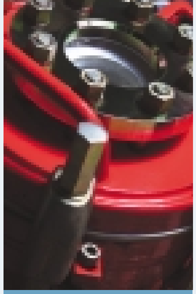


Autocatalyst development and the use of pgm

Significant changes in both the proportions of platinum, palladium and rhodium used in gasoline vehicle autocatalysts and in pgm loadings have occurred since the introduction of catalytic converters in the mid-1970s. This article dicusses the key influences on autocatalyst design and examines the process of catalyst development in the context of pgm use.

Emissions regulations and the pgm mix

The varying pattern of use of platinum, palladium and rhodium on autocatalysts over time has been intimately linked to the introduction and evolution of emissions regulations. Differences in these standards and how they are applied from country to country are instrumental in influencing pgm autocatalyst use.

Several other factors are also important, including:

- Fuel quality and the level of fuel impurities, which can reduce the effectiveness of autocatalysts.
- Wide variations in the types of vehicles and engine sizes produced (e.g. contrast the popularity of gasoline powered SUVs in the USA with diesel engined cars in Europe).
- Developments in engine design and electronic monitoring and control systems.
- Auto makers' strategies regarding pgm purchasing and use.

Catalytic converters were first fitted to cars in the USA and Japan in the mid-1970s in response to new emission standards, such as the US Clean Air Act Amendment of 1970. The first autocatalysts were oxidation catalysts, which convert carbon monoxide (CO) and hydrocarbons (HC) to carbon dioxide (CO_2) and water. These catalysts primarily used a mix of platinum and palladium.

The focus of regulation then turned to oxides of nitrogen (NOx) and new US regulations were phased in between 1981 and 1983. Because oxidation catalysts have little effect on NOx, the new standards resulted in the development and introduction of 'three-way catalysts' that simultaneously oxidise CO and HC while reducing NOx to nitrogen. The most common three-way catalysts fitted to cars in the 1980s contained platinum and rhodium in a 5:1 ratio, rhodium playing an important role in promoting the reduction of NOx.

Palladium came to the fore from 1989 onwards, as auto makers began using more durable palladium-based three-way catalysts to take advantage of the metal's price discount to platinum. In addition, the sudden spike in the price of rhodium to over $5,000 per oz in 1990 encouraged some manufacturers to utilise palladium-rich catalysts with lower rhodium loadings. Technological advances made by autocatalyst manufacturers enabled auto companies to be more responsive to the changing pgm price differentials.

The move to greater use of palladium gathered pace with the California Clean Air Act of 1990, the US Federal Tier 1 standards introduced in 1994, and the European Stage II regulations of 1996. These placed further limits on emissions levels, particularly for HC for which palladium is a highly-effective catalyst. The move into palladium was helped by reductions in the sulphur content of fuel in California, Europe and Japan.

Initially palladium loadings of two or three times that of platinum were required to maintain overall catalyst performance. However, as palladium was typically one-third to one-quarter of the price of platinum (averaging $88 versus $376 in 1991 for example) it was economical at much higher loadings.

The exceptionally rapid rise in auto company demand for palladium throughout the mid and late 1990s, coupled with disruptions to supplies from Russia, spurred the palladium price from around $200 at the start of 1998 to over $1,000 in January 2001. This triggered moves by some auto makers to shift a proportion of their autocatalyst pgm use back in favour of platinum. The subsequent reversal in platinum and palladium prices has created the financial incentive for the auto industry to re-examine greater use of palladium once again.

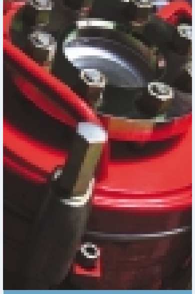
Influences on catalyst development

Car companies are already working with catalyst suppliers on vehicle models that will be launched in three to four years time and beyond, to meet the emissions regulations that will be in effect during these cars' lifetimes. The regulations stipulate what needs to be achieved in terms of emissions control and consequently influence many of the catalyst system parameters.

In addition to emissions legislation, other factors that will affect catalyst system designs include engine size, fuel type (gasoline or diesel), engine performance characteristics, and technical considerations such as the level of engine-out emissions, operating temperatures and exhaust system back pressure. Catalyst system design and layout (the number, size, shape and location of bricks, for example) will also be influenced by fundamental parameters such as the available space.

Although common components will be used as far as possible across a number of engine sizes, types, and even vehicle platforms, catalyst formulations and configurations and the calibration of engine control systems are tailored to individual models. Throughout the entire process the auto company, therefore, works very closely with the catalyst supplier in the design and formulation of an overall emissions control system that will meet the relevant emission standards at an acceptable cost.

Once a catalyst has been designed and the associated engine management controls have been calibrated, the system then has to be tested and approved by official certification bodies. After certification, changes to a catalyst system on a specific car model



cannot usually be made without it being re-certified.

In order to benefit from changes in pgm prices, auto manufacturers may re-examine the pgm loadings or ratios on an autocatalyst system after the vehicle model it is fitted to has entered production. However, catalyst design, testing and certification in association with calibration of the engine and on-board diagnostic systems typically takes many months and requires the input of highly qualified technical staff from both the auto manufacturer and catalyst supplier. It is complex, time consuming, and carries a significant cost to the car company.

Auto manufacturers, therefore, are reluctant to make major changes to pgm loadings once a specific model has entered production. By this stage the engine management and catalyst engineering teams will have long moved on to work on future models. Of course, knowledge gained and advances made in the development of a particular vehicle's catalyst system may be adapted and applied to subsequent models, and in this regard the process is evolutionary.

Advances in catalyst design

Substantial advances have been made in autocatalyst design and technology over the last 10 years and some have influenced pgm loadings. The most important trends can be summarised as:

Inspecting autocatalyst bricks on the production line at a plant in Shanghai.

- Improved thermal and chemical characteristics of the catalyst

A number of advances in pgm salts and washcoat formulations have enabled substantial improvements to be obtained in the efficiency of pollution conversion and in the thermal durability of catalysts. A key enhancement was the addition of ceria (cerium oxide) to the washcoat. This helped to stabilise the surface area of the washcoat and greatly improved oxygen storage capacity. The latter is crucial in maximising the ability of three-way catalysts to both oxidise HC and CO and reduce NOx, and also enables on-board diagnostic systems to evaluate the 'health' of the catalyst. Subsequently, catalyst manufacturers developed sophisticated catalytic formulations that contain all the active components in a single washcoat.

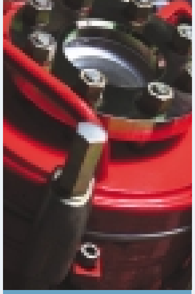
The production of catalytic materials with greater thermal durability and stability at high temperatures has also been achieved. High thermal durability is particularly important as a more thermally durable catalyst can be fitted much closer to the engine, where exhaust temperatures are higher and where it will reach light off (the temperature at which it becomes active and starts converting pollutants) more rapidly. This is critical as the pollutants emitted before the catalyst reaches light off account for the great majority of total emissions. The previous generation of catalysts with lower thermal durability had to be loaded with more pgm to counteract the possibility of degradation in performance over time.

- Closely tailoring catalysts to individual vehicle models

By optimising engine operating parameters (fuel combustion, the air:fuel ratio, exhaust temperature, etc.) in concert with close calibration of engine management systems and catalyst development, pgm loadings can be reduced compared to a one-catalyst-fits-all approach. Of course, improvements in engine design to reduce engine-out emissions will intrinsically lower the demands on the catalyst system and may also enable lower loadings of pgm to be utilised.

- Substrates with higher cell density and thinner walls

Five years ago a standard ceramic catalyst substrate contained 400 cells per square inch (cpsi) and the cells walls would have been around 0.125 millimetres thick. Today, substrates with 600 cpsi are common and some of 900 cpsi with walls less than 0.06 millimetres thick are in use. Similar advances have also been made in increasing the cell density of metallic substrates. This has an indirect effect on pgm loadings as a larger catalyst surface area can be incorporated into a given converter volume and this allows better conversion efficiency and durability. Alternatively, smaller converters with the same performance can be produced, making the catalyst easier to fit close to the engine where space is usually limited. This close-



coupling allows light off to be achieved more rapidly, enabling emissions limits to be achieved with lower pgm loadings. Substrates with thinner walls also heat up more rapidly, again reducing the time to light off.

Changes in pgm loadings

Thrifting in the context of precious metals and autocatalysts is generally understood to refer to the reduction of pgm loadings on a vehicle's catalyst system without compromising its ability to meet the relevant emissions legislation.

The rationale for thrifting is primarily economic: the goal is the most cost-effective catalyst system possible. Given their relatively high cost, efforts to thrift precious metals are a consequence of this drive, although strategic considerations – the security and reliability of pgm supply – are also relevant. In addition, thrifting of pgm can only be taken so far without impairing catalyst performance. For all auto companies the need to maintain 100 per cent compliance with emissions regulations is paramount. The development of sophisticated new autocatalysts by catalyst manufacturers has enabled the use of lower pgm loadings while still comfortably meeting the relevant emissions legislation.

The fact that auto manufacturers place different emphasis on the importance of pgm thrifting also has to be taken into consideration. Those for whom environmental 'leadership' is a key element of their marketing strategy may attach greater weight to meeting new emissions legislation ahead of the required deadlines than they do to pgm thrifting.

It is also useful to draw a distinction between pgm loading levels on individual catalyst bricks and the loading of pgm across the whole catalyst system of any one vehicle. Two brick systems are common, and it is not unusual for larger, high-performance passenger cars to be fitted with four to six catalyst bricks. The loading, choice of precious metals, and ratio of pgm used can vary substantially from brick to brick. It is the use of pgm across the system as a whole that is important.

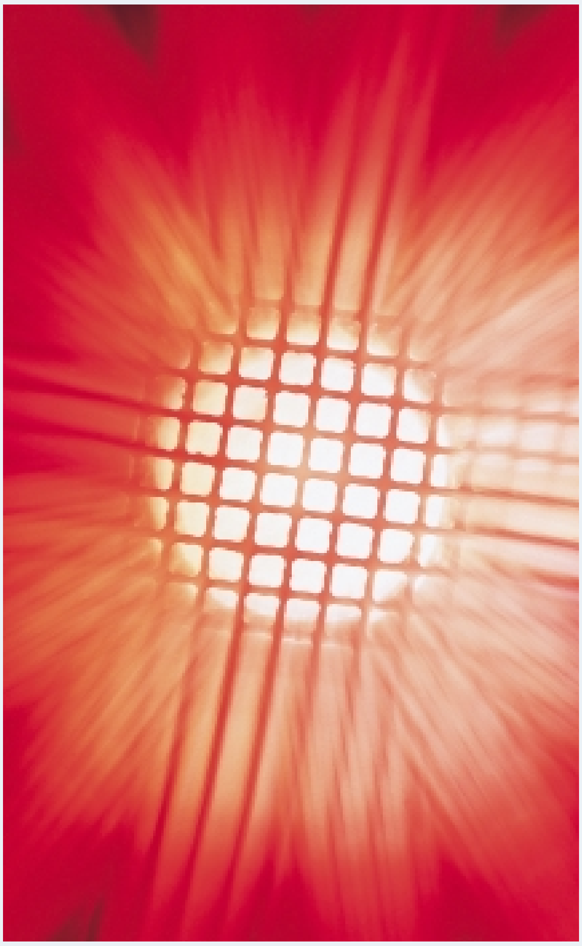
Dual certification – hard to justify

In light of the historical volatility in platinum and palladium prices, some auto companies have investigated the certification of both platinum and palladium-rich catalyst systems for the same vehicle model. Catalyst designers have responded by developing both palladium-rich and platinum-rich systems that meet existing emissions legislation, to enable car companies to adopt a more flexible approach towards pgm use. Dual certification would, in theory, allow a car manufacturer to have greater control over its pgm costs by switching from a platinum-rich catalyst system to a palladium-rich variant, or vice versa, when metal prices changed significantly (though this is only relevant to gasoline vehicles as diesels are dependent upon platinum-based catalysts).

However, the characteristics of the two metals such as reactivity, pollutant conversion efficiency and durability are not identical and a recalibration of the engine management systems and on-board diagnostics will normally be required. This, in turn, usually means that the entire system has to be recertified.

Auto manufacturers, therefore, have to assess whether the cost of developing and certifying two separate catalyst systems for the same car model will be offset by the potential benefits that may be gained through being able to switch from one to the other. This cost-benefit analysis requires car companies to take a view on how pgm prices will move over the coming 3 to 4 years or more – a tough proposition given their recent unpredictability.

Dual certification also has to be seen in the context of the strong desire by most auto companies to minimise costs. In this environment it is hard to justify the capital expenditure and the redeployment of resources required for additional catalyst engineering, testing, calibration and certification when there is no guaranteed financial benefit. Although attempts are being made to speed up and simplify the cost of the catalyst certification process, it will still have an associated cost that the auto maker is not guaranteed to recoup.



Close-up through an autocatalyst substrate. The development of substrates with thinner walls and a greater number of cells per inch has had a number of benefits for catalyst performance.