PALLADIUM USE IN DIESEL OXIDATION CATALYSTS

Automotive catalytic converters were first developed in the 1970s and were initially fitted to gasoline-fuelled automobiles in North America from 1975 in order to reduce the emissions of pollutants from these vehicles.

The first catalysts used a simple formulation of platinum deposited on aluminium oxide which in turn was coated onto a support material so that it could be placed in the exhaust stream of the vehicle. These designs were essentially two-way oxidation catalysts, so-called because they reduce tailpipe emissions of both carbon monoxide and hydrocarbons by oxidising them to carbon dioxide and water.

Later, researchers developed the now commonplace three-way catalysts (for gasoline vehicles) in order to meet tighter emissions legislation. In a three-way catalyst (TWC), carbon monoxide and unburnt hydrocarbons are oxidised at the same time as NOx emissions (a mixture of oxides of nitrogen) are reduced to water and nitrogen. Originally, TWCs used platinum and rhodium as the catalytically-active components. Palladium analogues of these platinum catalysts were developed later and have since become the dominant technology on light duty gasoline vehicles in most regions.

Volkswagen was the first company to fit platinum-based diesel oxidation catalysts – which were similar to the first gasoline two-way catalysts – to its diesel cars in 1989. In 1993, emissions rules were applied to new diesel passenger cars sold in the European Union and these catalysts began to be fitted as standard on new vehicles.

HOW DOES A DIESEL OXIDATION CATALYST WORK?

A diesel oxidation catalyst (DOC) functions by oxidising carbon monoxide and any unburnt hydrocarbons over a platinum group metal. Normally these reactions would only take place at very high temperatures but the use of a catalyst allows them to proceed at much lower temperatures. (In the oxygen-rich environment of a diesel engine exhaust, the reduction of NOx is hard to perform and there is little or no three-way activity.)

At ambient temperature, the catalyst will not oxidise either carbon monoxide or the unburnt hydrocarbons. However, as the temperature of the catalyst rises – when it is heated by hot exhaust gases almost immediately after the engine has started – both oxidation reactions begin to take place more quickly. The point at which this occurs is called the light-off temperature. Above this point, conversion efficiencies rapidly reach a steady state. Much of the development of DOCs has targeted the reduction of this light-off temperature in order to improve a vehicle's environmental performance, particularly when the catalyst is cold, soon after a vehicle's engine is started.

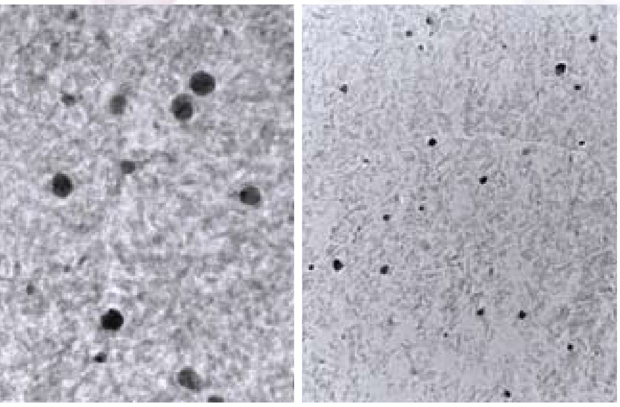
However, it is widely known that this catalytic performance will gradually worsen throughout the vehicle's lifetime. As the DOC ages, a variety of sulphur compounds derived from the diesel fuel can build up on its surface and poison its performance. Exposure to high operational temperatures also damages the catalyst's performance as the catalytically-active nanoscale platinum particles coalesce and their aggregate surface area decreases (a process known as sintering). With less of the precious metal's surface area exposed to the exhaust gases, the conversion efficiency falls too.

Development work has therefore been targeted at improving not only the "fresh" performance of platinum-based catalysts but also their "aged" performance. This has been achieved by optimising the size of the platinum particles in the catalyst and by strengthening the interaction between these particles and the base metal oxide materials used to support them.

WHY WAS PALLADIUM USED IN GASOLINE CATALYSTS BUT NOT IN DIESEL CATALYSTS?

The operating requirements for diesel catalysts are typically very different from those for three-way catalysts. Platinum has historically been favoured for use in diesel aftertreatment because the exhaust stream of a diesel engine is a highly oxidising environment and, under these conditions, palladium is readily converted to the less catalytically-active palladium oxide, whereas platinum remains in its metallic form. By comparison, in the more reducing environment of a gasoline engine's exhaust, palladium exists as the more catalytically-active palladium metal. As a result, palladium is generally a less active catalyst under diesel conditions than it would be in a gasoline vehicle.

The exhaust from a diesel engine is much cooler than that from a



The addition of palladium to a platinum diesel catalyst (above right) improves the thermal stability of the catalyst when compared to the platinum-only formulation (above left).

gasoline engine and this also has an effect. Both gasoline and diesel fuels can contain significant amounts of organic sulphur compounds which combust in the engine to form various gaseous sulphur species. These rapidly poison the performance of palladium catalysts. While platinum-based catalysts are also poisoned by these sulphur species, they are more tolerant to their presence.

In the higher temperature gasoline environment, desulphation often occurs spontaneously: in other words, the sulphates formed on the catalytic sites desorb in hot conditions and much of the catalyst's performance is restored. Unfortunately, in the cooler diesel environment this spontaneous desorption rarely occurs and palladium-based catalysts suffer deactivation by sulphur poisoning.

MOTIVATION FOR RESEARCH INTO THE INTRODUCTION OF PALLADIUM

Palladium is, compared to platinum, a less active catalytic material for these oxidation reactions. On its own in a diesel catalyst, it will often exist in its less active oxide form. It was therefore historically not the first choice of active metal for a scientist to use when developing a new catalyst. Fortunately for palladium demand, however, it has been known for some time that the addition of palladium to platinum in a supported catalyst can stabilise the catalyst, when it is heated, by forming bimetallic particles.

At the highest temperatures experienced by a diesel catalyst, platinum often sinters. As in a three-way catalyst, this means that the nanoscale platinum particles start to move around the support and merge to form larger particle aggregates with an associated loss of efficiency in the catalyst. The addition of palladium can stabilise the size of the precious metal particles when a catalyst is heated and thus ensure that the performance of the diesel catalyst is maintained at a high level for much longer.

Researchers have therefore attempted to use palladium alongside platinum in DOCs for a number of years to provide additional thermal stability. If this were achieved, the lifetime performance of a catalyst could be improved sufficiently to allow the use of a lower loading of platinum. Additionally, if the price of palladium were below that of platinum, the auto makers would potentially be able to improve the catalyst's performance in the real world and reduce costs at the same time.

OBSTACLES TO THE USE OF PALLADIUM IN DIESEL OXIDATION CATALYSTS

However, there were two major obstacles to the use of palladium in this way: one economic and one technical. The economic obstacle proved to be only temporary: while palladium was more expensive than platinum, the replacement of any platinum by palladium in a diesel catalyst was economically unattractive. However, since 2002 palladium has consistently been less expensive than platinum and its use has therefore been much more attractive to the car makers in purely economic terms.

The technical problem was more difficult to overcome. Palladium's catalytic activity is readily poisoned by sulphur and diesel fuel can contain significant amounts of sulphur-containing compounds. During the 1990s, for instance, diesel fuel in Europe could contain as much as 500 ppm of sulphur. However, the permitted level of sulphur has been steadily reduced and in 2005 the maximum sulphur content of European on-road diesel fuel was cut to 50 ppm. In February 2009 this fell again to only 10 ppm.

With sulphur levels falling this far, it became feasible to attempt to use palladium alongside platinum in diesel oxidation catalysts. Although research work had been ongoing for some time, the first public announcement of the development of such a platinum/palladium catalyst was made in 2004 and the very first commercial catalysts were fitted to vehicles during 2005.

The increased use of diesel particulate filters (DPFs) on European vehicles has also helped palladium make inroads into the light duty diesel sector. The soot which is retained in these filters needs to be removed regularly to avoid the build-up of high back pressure in the exhaust system. This is achieved by temporarily altering the engine's performance in order to raise the temperature of the exhaust gas to the point at which carbon is removed, a process known as regeneration of the filter. These high temperature regeneration events also increase the temperature of the DOC and, with careful design of the catalyst, allow sulphur to be removed periodically from the DOC's surface. As a result, sulphur build-up on DOCs is less problematic if a particulate filter is also fitted to the vehicle. The high temperatures experienced by the catalyst during this regeneration process mean that the thermal stability of the catalyst becomes more important where a filter is fitted, making the use of platinum/palladium technology more attractive.

LIMITATIONS OF PALLADIUM USE IN DIESEL EMISSION CONTROL

Platinum/palladium diesel catalyst formulations are now widely in use in Europe but there remain some limitations to their use, even where low sulphur fuel is available, meaning that platinum-only catalysts are still employed on many diesel vehicles.

Firstly, palladium is not an equally effective catalyst for each of the oxidation reactions it is required to perform. It is not particularly effective at converting some of the hydrocarbons present in diesel exhaust gas while platinum is a better catalyst for this reaction. However, palladium is an effective catalyst for the carbon monoxide oxidation reaction, particularly at high concentrations of this gas. In contrast, platinum's performance in this particular catalytic reaction is temporarily poisoned by high carbon monoxide concentration (i.e. it becomes less effective the more of the gas there is).

Secondly, even in those applications where palladium has a place, there is likely to be an upper limit to the ratio of palladium to platinum in the catalyst. The two metals do not normally exist as separate catalytic sites but rather as a mixture of alloys. While the presence of palladium can provide much-needed thermal stability in a catalyst, the use of some platinum remains important in providing high catalytic activity for some of the oxidation reactions.

Finally, the role of a diesel oxidation catalyst has become progressively more complex as emissions legislation has tightened. Where simple oxidation of hydrocarbons and carbon monoxide was the role of the DOC, a limited range of catalytic formulations was employed. In current systems, a DOC can also be required to convert NO to NO_2 or to burn large quantities of fuel to heat the exhaust system quickly and it can be combined with a range of other types of aftertreatment. With a wider range of possible roles for the DOC, no single catalyst formulation can be universally applied.

FUTURE DEVELOPMENTS IN THE USE OF PALLADIUM

While the platinum price fell heavily in late 2008, the palladium price fell too and a considerable price differential remains between the two metals. As a result, we expect palladium to make further inroads into the diesel sector as platinum/palladium formulations are introduced on an increasing proportion of European vehicles.

There is a considerable amount of ongoing research looking at increasing the use of palladium in place of some of the platinum in diesel oxidation catalysts and even in diesel particulate filters. A typical oxidation catalyst formulation currently in use might have a platinum:palladium ratio of 2:1 in weight terms (or about 1.2:1 in atomic terms). The launch of catalysts containing equal amounts of platinum and palladium seems now to be inevitable and further development beyond this ratio may be possible in some cases, although it may not prove possible to apply such technology universally.

The market share of platinum/palladium catalysts has also increased in the last few years, adding to palladium demand and helping to restrict the rapid growth in platinum demand which would otherwise have occurred. With the global market for diesel vehicles expected to expand over the medium term, good prospects exist for enhanced demand for both metals in the future too.

The maximum permitted sulphur content of on-road diesel fuel varies between different markets but is decreasing everywhere.