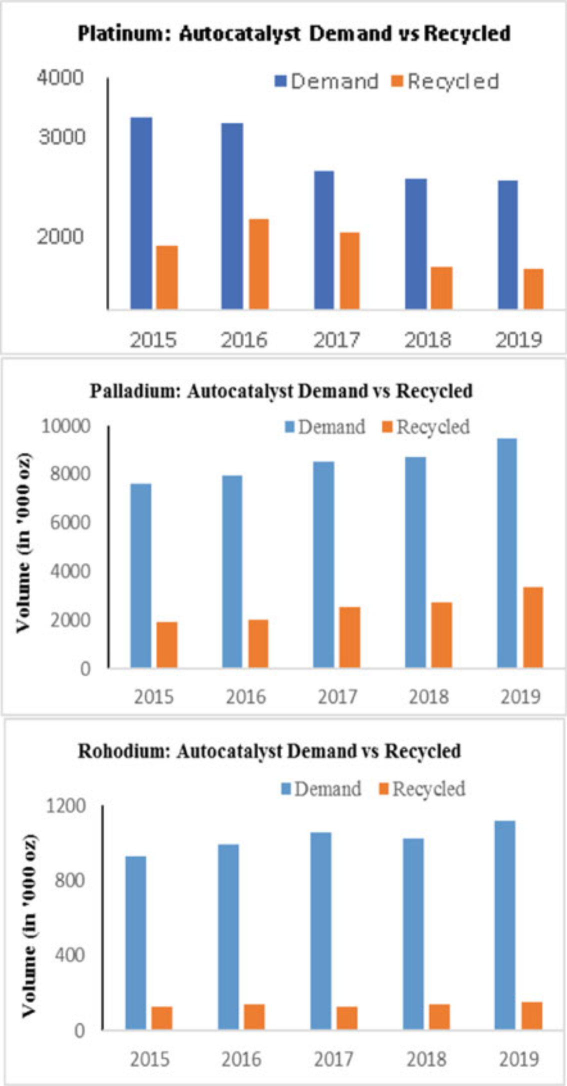
noble metals. There is ample amount of research already available on the topic of PGM recycling and reuse, the current research reviews the developments made in the methods of recycling, reuse, and alternative catalysts tested in place of PGMs. The current study also presents experimental results of catalytic activity of alternative catalysts such as Cu-COK12, Cu- Nb_2O_5, Cu-YZeolite, and Cu-ZSM5 using DeNO$_x$ (Direct decomposition of NO$_x$) technology.

17.2 Current Scenario of the Use and Recycling of PGMs from Catalytic Converters

As discussed in the earlier sections that the demand of PGM are higher than supply, hence the idea of recycling the PGMs would be great. Figure 17.6 shows the trends of demand volume and PGMs recycling volume being performed in recent times.

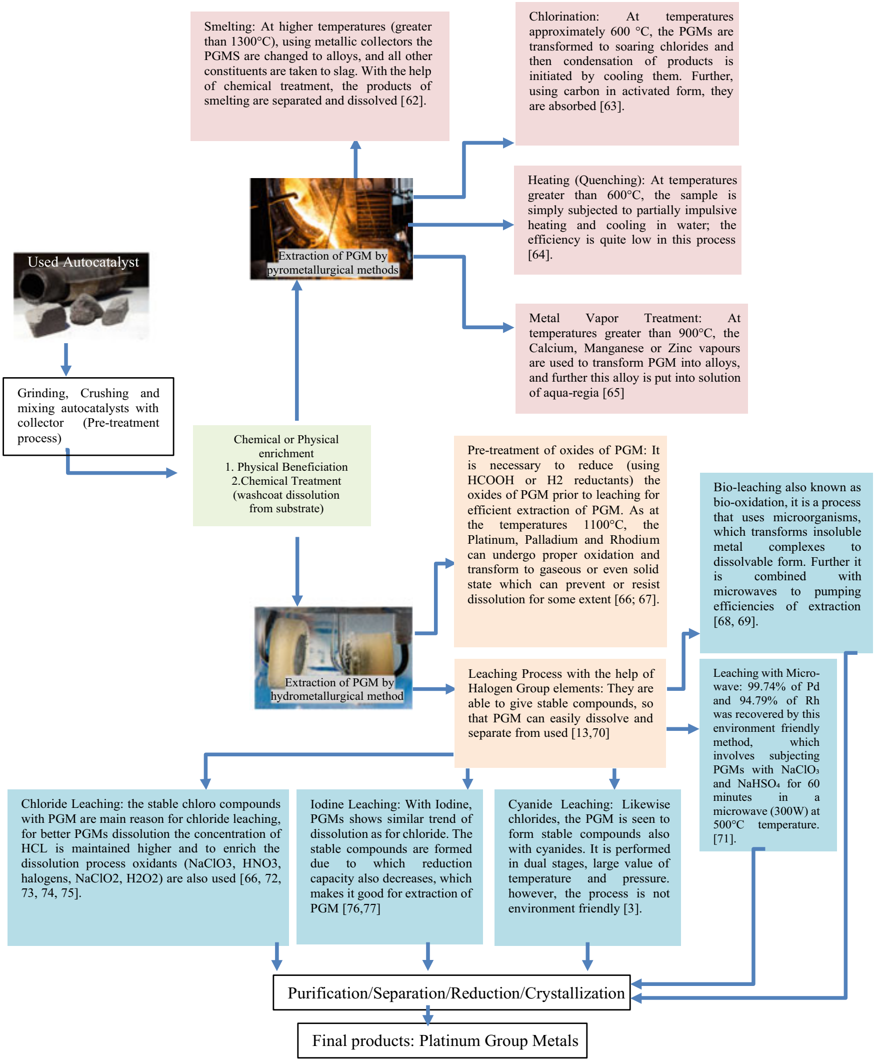
Figure 17.6 shows that the amount of PGMs obtained from the recycling of autocatalysts is very small as compared to their total demand in the autocatalysts industry. This low fraction of the extraction of PGMs from the autocatalysts adds more to its demand and supply gap. This percentage needs to be increased so that the maximum possible share of demand as autocatalysts gets fulfilled by recycling the old autocatalysts from discarded automobiles.

Fig. 17.6 Trends of demand volume and PGMs recycling volume, being performed in recent times [21]



17.3 Methods of PGM Recycling

The recycling of PGMs in catalytic converters has been of particular interest to many researchers [10, 56–61]. It is considered that the recycling of autocatalysts from the catalytic converter takes less effort than to purify or separate them as compared to the ones taken out directly from mineral ores. Additionally, it is also a fact that the content of PGM is higher when recycled from spent autocatalysts as compared to the ones extracted directly from the earth [51]. Figure 17.7 gives a flowchart of the



Grinding, Crushing and mixing autocatalysts with collector (Pre-treatment process)

Chemical or Physical enrichment
1. Physical Beneficiation
2.Chemical Treatment (washcoat dissolution from substrate)

Smelting: At higher temperatures (greater than 1300°C), using metallic collectors the PGMS are changed to alloys, and all other constituents are taken to slag. With the help of chemical treatment, the products of smelting are separated and dissolved [62].

Chlorination: At temperatures approximately 600 °C, the PGMs are transformed to soaring chlorides and then condensation of products is initiated by cooling them. Further, using carbon in activated form, they are absorbed [63].

Heating (Quenching): At temperatures greater than 600°C, the sample is simply subjected to partially impulsive heating and cooling in water; the efficiency is quite low in this process [64].

Metal Vapor Treatment: At temperatures greater than 900°C, the Calcium, Manganese or Zinc vapours are used to transform PGM into alloys, and further this alloy is put into solution of aqua-regia [65]

Pre-treatment of oxides of PGM: It is necessary to reduce (using HCOOH or H2 reductants) the oxides of PGM prior to leaching for efficient extraction of PGM. As at the temperatures 1100°C, the Platinum, Palladium and Rhodium can undergo proper oxidation and transform to gaseous or even solid state which can prevent or resist dissolution for some extent [66; 67].

Leaching Process with the help of Halogen Group elements: They are able to give stable compounds, so that PGM can easily dissolve and separate from used [13,70]

Bio-leaching also known as bio-oxidation, it is a process that uses microorganisms, which transforms insoluble metal complexes to dissolvable form. Further it is combined with microwaves to pumping efficiencies of extraction [68, 69].

Leaching with Micro-wave: 99.74% of Pd and 94.79% of Rh was recovered by this environment friendly method, which involves subjecting PGMs with $NaClO_3$ and $NaHSO_4$ for 60 minutes in a microwave (300W) at 500°C temperature. [71].

Chloride Leaching: the stable chloro compounds with PGM are main reason for chloride leaching, for better PGMs dissolution the concentration of HCL is maintained higher and to enrich the dissolution process oxidants (NaClO3, HNO3, halogens, NaClO2, H2O2) are also used [66, 72, 73, 74, 75].

Iodine Leaching: With Iodine, PGMs shows similar trend of dissolution as for chloride. The stable compounds are formed due to which reduction capacity also decreases, which makes it good for extraction of PGM [76,77]

Cyanide Leaching: Likewise chlorides, the PGM is seen to form stable compounds also with cyanides. It is performed in dual stages, large value of temperature and pressure. however, the process is not environment friendly [3].

Purification/Separation/Reduction/Crystallization

Final products: Platinum Group Metals

Fig. 17.7 Flowchart of the steps involved in common techniques of extraction of Platinum group metals from the catalytic converters

steps involved in common techniques of extraction of platinum group metals from the catalytic converters.

17.3.1 HydroMetallurgy

Hydrometallurgy is the most basic and common metallurgical process of PGM extraction from the autocatalysts. In this process, the catalytic carrier is first immersed into a solution of chlorides, nitrates, aqua regia, etc. Consequently, PGMs get converted into their respective chlorides (MCl6-2). The obtained solution is then concentrated and separated by electrolytic decomposition of the metal chloride complexes.

Dissolving PGMs in common acids is not easy, as they show high chemical inertness. Hence, aqua regia solution (firmly acidic) is availed to dissolve PGMs. The presence of nitric acid helps as a reducing agent as the reducing potentials for the formation of the chloride complexes of the PGMs is quite high. About 90% of the PGMs used in a car's catalytic converter get extracted by this process. However, processing takes considerable time due to slow phenomenon of PGMs dissolution in solution of aqua regia. Also, a lot of liquid waste gets created in this process which may be hazardous due to the presence of strong metals [67].

17.3.2 PyroMetallurgy

It is second most used common way for the extraction of PGMs from the catalytic converters. In this method, the catalyst carrier is first ground to break up its surface. It is then melted with additional metal collectors, forming PGMs alloys and metal collector, together with the slag. Further, the metal alloys are purified to yield pure PGMs, and the slag is removed simultaneously.

For the choice of collector metal, several properties like melting point, mutual solubility, and chemical properties between PGMs and collectors have to be considered thoroughly. Mostly copper, nickel, lead, and iron are considered good collector. This technique has many advantages like a lesser investment, low melting temperature, a simple refining process, and simple operation. However, it has a disadvantage of low extraction of rhodium and also by the formation of lead oxide, as it is a toxic waste added into the environment [13].

17.3.3 Pressure Cyanidation

The use of pressure cyanidation is a potential way of extracting PGMs from the automotive catalytic converters. In this method, the spent catalyst is first pre-treated with pressure alkaline leaching. The metal concentrate so obtained is then once again treated with two stages of pressure cyanide leaching. It is then followed by the zinc cementation process giving out concentrates of the respective precious metals. And ultimately, the PGMs are separated by electrolytic decomposition of the metal concentrates [3]. Although it can be categorized under the hydro-metallurgical process, the pressure cyanidation process is, however, more complex and advanced. Firstly, the selective dissolution of base metals by the acidic leaching process was done with elevated pressure conditions, keeping nearly all the precious metals in residue of iron. However, its results were not very satisfactory, partly due to the uncertainty of extraction of PGM, high reagent consumption, lesser rhodium recoveries, and severe pollution, etc. The organization of the United States Bureau of Mines consequently executed investigations on convalescing the platinum group metals by cyanide leaching at high temperatures. The recoveries reported were not much high and also the cyanide exhaustion was quite high in the process of leaching. Thus, a conclusion was made that new pertinent pre-treatment methods are much needed. Chen et al. [6] suggested a new method of pre-treatment, where followed by the 2 stages of leaching of pressure cyanide, the automotive catalysts are pre-treated with pressure alkaline leaching. This leads to a very high number of recoveries of platinum, palladium, and rhodium [3].

17.3.4 Industries Involved in Recycling

The art of recycling catalytic converters has now become well known and gained the focus of industrialists globally. Some used catalytic converters are shown in Fig. 17.8. The processes discussed above in Sect. 17.3 are employed to extract PGMs from them and use them to make fresh catalytic converters.

Different companies have now begun works to recycle the old, discarded autocatalysts used in automobile vehicles to extract these metals back. Currently, most of the companies that have been involved for production of PGMs are also actively growing a facility for the recycling of catalytic converters to extract back the used PGMs. Some companies are listed in Table 17.7.

Among the above-listed companies, the Umicore Autocatalysts recycling is the most established name in the entire world that works to extract back the PGMs from the used autocatalysts with its plants in Germany, Brazil, the U.S.A., Belgium,

Fig. 17.8 Some used catalytic converters before process of PGM extraction [59]

Table 17.7 List of few PGM recycling companies around the world

Stillwater mining company	USA
Umicore Autocatalysts Recycling	Belgium
Alpha Recycling	USA
Power Metal Recycling	USA
Environmental Solutions (Asia) Pte Ltd	Singapore
Evciler	Turkey
Sufimet spa	Italy
Duesmann & Hensel Recycling	Germany
European Metal Recycling Ltd	England

etc. Moreover, researchers have studied to substitute PGMs with different noble and non-noble metal catalysts as discussed in the next section.

17.4 Alternatives of Platinum Group Metals as Autocatalysts in Catalytic Converters

some potential catalysts, to replicate PGMs in the catalytic converters. Following Table 17.8 shows the work of researchers since many years for the development of reliable and low-cost solution for exhaust gas treatment. Selected PGM alternatives are discussed in this section.

17.5 Alternative Methods/Techniques

17.5.1 Selective Catalytic Reduction (SCR)

The selective catalytic reduction can control the nitrogen oxides emissions, and the technology involves a reducing agent coupled with catalyst which needs to be injected in the exhaust gas flow stream [100]. Anhydrous ammonia, liquid ammonia, and urea can be used as the reagent for the reduction of NO_x. The use of liquid ammonia is preferred over anhydrous ammonia, as it is safer to store and is not toxic [101]. The initially manufactured SCR catalyst system was comprised of TiO_2 anatase containing active components (mostly V_2O_5 & WO_3). However, toxicity of vanadium and need of catalyst activity at elevated temperatures gave an idea to focus on another type of research, for example, the highly active metal zeolites [102].

Nowadays, catalysts are generally metal-based zeolites like iron, copper, chromium, etc. The NO_2 is generated at just the center of metals on these metal exchanged zeolites, whereas the selective catalytic reduction reaction occurs inside zeolite lattice. On these metal-exchanged zeolites, the NO_2 is produced at the

Table 17.8 Studies performed by researchers regarding alternatives for platinum group metals

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
Au-TiO_2	FTIR, BET	Catalyst Used: 1% Au-TiO_2, Gas Used: CO for 30 min at 300 K, Conversion of CO: 50–70%, Time: 3–15 h	For CO oxidation at normal room temperature, Ti-based gold catalysts show good activity. Pretreatment (calcination/high and low temperature reduction) of Au impregnated TiO_2 shows good catalytic activity	[78]
Cu-ZSM5	XRD, BET	Experimental method: direct and continuous decomposition of NO_x. Harda et al., used pulsating heating in presence of water vapor	Conversion of NO is focused in this research, and CuZSM5 catalyst is explained as a potential catalyst for nitrogen oxide decomposition	[79–82]
$K/A^{2+}B_2^{3+}O_4^{2-}$	TGA, XRD	Sample used: Soot Catalyst Mixture, Catalyst Used: K_2CO_3, K_2Mn_2Od, and KO_2, Experimental Method: TGA, Temperature Range = 200–600 C, Gas Used: Balanced oxygen is used at flow rates of 80 and 120 ml/min. Catalyst Amount = Ratio of 1 g soot and 9 g of catalyst is used and TGA was performed, it was observed that for every run the combustion of only 0.5 mg took place	Spinel kind oxides, if doped with alkali metals, they enhances the reactivity of these oxides to some extents. The K_2CO_3, K_2Mn_2O8, and KO_2 catalysts were subjected to the stability tests, and due to potassium sublimation a potassium degradation was observed while undergoing the soot combustion	[83]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
$La_{0.8}Sr_{0.2}$ 'X'O_3	XRD, BET	Sample used: catalysts used involved 'X' = Co, Mn, Fe, Cr, Cu in different concentrations in the catalyst. Experimental Method: passed the NO balance He gas at 15 ml/min, through flow reactor. The catalyst was placed in the reactor, and Gas chromatography machine was used to determine the reactivity of catalysts	It was observed that the catalytic activity was dependent on the concentration and composition of catalysts, oxide ion vacancies, and cation sites. It was concluded that oxides of Co-based pervoksites are potential catalysts for NO abatement	[84]
Co, K/MgO	BET, TPR, FTIR, XRD, XPS	Sample Used: Soot Catalyst Mixture, Catalyst Used: Co, K/MgO, Experimental Method: TPO, Temperature Range = 200–450 C, Gas Used: 6% O_2 in N_2, Catalyst Amount = 7 mg. Potassium Content Used: (1.5, 4.5 and 7.5 wt%)	At the temperature of 400 °C, the 1.5 wt%, 4.5 wt%, 7.5 wt% of K, and 12 wt% of Co were calcined for diesel soot combustion. The catalyst combination calcined at 700 °C, comprising of 7.5 wt% of K, sustain more to show good catalytic activity; the CO conversion into CO_2 was effective using Co, K/MgO at soot burning temperatures	[85]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
MoO_3/support; V_2O_5/support	TPR, CHN analysis	Type of Soot: size of 28 mm particle carbon black; BET for SA: 80 m^2/g; The Carbon, Nitrogen, and Hydrogen analysis found that C = 97.99 wt.%, N = 0.06 wt.%, H = 1.12 wt.%) were present, Gas Used: 10% O_2 + 1000 ppm NO_2 + 100 ppm SO_2 + 7% H_2O in N_2, Flow Rate = 500 ml/min, Temperature Range: 80–750 C, Experiment: Fixed Bed Reactor	TPR analysis was performed on supports like ZrO_2, MCM-41, HZSM-5, Al_2O_3, SiO_2, SnO_2, Cordierite, and Nb_2O_5. The O_2 and NO_2 were used as oxidants. It was observed that higher reactivity was achieved with the help of oxides with high vapor pressures and low values of melting point. The research concluded that among all the catalysts (V_2O_5/support and MoO_3/support) tested, the most reactive were V_2O_5/MCM-41 and MoO_3/SiO_2 catalysts	[86]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
Metal Chlorides (such as CuCl, $PbC1_2$, Pb, OCl, FeOCl, and BiOCl)	TGA	Soot Used: Printex-U soot, Sample Used: 4 milli gram catalyst, 2 milli gram soot and 54 milli gram SiC, Gas Used: 21 vol percent Oxygen balance Nitrogen, Flow rate: 50 ml/min, Soot Conversion: 20–60%, Catalyst Used: CuCl, $PbC1_2$, Pb, OCl, FeOCl and BiOCl, Temperature = 550 K (CuCl), 610 K (PbCl, Pb, OCl) and 645 K (FeOCl, BiOCl)	TGA analysis was performed to see the oxidation of soot (in loose contact). Most active metal oxychlorides were of Bi, Cu, Fe, and Pb. Metal chlorides like CoCl2, $BaCl_2$, NiCl2, and CaCl2 showed less catalytic activity because of high melting point. HgCl2 (or other highly volatile metal chlorides have shown zero or no catalytic activity. Using metal chlorides for oxidation of soot is in question as due to decomposition or evaporation, there is an activity loss and instability is also present	[87]
MnOx-CeO_2	TGA, FTIR, XRD	Soot Used: collected the carbon black from tail pipe of EURO II diesel, Catalyst Used = MnOx-CeO_2, Gas Used = 10 percent Oxygen, 5% H_2O, 1000 ppm NO, balance N_2, Flow Rate: 140 ml/min, Experiment: TPO, TG-FTIR and flow reactor experiment	Observed soot oxidation activity of catalysts was higher for 330–400 °C. Higher activity was observed when content of cerium was higher in the catalysts. At SO_2 trap downstream, these catalysts find their applicability as they are prone to sulfur poisoning	[88]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
K/$CuFe_2O_4$	XRD, XPS, TPR	Soot Used: <5 weight percent of SOF dry soot was used. Experimental Method: TPR, Gas Used: Helium balanced 0.5% NO ± 5% O_2 Catalyst Amount: 5% weight of soot in the catalyst	For the abatement of diesel soot and NO_x, adding K on $CuFe_2O_4$ was found effective, and in the same scenario if platinum, Vanadium, and some other alkali metals, the catalytic activity was not enhanced. Amount of potassium doping was crucial in the catalytic reactivity of $Cu_{1-x}K_xFe_2O_4$	[89]
La-K-Mn-O perovskite-type oxide	TPR, XRD, BET	Catalyst Used: La–K–Mn–O, Experiment: NOx–soot removal reaction, Method: TPR, Catalyst Amount: 5% weight of soot in the catalyst. Gas: Helium balanced 0.5% NO ± 5% O_2. Flow Rate: 20 ml/minute on TCD Gas Chromatograph	XRD analysis of $La_{1-x}K_xMnO_3$, and solubility limit of K was found in range of 0.20–0.25. As a byproduct of processing pervoksites La-K-Mn-O, the $K_2Mn_4O_8$ was found, which is also a potential candidate for diesel soot and NO_x abatement. Analysis concluded that oxides of La-K-Mn-O are favorable for diesel soot and NO_x abatement	[90]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
Cu/K/Mo/Cl	XRD	Catalyst Used: Cu/K/Mo/Cl catalyst (K, Cu, (MOO, 3)) with model soot (Printex-U), Composition: 10.3 weight percent of Cu, 8.3 weight percent of MO and 6 weight percent of K. Experimental Analysis: DRIFT and XRD	In the ball mill, the catalysts in tight contact with soot performed well and highly active within the temperature range of 665–720 K, and for oxidation of soot in loose contact or 'mixture with spatula', this temperature goes high to 790 K. Specifically, for tight contact the oxidation of soot occurs at the 683 K	[91]
CuO-CeO_2	XRD, BET, TPO	Catalyst Used: Mixed oxides such as Cu–Ce–Zr; Cu–Ce; Ce–Zr, and CeO_2. Soot: Printex-U (Degussa), Experimental Method: TPO, Catalyst Amount: 1:10 ratio of soot and catalyst. Experimental Setup: Placed in reactor with 1000 ppm gas of nitrogen oxide and 9.5% of oxygen in nitrogen at a flow rate of 500 cm^3/min	The 'aging (air flow for 20 h' time)' experimental investigation of CuO-CeO_2 at the temperature of 800 °C, the rate of oxidation of diesel soot due to this catalyst in both forms the loose and tight contact, reached maximum at 419 °C and 321 °C respectively. The catalyst CuO-CeO_2 seems good candidate for oxidation of soot and nitrogen oxides removal, as selectivity for production of CO_2 reached to approximately 100%	[92]

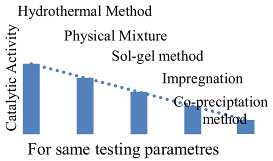
(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
MnO_x-CeO_2-Y_2O_3	XRD, N2 adsorption-desorption, Raman Spectroscopy, H_2-TPR, NO-TPO, X-ray Photoelectron spectroscopy, Soot TPO, BET	The Y doping in the different weight percentages (0, 1, 3, 6, and 10 wt%) was done in MnOx-CeO_2-Y_2O_3. The mixture was kept into dry air flow in observation for 12 h at a temperature of 800 °C. Gas: 800 ppm of Nitrogen oxide with 10% balanced oxygen/nitrogen (500 cm^3 min^{-1}, at a Gas Hourly Space Velocity of 30000 per hour) Experimental Method: TPO, Catalyst Amount: 1:10 mixture of soot and catalyst	The maximum oxidation of soot is observed at weight percentages of 6 and 10%	[93]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
$Ce_{0.5}Fe_{0.3}Zr_{0.2}O_2$	XRD, RAMAN, H2-TPR	Sample Used: Soot and catalyst mixture, Soot used: Printex-U (Degussa), Catalyst used: CeO_2-ZrO_2-Fe_2O_3 mixed oxide catalysts, Experiment method: TPO, Soot Amount: 15 mg, Catalyst Amount: 150 mg, Temperature Range: 25–600 C, Gas Used: 10% O_2/N_2	For combustion of soot, the maximum stability and activity were achieved for aging sample for 10 h at a temperature of 800 °C, which is due to good oxygen concentration vacancy of ferric oxide and its property of having surface reducibility. The prepared catalysts implemented different methods of preparation, and the activity of catalyst was comparatively analyzed as follows: 	[94]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
K/$Ce_{0.65}Zr_{0.35}O_2$/cordierite	BET, XRD, SEM, XPS, LRS	Sample used: Soot Catalyst Mixture, Soot Used: Found from vessel of glass after igniting diesel sample. Catalyst Used: Potassium-promoted $Ce_{0.65}Zr_{0.35}O_2$ monolithic catalysts, Experiment method: TPO, Gas Used: N2, Temperature Range (catalytic combustion of soot by Nitrogen oxide/Oxygen): 25–600 C	Studied the combustion of spatular mixture of catalyst and soot by repetetive TPO runs. After ten runs, due to loss of potassium at high temperatures, authors quoted a deactivation, whereas activation was observed when potassium was not present in the mixture. In the presence of NO/O_2 with K/CeO_2/cordierite (comparatively more active) and K/$Ce_{0.65}Zr_{0.35}O_2$/cordierite, the soot burning hiked. In tight contact the $Ce_{0.65}Zr_{0.35}O_2$ activity was greater as compared to CeO_2	[95]
FSP-Mn_3O_4	XRD, PXRD, SEM, NH_3-TPD, H_2-TPR, NDIR, TPO, TPD	Sample Used: Soot and Catalyst mixture, Catalyst Used: Flame spray pyrolysis is used to originate the catalysts such as Mn_2O_3, Mn_3O_4, and MnO_2 Experiment method: TPO, Temperature Range: 25–750 C, Gas Used: 10 volume percent Oxygen and 90 volume percent Nitrogen	TPO was employed to check the activity of catalyst and soot mixture in loose and tight contact. Among all catalysts samples investigated, FSP-Mn_3O_4 performed best. FSP-Mn_3O_4 was later coated on DPF, the oxidation of soot occurred at the temperature of 350 °C, prooving the catalyst a potential candidate for real-time continuous diesel soot oxidizer	[96]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
Alkali doped Fe_3O_4	XRD, FTIR, TPO	Sample used: 0.006 g soot (type: Degussa Printex80) and 0.050 g catalyst, Catalyst used: Fe_3O_4 (more than 98% Aldrich) with carbonate alkali (alkali metals = Li, Na, k, Cs), Experiment method: TPO, Temperature Range: 25–700 C, Gas used: 5% O_2 in He, Catalyst amount: ratio of 1 g soot to 8 g catalyst	It is observed that controlled alkali doping can increase the catalytic ability of magnetite for the combustion of soot. Li < Na < K < Cs is the sequence in which the alkali promoters increases promotional effects (coherent with the ionic radiis of these promoters)	[97]
K-doped manganese and iron spinels	XRD, ATR-FTIR, RAMAN, TPO	sample used: 0.006 g soot (type: Degussa Printex80) + catalyst, Catalyst used: iron doped K_2SO_4, KOH, CH_3COOK, KNO_3 and K_2CO_3 KOH, K_2CO_3, KNO_3, CH_3COOK, and K_2SO_4 with manganese spinels, Experiment method: TPO, Temperature Range: 25–700 C, Gas used: 5% O_2 in He, Catalyst amount: 1:8 of soot and catalyst	The increase in activity of combustion was observed when KNO_3, KOH, and K_2CO_3 was used. But a decreasing activity was observed for K_2SO_4 (shown as $\Delta T50\% \approx 25$ °C). Additionally, $\Delta T50\% \approx 150$ °C was observed for KNO_3 and $\Delta T50\% \approx 80$ °C for K_2CO_3, and for CH_3COOK and KOH and CH_3COOK, it was $\Delta T50\% \approx 40$ °C. It was also observed that higher the K content, higher is the potential for soot combustion	[98]

(continued)

Table 17.8 (continued)

Catalysts used	Characterizations performed	Experimental conditions	Remarks/findings	References
Nanostructured $Ce_{0.7}Mn_{0.3}O_2-\delta$ (CM) and $Ce_{0.7}Fe_{0.3}O_2-\delta$ (CF) solid solutions	Raman, XRD, TEM, ICP-OES, TGA-DTA, SEM-EDX, FT-IR, H_2-TPR, UV-vis DRS, HRTEM, BET, XPS	Sample used: Soot Catalyst Mixture, Catalyst Used: $Ce_{0.7}Mn_{0.3}O_{2-1}$(CM) and $Ce_{0.7}Fe_{0.3}O_{2-1}$(CF), Experimental Method: TG-DTA, Temperature Range = 573–1073 K, Gas Used: nitrogen atmosphere(50 ml min^{-1}), Catalyst amount: 15 mg	Soot oxidation capability of $Ce_{0.7}Mn_{0.3}O_2$ (CM) and $Ce_{0.7}Fe_{0.3}O_2$ (CF) was compared with CeO_2-ZrO_2 (CZ)'s catalytic activity. It was observed that Fe and Mn in ceria solution resulted in increased soot oxidation activity. As compared to ceria in pure form the $Ce_{0.7}Mn_{0.3}O_2-\delta$ (CM) and $Ce_{0.7}Fe_{0.3}O_2-\delta$ (CF) found more thermally stable. The research concluded CM as best catalyst among tested ones	[99]

metal centers, while the SCR reaction itself takes place within the zeolite framework. Because the NO_2 is destroyed as soon as it is produced in the SCR method, it doesn't appear as gas-phase NO_2 [103].

The main reactions for this process are:

$$2NO + 2NH_3 + {}^{1}/_{2}O_2 \rightarrow 2N_2 + 3H_2O$$

$$NO_2 + NO + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

17.5.2 NO_x Traps

NO_x traps or absorbers are applied to reduce the NO_x emissions from the automotive exhausts. Various metal-based Zeolites were employed as adsorbents in this study, and their unique characteristics in a variety of applications such as ion exchange, adsorbents, and catalysts have piqued the interest of automotive industry makers [104, 105].

Das et al. [106] developed iron-exchanged X-zeolite and investigated it in real-time exhaust of SI engine. For NO_x, the conversion efficiency of 55.8% was achieved, and the conversion of 57.4% was reported for CO. A numerical mathematical equation model for assessing the actions of a catalytic converter incorporating the Fe-X catalyst was also created [107].

17.5.3 $DeNO_x$ (Direct Decomposition of NO_x)

The direct decomposition of NO_x has been in research since a long time due to its easy applicability to break NO into nitrogen and oxygen with the help of catalysts. The direct decomposition of NO_x method do not employ a reducing agent and deals in temperature less than 1000 °C while decomposing the NO, hence known to me thermodynamically favorable method [108]. The method includes conversion of NO to Nitrogen and Oxygen (as shown in reaction below) at the catalyst's surface, with N desorbing as N_2 and O remaining strongly attached at surface of catalyst.

$$2NO \rightarrow N_2 + O_2$$

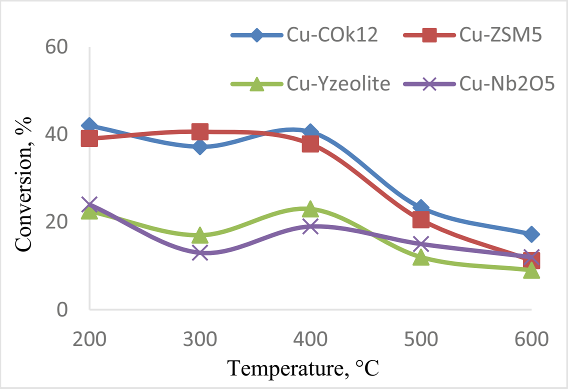
The dissolution and absorbance of NO occur efficiently on surface of transition metal. The direct decomposition of NOx has widely been studies for PGM metals. There's also an article there in 1920s that stated that at a temperature of approximately 800 °C, $DeNO_x$ progressed on the surface of platinum metal [109], and though research that time in this area slowed due to lack in activity of catalyst and necessary catalysts just weren't readily available to recompense platinum metal. Also in early 1990s, the studies shown that Cu-ZSM-5, Ag/Co_3O_4, $Pd/MgAl_2O_4$ and perovskite-type oxides shown good activity for decomposition of nitrogen oxides, so researchers focused on the rare earth metals and the compounds of the oxides of pyrochlore [110–115].

17.6 Future Scope and DeNO$_x$ Results Using Non-noble Metal Catalysts

The use of emission control techniques is however depends on particular characteristics associated with different engines. Certain modifications in the discussed techniques might improve the control of the engine exhaust emissions. For example, for lean-burn Spark Ignition (SI) and Compression Ignition (CI) engines, the three-way catalyst system is not effective for reducing NO_x emission. This is because the reducing catalyst is used up in reducing the high level of O_2 in diesel exhaust gases. To overcome this problem, other techniques such as Selective Catalytic Reduction (SCR), in which ammonia is used as a reductant and metal oxides as an oxidizer [101], are applied. Also, NO_x traps or NO_x adsorbers are applied, in which different metal-based zeolites are used as an adsorbent [104].

Authors have conducted a study for direct decomposition of NOx using alternative catalyst to PGMs. The experimental tests were based on the development of non-noble metal-based catalysts in order to provide a low-cost solution. The catalysts Cu-COK12, Cu- Nb_2O_5, Cu-YZeolite, and Cu-ZSM5 were prepared by the standard wet impregnation method, the supports ZSM-5, Y-Zeolite and Nb_2O_5 were obtained from Zeolyst International, the Netherlands, and COK12 support was prepared in the laboratory of CSIR-Indian Institute of Petroleum, Dehradun, India. Furthermore, the reactivity tests of prepared catalysts toward NO decomposition were performed with the help of a quartz glass fixed bed reactor setup. This experimental setup at the laboratory of EATA, AFLAD, and CSIR-Indian Institute of Petroleum consists of quartz reactor, thermocouples, mass flow controllers (MFCs), furnace, gas shut ON/OFF valves, gas regulators, and temperature control units. Helium and nitrogen gases were simultaneously used as purging agents to remove the impurities in the gas lines and fixed bed reactor. The prepared catalyst (of amount 250 mg) was placed on the quartz wool (fixed bed) and NO gas was made to pass through the fixed bed reactor; this fixed bed reactor was placed in a furnace to maintain the temperature of the reaction from 200 to 600 °C. For this case, the flow rate of NO was maintained (using mass flow controllers) at 100 ml/min. Similarly, for each catalysts, the tests were performed at a NO flow rate of 100 ml/min, and temperature of furnace was varied from 200 to 600 °C. The reacted NO gas coming out of quartz fixed bed reactor was then taken into DANI Master Gas Chromatography machine, equipped with the thermal conductivity detectors, and the output was seen in the form of voltage signals with the help of Clarity software attached with the DANI Master GC.

Fig. 17.9 Percentage conversion of NO by catalysts at 100 ml/min flow rate



The interpreted results are hence plotted for the percentage conversion versus the temperature as shown in Figure 17.9.

Figure 17.9 shows the catalytic activity of Cu-COK12, Cu- Nb_2O_5, Cu-YZeolite, and Cu-ZSM5 at the NO flow rate of 100 ml/min. The reactivity of Cu-COK12 and Cu-ZSM5 remains approximately 40% at lower temperatures and falls down with subsequently higher temperatures; but, the reactivity of Cu-YZeolite and Cu-Nb_2O_5 remains low. Moreover, in order to enhance the catalytic activity and to accomplish the aim to get comparable reactivity with platinum group metals, the further investigations are planned to vary the flow rates of NO and the non-noble metal catalyst weight. In the future, it is planned to calculate the dependence of NO decomposition activity of catalysts in terms of space velocities. This study can be extended for developing the diesel oxidation catalysts for the abatement of HC, CO, and particulate matter emissions.

17.7 Conclusions

Platinum, palladium, and rhodium, have powerful catalytic abilities. Additionally, platinum metals are naturally beautiful, which elevates their value as jewelery in many cultures. The automotive sector is anticipated to have a substantial impact on future PGM demand, while important Asian nations like China are anticipated to have significant rise in jewelery market for platinum. Along with the expansion of the world economy, there is also anticipated growth in the demand for platinum metals for industrial uses. These metals, which are utilized in electronic components and automotive catalytic converters, are increasingly being recycled because of recent increases in PGM costs. PGM recycling often begins with scrap refiners, which gather scrap materials such used catalytic converters and electronic components that contain PGMs to recover the precious metals. To further improve the quality of the recycled material, other refiners often purchase the recovered PGM material.

Technological developments that rely on the catalytic capabilities of PGMs, such as fuel cells, become more extensively employed across the globe, the market for recycled platinum metals is anticipated to rise over the upcoming years. The study highlights the following conclusions:

- The high demands of the PGMs emphasize the need to recycle the catalytic converters for the chemical extraction of these precious metals used as autocatalysts.
- The gap between total gross supply and total gross demand of PGMs is around 30%; this is what it makes them precious.
- Only about 32% of the demand for PGMs as an autocatalysts gets fulfilled by recycling from used catalytic converters. This percentage should be increased with a target to achieve above 90% recycling.
- The use of PGMs in catalytic converters can be reduced by replacing them with other materials and techniques like nickel oxide, titanium dioxide, CeO_2 composite catalysts, Cu/Cr Oxide Catalysts, zeolites, selective catalytic reduction, NOx traps, etc.
- A direct decomposition of engine exhaust is possible using alternative catalyst to PGMs with comparable reactivity with platinum group metals.
- The current research showed an experimental investigation on NO decomposition activity using Cu-based non-noble metal-based catalysts through $DeNO_x$ technology. The maximum reactivity achieved was for Cu-COK12 and Cu-ZSM5, it remains approximately 40% at lower temperatures.

In the future, the plan will be to find ways to increase the reactivity of the catalysts, so that we can add to the research of alternative catalysis. Using non-noble metal catalysts instead of PGMs would be a great breakthrough in this area of research.

Acknowledgements The work was supervised by Dr. Atul Dhar, School of Engineering, Indian Institute of Technology Mandi, H.P., India. The research was performed with the collaboration of CSIR-Indian Institute of Petroleum, Dehradun, U.K., India, Indian Institute of Technology Mandi, H.P., India, and Centre of Earth Observation Science, School of Applied Sciences, University of Brighton, Brighton, BN24GJ, United Kingdom.

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

Credit Author Statement M.K. Shukla: Conceptualization, Methodology, Visualization, Writing- Original draft preparation; **Balendra V.S. Chauhan**: Investigation, Draft preparation, Writing and Editing; **Dr. Thallada Bhaskar**: Data curation, Visualization and Supervision; **Dr. Atul Dhar**: Validation, Supervision, Reviewing and Editing; **Dr. Ajitanshu Vedratnam**: Visualization, Draft preparation, Editing.

Abbreviations

ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
BET	Brunauer–Emmett–Teller
CHN	Carbon Hydrogen Nitrogen analysis
CI	Compression ignition
CO	Carbon monoxide
$DeNO_x$	Direct decomposition of NOx
DPF	Diesel particulate filter
FSP	Flame spray pyrolysis
FTIR	Fourier Transform Infrared Spectroscopy
H2-TPR	Hydrogen-temperature programmed reduction
HC	Hydrocarbons
HRTEM	High-Resolution Transmission Electron Microscopy
ICP-OES	Inductively coupled plasma—optical emission spectrometry
LRS	Laser Raman spectroscopy
MFC	Mass flow controller
N_2O	Nitrous oxide
NDIR	Nondispersive infrared sensor
NH_3-TPD	Ammonia-Temperature programmed desorption
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO-TPO	Nitrogen oxide- Temperature programmed oxidation
NOx	Nitrogen oxide gases
PGM	Platinum group metals
PM	Particulate matter
PXRD	Powder X-ray diffraction
ROW	Rest of World
SA	Surface Area
SCR	Selective catalytic reduction
SEM	Scanning electron microscope
SEM-EDX	Energy-dispersive X-ray spectroscopy
SI	Spark ignition
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TGA-DTA	Thermal gravimetric analysis -Differential thermal analysis
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
UHC	Unburnt hydrocarbons
USA	United States of America
UV vis DRS	UV–vis diffuse reflectance spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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