

# Substantial Emission Control Progress to Meet Future Legislation

## SELECTIVE REPORT OF THE 1994 INTERNATIONAL SAE CONGRESS

The February Congress of the Society of Automotive Engineers (SAE) is traditionally the focal point for those involved in the field of emission control. It is the main annual opportunity for presentation of technical papers associated with mobile source emissions and their treatment. The 1994 conference, which was held in Detroit from 28th February to 3rd March, proved to be one of the strongest Congresses ever held, with literally dozens of papers devoted to emission control, and therefore to the development and application of autocatalysts containing the platinum group metals.

Forthcoming legislation in California, the so-called LEV (Low Emission Vehicle) scheduled to come into effect in 1997, the prospect of further tightening of the European exhaust emission limits in 2000, and also perhaps the driving force of fiscal incentives, have caused the technology to race to meet these demanding automotive emission standards.

Although this review focuses upon three specific papers concerned with platinum group metals, it is important to note that the relative stringency of current and forthcoming emissions legislation now means that much greater emphasis is placed upon a *system* approach to emission control, as compared with the contribution from individual components. This was a recurrent theme throughout the technical presentations and papers. Several papers were given, for example, which discussed the potential for platinum and rhodium catalysts in combination with electrically heated supports or burner systems; the objective being to enable catalytic activity, especially hydrocarbon reduction to begin within seconds after vehicle start-up.

The past three or four years have seen an increasing interest in the prospects for using palladium in automotive emission catalysis. The use of palladium is not new, having been used in oxidation catalysts (to oxidise carbon monox-

ide and hydrocarbons) in the United States in the mid 1970s and early 1980s. However, palladium has not been widely used in three-way catalysts (for the simultaneous control of carbon monoxide, hydrocarbons and oxides of nitrogen) for two main reasons: first palladium is generally more susceptible to poisoning by lead and sulphur than either platinum or rhodium, and second, palladium can form alloys with rhodium thereby suppressing the catalytic activity of the rhodium. Nevertheless, the lower cost of palladium, compared with that of the other noble metals, and the fact that palladium does have specific desirable catalytic properties have contributed to its continuing development.

### Palladium-Only Three-Way Catalysts

Three papers in particular considered palladium, the first being "Development of Palladium Only Three-Way Catalyst Technology" a joint publication of work done by the Ford Motor Company, the Engelhard Corporation and Johnson Matthey, and presented by J. S. Hepburn from Ford (SAE 941058), which described recent developments. The original objective of the research was to utilise the high temperature durability properties of palladium to provide a more thermally stable washcoat for use in close coupled automotive catalyst applications. Initial work used alkaline metals and rare earth oxides in conjunction with palladium to obtain a catalytic performance similar to that of rhodium. This was achieved by the construction of stable catalytic sites comprised of specific ions in close proximity to palladium atoms, which has the effect of promoting the dissociative chemisorption of nitric oxide and enhancing the water gas shift reaction, that is, it provides hydrogen to reduce nitric oxide.

First generation palladium-only three-way catalyst formulations demonstrated improvements, when compared to current three-way catalyst

technologies, in the hydrocarbon light-off and in an equivalent reduction of the nitrogen oxides. Second generation development focused upon improvements in the oxygen storage capability of the catalyst system to achieve an improved conversion capability for carbon monoxide and nitrogen oxides. Additional optimisation in the positioning of catalytically active sites further improved the water gas shift reactions described earlier.

Vehicle and laboratory reactor testing demonstrated the relative performances of palladium-only and palladium-rhodium catalyst formulations after ageing at various high temperatures. Data were presented showing that a palladium-only catalyst at 1200°C can have a broadly equivalent performance to a palladium-rhodium catalyst aged at 1000°C. The paper concluded that, when used in Ford vehicle applications, the palladium-only catalyst formulations demonstrated the capacity to reduce substantially the tailpiece emissions of hydrocarbons, carbon monoxide and oxides of nitrogen and this technology will be released into limited production in 1995.

### **Durability Aspects of Palladium Only Catalysts**

Aspects of palladium-only three-way catalysts were reviewed by M. Härkönen and colleagues from Kemira Metalkat Oy in their paper, "Performance and Durability of Palladium Only Metallic Three-Way Catalyst" (SAE 940935). A palladium-only formulation, designed specifically for low temperature light-off and high temperature application, with a relatively high metal loading per catalyst, was found to be superior for the conversion of hydrocarbons, when compared with a conventional platinum-rhodium three-way catalyst. It was noted however that the control capability for oxides of nitrogen was lower than that of a platinum-rhodium system. Differences between palladium-only and platinum-rhodium catalyst performance are caused by changes to the air:fuel ratio of the engine. Higher air:fuel perturbation amplitudes showed that there was a capability for improving the conversion of nitrogen oxides using palla-

dium-only catalysts without compromising other catalytic properties. In addition the performance of the catalyst can be further optimised by calibrating the air:fuel ratio exactly for this system.

### **Extensive Work on Tri-Metal Catalysts**

This result tends to suggest that the use of palladium-only or palladium containing three-way catalysts will be specific to each application, and this was one of the main conclusions from the third paper which considered palladium, "Recent Trends in the Application of Tri-Metal Emission Control Catalysts" a joint paper from Degussa AG, International Catalyst Technology Co. and Nippon Shokubai Co. Ltd., which was presented by E. S. Lox of Degussa (SAE 940928).

The authors noted that the catalyst-relevant properties of fuels available in the United States of America and in European markets have improved considerably, and especially that the lead content has decreased. Advanced engine management systems are now available which allow a much tighter control of the air:fuel ratio. In addition the use of air pumps to add air to the exhaust to give a net oxidising exhaust gas composition at engine start-up creates a condition which is advantageous to palladium.

The report described an evaluation of combinations of various noble metals: platinum/rhodium, palladium-only, palladium/rhodium and platinum/palladium/rhodium for a range of loadings and ratios. The catalysts were evaluated under a range of test conditions, including synthetic gas, engine bench and by vehicle evaluation.

The effect of hydrocarbon speciation upon the catalytic activity was highlighted. Under lean conditions, palladium exhibits lower light-off temperatures for an olefinic hydrocarbon (butene) than platinum or rhodium based catalysts. Increasing the partial pressure of the oxygen lowers the light-off further. However palladium has no advantage over platinum for the light-off of a paraffinic hydrocarbon (butane) and the light-off temperature of a paraffinic hydrocarbon is not affected by an increase in the partial pressure of oxygen.

Thus the authors note that the improvements in the performance of engine hydrocarbon light-off, observed for palladium-only catalysts when used in conjunction with a secondary air-pump, are due to the present generation of gasoline engines emitting a higher proportion of olefinic hydrocarbons from utilising the currently available fuel specifications.

The performance of three metal autocatalyst systems was also considered in this paper. The authors noted that to combine platinum, palladium and rhodium into one catalyst would involve complex impregnation techniques. Therefore for this study combinations of different metal catalysts within the vehicle exhaust system were evaluated. Results indicate that the best conversion performance for carbon monoxide and hydrocarbons is achieved with those systems that place a palladium catalyst first, but

the best compromise for simultaneous conversion of carbon monoxide, hydrocarbons and oxides of nitrogen is achieved by using a platinum-rhodium catalyst followed by a palladium-only catalyst. Within the context of European legislative requirements it was demonstrated that a platinum-rhodium catalyst followed by a palladium-rhodium catalyst gave the best results. However, in the context of United States legislative requirements it is noted that a single catalyst combining all three noble metals gives the best vehicle test results.

The Congress held this year has shown the determination and capability of the automobile manufacturers to meet the forthcoming stringent emission standards. It has also demonstrated that the use of platinum group metals can meet this challenge for application in vehicle exhaust systems. C.J.

## Encapsulation of Palladium Crystallites in Carbon

The growth in carbon nanotechnology has produced carbon in the form of giant clusters, large nested fullerenes, bamboo-like structures and nanotubes. Metals and metal carbides have been successfully included into these structures, and carbon clusters in tubular form encapsulating a metal are expected to result in new technology. However, encapsulating a metal has generally been selective with respect to the metal.

Palladium is an important catalyst and is used in many chemical reactions, often supported on carbon. Now a researcher at the DuPont Company in Delaware, has succeeded in encapsulating cubic palladium crystals inside giant carbon clusters and produced worm-like carbon nanotubes ("nanoworms") (Y. Wang, "Encapsulation of Palladium Crystallites in Carbon and the Formation of Wormlike Nanostructures", *J. Am. Chem. Soc.*, 1994, **116**, (1), 397-398).

The carbon-encapsulated palladium was found in the cathode deposit produced from arcing between a hollow carbon anode filled with palladium oxide/graphite cement paste and a carbon cathode within a chamber filled with flowing helium at 500 Torr. The ratio of the palladium oxide:carbon, in weight per cent, was from 0.05 to 1.0. The worm-like structures were mainly observed in the core of the cathode deposit and rarely found in the shell.

Deposits formed at the tip of the cathode were analysed by transmission electron microscopy.

The head region of the "worm" was examined by energy dispersive X-ray analysis and was found to consist of palladium encapsulated in carbon clusters; electron diffraction of the body of the "worm" showed that it consisted of many sections of carbon tubes 20-50 nm in diameter and several hundred nanometres long. The tubes had mostly cone-shaped internal voids, with the tip of each void always pointing to the back of the worm.

Palladium appears to act as the seed for the growth of the "nanoworm"; the cone-shaped internal void being the result of tube closure caused by pentagonal ring formation due to the presence of palladium. Each closure is followed by new growth from the outer layer which forms the next section. This periodic tube closure and regrowth eventually produces the worm-like structure. Some worm-like bodies were without palladium in the head, but the internal cone-shaped voids indicated that palladium had once been present.

As it is already known that chemical methods and electron beam radiation can open the ends of nanotubes and nanowires it is suggested that such carbon-encapsulated palladium could become very useful. The carbon protects the palladium in a pristine form and only needs to be able to release it periodically under controllable conditions. This would allow the palladium to be introduced into a chemical reaction with regulated and timed release.