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Noble metal catalysts for monolithic converters

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ABSTRACT

Catalytic combustion of pollutants released from the vehicular exhaust is one of the best methods to decrease their concentration before their release to the atmosphere. The catalyst help to bring about the reduction of these pollutants at a much lower temperature as compared to homogenous combustion reactions. In this paper a review about the noble metal catalysts used for gasoline vehicles is carried out. These noble metal catalysts although expensive and limited in supply are the best option for reduction of the pollutants hydrocarbons, carbon monoxide and oxides of nitrogen released from the vehicular exhaust.

Key words: Catalyst, noble metals, activity, converter, deactivation.

INTRODUCTION

The performance of the catalytic converter is highly dependent upon the types of catalyst or combination of catalysts used in the assembly. The rate of chemical reactions is affected by the presence of catalysts. Catalysts act as agents that reduce the activation energy of the reaction of interest, generally without being transformed throughout the reactive chain [1, 2]. Noble metals and metal oxide catalysts are mostly used for carrying out the reactions in the converters. The earlier converters from their invention in 1960’s to 1970’s employed both metal oxides and noble metals for catalytic conversion.

Much of the earlier research and development on automotive catalysts, prior to commercialization in the 1975 time frame, was devoted to non-noble metal catalysts also called the base metal catalysts, largely due to concerns over the cost and availability of noble metals.

However, it became apparent that the base metals catalysts comprising of oxides of Ni, Cu, Co, Mn, and Cu/Cr etc lacked the intrinsic reactivity, durability, and poison resistance required for automotive applications [3].

The major disadvantage of the base metals was that they were found to be very sensitive to sulphur poisoning [4, 5]. They were sensitive to thermal degradation at high temperatures. Their irreversible interaction with aluminia (support material) resulted in their permanent deactivation. Their conversion activity was found to be much less as compared to noble metals [5] particularly at low temperatures. They are found to be more sensitive to flow variations and require a much larger converter space volume as compared to the noble metals.

Noble Metals

The noble metals are also referred to as the precious metals or platinum group metals. They are favoured as the active catalytic materials in automobiles [4] due to their excellent thermal stability, their lower tendency to react with support materials (compared to the base metals), and their ability to process gas streams containing upwards of 1000 ppm (by weight) sulfur without being transformed to bulk sulfates [3]. The noble metals showed highest catalytic activity and thus initiated catalytic oxidation of fuels at lowest reaction temperatures [6]. These reactions take place on the surface of tiny metal cryatals in the catalyst coating [7].

Platinum and palladium are preferred over other noble metals for oxidation reactions. As compared to them all other noble metals exhibited higher volatility [5] due to high temperatures and high velocity of the gases encountered during exhaust gas treatment, which was undesirable [6].

The reduction of NO over platinum, a major active phase of three-way catalysts was difficult [8] due to low dissociation abilities of most platinum crystal planes. In fact this was one of the major reasons for introduction of rhodium in catalyst formulations [9].

The factors that chiefly lead to their increased use are that only the precious metals had the required activity needed for the removal of the pollutants in the very short residence times dictated by the large volumetric flows of the exhaust in relation to the size of catalyst which could be accommodated in the available space [10]. The precious metals were the only catalytic materials with the requisite resistance to poisoning by residual amounts of sulphur oxides in the exhaust. The precious metals were less prone but not entirely immune to deactivation by high-temperature interaction with the insulator oxides of Al, Ce, Zr, etc., which constitute the so-called high surface area "washcoat" on which the active catalytic components are dispersed [10]. In addition to these factors choice of the noble metal loading in the converter is also dependent on the noble metals cost, easy availability, variable operating temperature etc.

Initially in USA in the years 1975-1980, platinum (Pt) and palladium (Pd) were used as oxidation catalysts in the ratio 5 (Pt) : 2 (Pd) at a typical loading of 50-70 g/ft^3. Rhodium (Rh) was introduced with the advent of the three-way catalysts, having considerably better activity than Pt or Pd for the catalytic reduction of the oxides of nitrogen [11]. When sufficient Rh is present the participation of Pt in NO removal is minimum [12]. The amount of precious metal loadings are 30-100 g/ ft^3 for Pt, 0-120 g/ ft^3 for Pd and 5-10 g/ ft^{3}for Rh [12].

The commercially used three way catalytic converters formulations contain Pt/Rh, Pt/Pd/Rh (trimetal), Pd-only, and Pd/Rh noble metal combinations [10] as shown in Table 1. It is not uncommon to find two formulations in use on the same vehicle like Pd-only as a light-off catalyst and Pd/Rh as downstream underbody catalyst.

Table 1. Metal contents of different catalyst loading [13]

Catalyst Type	**Loading**		**Ratio**	**Individual Metal Loadings (g/l)**		
	g/l	**g/ft^3**		**Pt**	**Pd**	**Rh**
Pt : Rh	1.41	40	5 : 1	1.17	-	0.24
Pt : Pd : Rh	3.35	95	1 : 14 : 1	0.21	2.93	0.21
Pd	4.94	100	-	-	4.94	-
Pd : Rh	3.53	100	14 : 1	-	3.29	0.24

The fuel quality still plays an important role in the choice of catalyst formulation for a particular market due to presence of residual Pb levels, sulphur concentration. As all of the formulations have improved over time, decisions regarding the choice of the noble metal and loading are becoming more and more based on cost factors. In order to reduce pollution the thickness of the washcoat containing the noble metals has to be increased. But this results in increase of sulphur emissions and also the cost of the converter.

The catalyst structural design consists of making multiple layers of catalysts with platinum and rhodium segregated in different layers. Fig. 1 shows schematic placing of noble metals in the washcoat. It represents the corner of a monolith catalyst cell in which the lower layer of catalytic materials contains platinum and alumina, and the upper layer contains rhodium on cerium dioxide.
Properties of some commonly used noble metals are listed below:

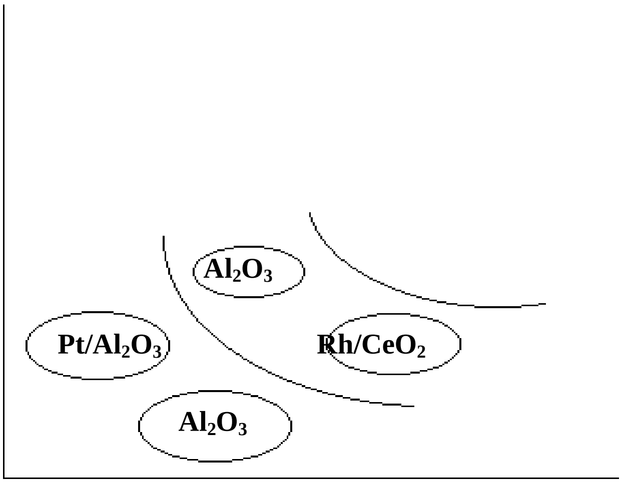

Fig. 1 Schematic placement of noble metals in the washcoat

Platinum

Platinum was one of the earliest catalysts to be used to bring about most effective oxidation of carbon monoxide (CO) and hydrocarbons (HCs) during stoichiometric and lean conditions (more oxygen).

The high activity of this metal and of its other group-VIII metals is mainly due to their partially unfilled d-electron bands, which have bond energy levels that are suitable for breaking bonds of adsorbed molecules. Pt increases the oxygen uptake rate in ceria (it does not increase oxygen storage appreciably) and promotes water gas shift reactions [14].

The limitations of Pt include its tendency to get strongly poisoned by sulphur [12], poor high temperature stability and therefore it tends to age badly [14]. Also its scarcity and high price do not make it economically feasible for its large-scale use in catalytic converters and therefore the possibility of other materials replacing it have to be looked into.

RHODIUM

Metallic rhodium has proven to be one of the best catalysts for the conversion of NO_x to molecular nitrogen, a critical step in pollution control processes [2, 8, 15, 16]. It offers better NO_x reduction in presence of traces of O_2 or SO_2 than Pt and Pd. It even showed some NO reduction activity when air fuel ratio is slightly lean of stoichiometric [12].

As compared to Pt, Rh is much less inhibited by CO but Rh cannot be used alone to convert all three components effectively. It is also is less prone to poisoning by sulphur compounds and also produces less NH_3 [12] but is severely poisoned by lead compounds. Rhodium is good at promoting the water gas shift reactions and shows resistance to sintering [14].

PALLADIUM

Within the family of precious metals palladium is significantly less expensive and more easily available than either Pt or Rh owing to sources outside South Africa, such as Russia, Canada, and US. Its commercial use was thwarted by technical limitations, namely its increased sensitivity to poisoning by lead and sulphur, being much more compared to that of Pt and Rh [12, 14]. Sulphur decreases its ability to convert CO and HC in the net reducing exhaust gas conditions [12], thereby narrowing the air fuel ratio window. The other limitations include the decomposition of palladium oxide to metal if the workable temperature exceeded 800^0C as shown by equation (1) [17, 18]. In order to increase its workable temperature limit some suitable promoter needs to be add at the time of the washcoat formation [18]. In addition to these factor, the use of Pd in three way emission control catalysts was limited to applications where targets for conversion of CO, HCs and NO_x were lower than 90% [12].

$$2\,PdO \rightarrow O_2 + 2\,Pd \qquad (1)$$

By the late 1980s, residual lead levels in US unleaded gasoline had dropped to levels at which Pd could be implemented as a substitute for Pt. Also the reduction of fuel sulphur to levels below 50 ppm in California reformulated fuels was another important factor in opening the door to widespread use of Pd-only catalysts [12]. While increased use of Pd as a substitute for Pt took some of the pressure off of Pt. It was felt that higher loadings of Pd deployed in ways different than before could also be used as an alternative to Rh. At one point, Allied Signal researchers claimed equivalence between a Pd-only catalyst at 56.7 g/ft^3 loading and a 5:1 Pt/Rh catalyst at 20 g/ft^3 [10, 19].

Palladium was found to favor CO-O_2 reaction more than CO-NO reaction as opposed to rhodium [12]. Depositing Pd directly on the oxygen storage capacity component enhances the oxygen exchange kinetics and capacity and helps to promote CO oxidation and water gas shift reactions. Separating the Pd from the CeO_2 results in better NO_x reduction and HC oxidation.

New ways of promoting Pd were also developed, mostly involving rare earth oxides such as lanthana and ceria [20] which enhanced NO_x reduction and imparted greater tolerance towards Pd deactivation by SO_x. In contrast to Pt (and Rh at levels normally employed), Pd itself contributes to oxygen storage [18], by its ability to undergo a redox cycle under exhaust conditions. This source of oxygen storage persists even under severe aging conditions in which the oxygen storage due to rare earth oxides is largely lost. Palladium is found to be more effective as compared to Pt for reduction of methane emissions.

In the year 1989 Ford introduced Pd/Rh catalysts in some of its models in California, replacing the long-standing use of Pt/Rh in three-way catalysis (TWC) formulations. The use of Pd/Rh catalyst technology quickly spread within US. Addition of small amounts of palladium to the rhodium catalyst (Pd:Rh ratio 1:1) had no effect on catalytic activity whereas addition of large amount (Pd:Rh ratio 14:1) decreased CO and especially NO_x activity under rich air-fuel conditions [13]. The Pd/Rh catalyst used needed improvement in techniques for segregating Pd and Rh into separate washcoat layers [21, 22] so as to prevent the deleterious formation of bimetallic Pd-Rh particles which would otherwise cause undesirable deactivation of the catalyst. Introduction of Pd/Rh catalysts in Europe and other markets has been much slower due to a much more gradual process of eliminating the sale of leaded fuels.

Environmental awareness in the late 1980s in US led to the Clean Air Act of 1990 and a corresponding enactment of stricter emission regulations in Europe. Pd was found to produce faster light-off under net oxidising conditions, this could further lead to significant reduction in emissions during cold start. As Pd catalysts are well known to be thermally durable [23], it could be positioned close to the exhaust manifold whereas Rh containing converter could be placed at a downstream location to protect it from high temperature thermal deterioration [24]. This modified arrangement in washcoat along with closed-coupled converter could help a lot in achieving LEV (low emission vehicle) standards.

However with improvement in fuel quality (i.e., reduced levels of lead, reformulated fuel), better engine control of the air to fuel perturbations and improved catalyst formulations it was found that palladium along with certain base metal oxides like ceria and lanthana, can be used to meet tighter future emission regulations during start-up [9, 10, 25] and at higher operating temperatures as high as 1000^{o}C [12].

Structural designs were used in the early 1990’s in palladium-only catalysts to overcome the limitations of using a single catalytic metal. Fig.2 shows a schematic representation of such a catalyst where the lower layer contains palladium on cerium dioxide, and the upper layer contains palladium on alumina By use of these structural design techniques a better performance of the palladium catalyst under cold start conditions by lowering the catalyst light off temperature was obtained [9]. Fig.3 show the improvements in light-off temperature and the higher conversions obtained when the Pd catalyst is heated.

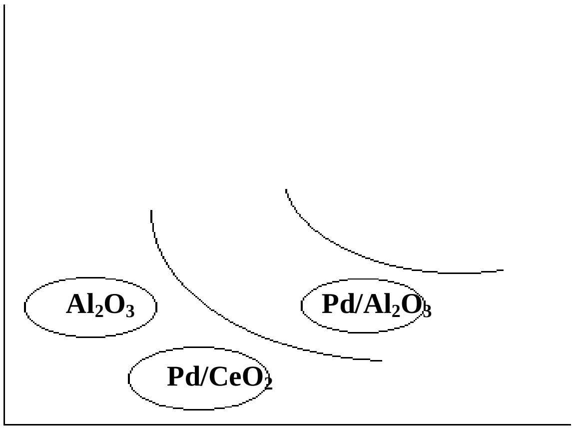

Fig.2 Schematic representation of palladium catalyst when used alone

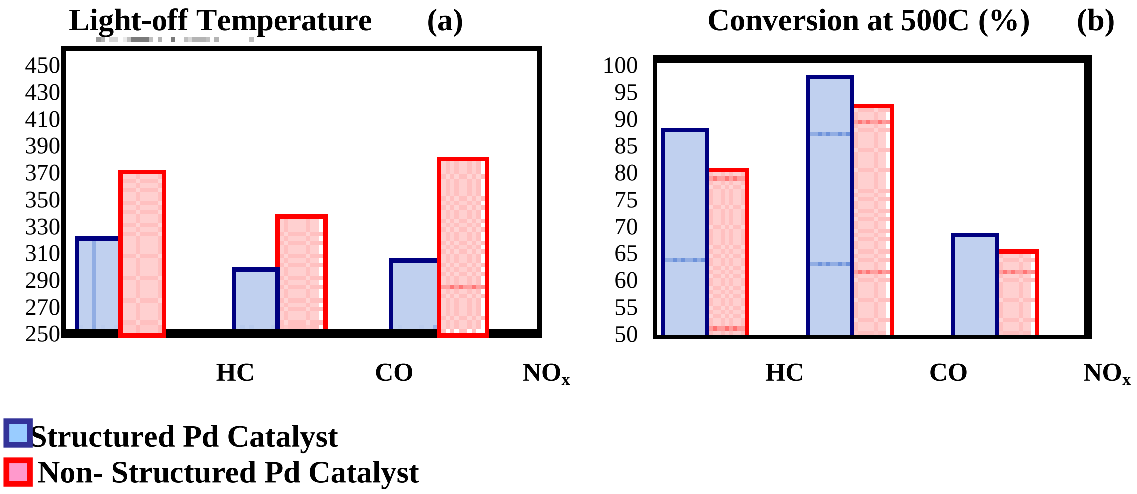

Fig.3 (a) Improvements in light-off temperature and (b) the higher conversions obtained when the palladium catalyst is heated [9]

The use of Pd catalysts at high metal loadings became very common in the mid to late 1990's causing a large escalation in palladium price, peaking at the end of 2000. This resulted in a significant increase in price of the catalytic converter. This was obviously undesirable to the car manufacturer and to the vehicle buying public. Significant pressures were placed on reducing the Pd use in catalytic converters to achieve cost-effective performance by substituting part of the Pd with low levels of Pt and Rh [9].

IRIDIUM

Iridium exhibits ability to catalyze NO reduction under net oxidising conditions [2], but due to its lower availability than Rh and its tendency to form volatile oxides in exhaust environment, it was not used as automobile catalyst [12].

RUTHENIUM AND NICKEL

A number of studies were carried out at Ford and elsewhere during the early to mid-1970s exploring the effectiveness of stabilizing ruthenium (Ru) against volatilization by deploying it in the form of various pure ruthenate compounds ($MRuO_3$, where M=Ba, Sr, La) and also substituted ruthenates such as $LaNi_xRu_{1-x}O_3$ and $BaMn_xRu_{1-x}O_3$. Although impressive gains in stability were realized, they came at the expense of slightly reduced activity for NO reduction, and more importantly, significantly increased NH_3 selectivity. Thus, stabilizing Ru undid the key reason for considering it in the first place, and a Ru-based NO_x reduction catalyst never made it to production [3].

COPPER /ZEOLITE

It consists of copper impregnated zeolite showing reasonable lean NO_x activity [26]. Lean NO_x conversion as high as 45% could be attained using Cu/ZSM-5 catalyst to treat exhaust of a lean burn gasoline engine. The HCs are used to bring about conversion of NO_x and operates best in temperature range 400-500^oC as the conversion decreases on further increase of temperature [27]. The serious disadvantage of this catalyst is its vulnerability to deactivation by sulphur oxide poisoning [21].

DEACTIVATION OF CATALYST

Variation in the noble metal loading along the converter length is found to strongly influence the solid temperature profiles during converter warm-up [28, 29, 30]. Higher metal loading (with loading six times that of base loading) in the front region (20 to 30 mm of front face) improves conversion characteristics and has the same warming-up conversion performance as that of uniform high loading throughout [29, 30] stated that axially non-uniform catalyst distribution is favoured as it can induce favorable interaction among mass and heat transfer reaction.

Aging decreases the converter catalyst activity with time. It is caused due to conditions like high temperatures or poisoning [1, 31] encountered during working operations. It is difficult to determine the degree to which each process contributes to the loss of activity. A rate expression accounting for noble metal sintering was proposed [31]. For aged catalysts front and center of the catalyst show lower activity due to poisoning whereas the entire central channels of the converter is more prone to thermal deactivation as compared to the pheripheral channels [1, 32].

Oxidizing atmosphere or even switching between oxidizing and reducing atmospheres also accelerates aging process [33]. There are many materials in exhaust gases that can slowly poison the catalyst, by reacting with active material or by physically blocking it. The engine oil, fuel and air contain a number of inorganic substances that accumulate on the catalyst and thus reach considerable amounts after years of driving and cause reduction in activity of catalytic converters. It was observed that the fresh catalyst is less sensitive to different operating conditions as compared the aged one.

The effect of sulphur poisoning in a converter is dependent on the precious metal loading, the oxidation state and catalyst preparation procedure. Base metal oxide catalysts are inhibited by sulphur to such a great extent that they cannot alone be used in automobile catalyst applications. The order of sensitivity of noble metals to sulphur poisoning [12, 14] is:

$$Pd > Pt > Rh \qquad (2)$$

Platinum and rhodium are found to rapidly recover from lost activity due to sulphur poisoning on removal of sulphur from feed whereas palladium does not recover at all. The oil refining industry has not actively focussed on the removal of sulphur from fuel, despite moderate cost of processing [33]. Presence of nickel in the washcoat can some what reduce the sulphur poisoning problem, as it is capable of suppressing H_2S formation [10, 12]. Due to these adverse effects of sulphur there is a need for its removal by oil industry.

Lead is used in petrol as an anti-knock agent or octane booster in the form of tetraethyl lead (TEL) and tetramethyl lead (TML). Such fuels require a halide scavenger to remove lead which would otherwise accumulate in the combustion chamber or spark plugs or on the valve surfaces. Both lead oxide and halide forms get attracted to precious metal sites. The deposition of lead is a complex process. It occurs predominantly on the outer surface of the washcoat near the front of the converter, but may also penetrate the washcoat, more extensively at all positions. Lead poisoned catalyst showed a considerable decrease in the selectivity of nitric oxide reduction [34]. Phosphorous and zinc are typical components in lubricating-oil additive (antiwear compound such as zinc dialkyldithophosphate (ZDP) etc [35] that cause most severe damage of catalyst [33, 36]. Zinc deposition is observed in the washcoat layer of the catalyst whereas phosphorus existed on the surface of the washcoat [34].

Fuel doped with tributyl phosphate (TBP) was found to result in lower HC activity [35]. Deposition of phosphorus usually follows a shell progressive model with blockage of micropores passages leading to noble metal sites [34]. Eventually total coverage due to formation of phosphorus containing glass like deposits and due to reactions with support obstructs access to active sites in the catalyst [24, 35, 37] leads to reduction in performance of the converter.

Zinc contributes to loss of catalytic activity in the converter at low temperatures by formation of glazes [4, 35]. Zinc contamination is a major cause of loss of area, and therefore of activity, especially in the front of the converter. The oxygen storage capacity was not strongly affected by deactivation caused by phosphorus and zinc [38]. Phosphorus and zinc poisoning may get affected and even inhibited by other additives in engine oils, such as calcium, magnesium sulfonates [24, 35].

High operating temperatures cause not only a loss of support surface area and support phase transformation [6], but also sintering of noble metals and loss of rhodium function [24]. Exposures to high temperatures results in transformation of a large number of relatively small supported noble metal particles into smaller number of much larger particles. This results in a net effect of reduction in overall noble metal surface area and hence less number of active sites. Noble metal sintering becomes appreciable over 600^0C and above 1000^0C the support material starts to collapse [33]. This causes blocking and embedding of active material in the converter assembly. Some oxygen storage capacity is lost due to ceria forming large crystals with decreased surface area. As a result, the contact area between the metals and ceria, important to their synergistic reduction [39], is decreased.

The stability against deactivation can be improved by proper choice of catalyst. Zirconia mixed with ceria improves the thermal stability of the converter. Also alloy formation between different metals can be restricted by formulation of active materials in separate washcoat layers. The surface loss of cerium at high temperature in oxygen-rich atmospheres can be retarded by use of La, Nd or Y as stabalizers [12].

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