

# Exhaust Gas Pollution Control

## FURTHER PROGRESS IN PLATINUM METALS CATALYSIS TO REDUCE EMISSION LEVELS

The Third International Congress on Catalysis and Automotive Pollution Control (CAPOC3) was held in Brussels from 20th to 22nd April 1994. This conference goes from strength to strength, and the event this year contained four plenary lectures, twenty-five oral presentations, and fifty-four posters – a substantial increase on CAPOC2, which was held in 1990. A measure of the international importance of the event is that both scientific contributions and attendance came from all parts of the world, and the conference can now be considered to be among the most important dealing with the subject of automotive pollution control by catalysis.

A high proportion of the papers presented referred to catalysis by the platinum group metals. However, it is only possible to review a very limited selection of them here.

K. C. Taylor of General Motors, reviewed the results of controlling emissions from motor vehicles in the U.S.A. over the period 1975–90 as a function of the total emissions inventory, showing that the contribution from the motor car had been significantly reduced. This trend was projected to continue through the 1990s as the older, more polluting vehicles were replaced by vehicles meeting the newer standards. Other factors, for example use of reformulated fuels and enhanced inspection and maintenance standards, will also play a part, but she suggested that further controls will probably realise only limited improvements in air quality. Two subsequent scene-setting papers by K. P. de Jong of Shell Research and P. Eyzat of Ecole National Supérieure du Pétrole et des Moteurs, examined the historical and future roles of fuels and automotive engines, respectively.

### Modelling and Mechanisms

Although platinum group metal catalysts, principally based on platinum and rhodium, have been successfully used in some parts of the world

for well over a decade, there is still considerable interest in understanding the complex mechanisms involved over the catalyst surface. By using mechanistic and kinetic information to model catalyst performance, it is hoped that it will be possible to predict how the increasingly stringent emission requirements of the future might be met. Furthermore, the use of modelling techniques gives the possibility of reducing the expensive experimental programmes currently being run by both automotive engineers and catalyst chemists around the world.

This was explored in two enlightening and entertaining papers presented by D. Schweich and his co-workers from Laboratoire de Génie des Procédés Catalytiques, CRNS-CPE, who described their experiences in modelling three-way catalytic converters, and compared the data obtained from their model with laboratory generated experimental data. It was pointed out that in order to develop a successful model the most crucial factor was the availability of good kinetic data.

In practice, automotive catalysts operate not in steady state conditions, but under a series of transient conditions. The changing nature of the gas composition can have a major influence on the composition of the catalyst surface. These effects are sometimes best studied using synthetic gas mixtures and an experimental rig, which is more readily controllable than a complex car engine.

A number of papers described the use of synthetic gas to investigate various aspects of auto-catalyst reaction phenomena, including that by C. Howitt, V. Pitchon, F. Garin and G. Maire of Université Louis Pasteur, who reported on the state of platinum/rhodium catalysts during cycling experiments (rich, stoichiometric, lean). These authors concluded that under the influence of the reacting gases, particularly oxygen, extensive surface rearrangement can occur, such

that in a reducing or stoichiometric environment the activity is that of reduced rhodium and platinum, whereas under lean conditions the activity is due entirely to platinum.

### **Thermal Ageing and Sulphur Poisoning Effects**

With the forthcoming lower emission limits in mind there were several papers concerned with the effects of thermal ageing and poisoning of three-way platinum group metal catalysts. In particular poisoning by sulphur species which arises from combustion of fuel sulphur was highlighted. D. D. Beck and J. W. Sommers of General Motors compared the effects of sulphur on thermally aged commercial palladium and platinum/rhodium catalysts. This study showed that increasing the sulphur level in the exhaust gas adversely affected light-off and warmed-up activity of both catalysts to a similar degree, and that this effect was more pronounced under rich conditions than under lean conditions. The magnitude of the reduction in performance for nitrogen oxides control and propylene removal under stoichiometric conditions was significantly greater for the palladium catalyst than for the platinum/rhodium system. In addition, the effects of the sulphur poisoning on platinum/rhodium were reversible, whereas the palladium catalyst only partially recovered when sulphur was removed from the gas stream. The role of ceria, present in most current three-way catalyst formulations, in absorbing sulphur species was described by S. Lungren, G. Spiess, O. Hjortsberg, E. Jobson, I. Gottberg and G. Smedler of Volvo. Under reducing conditions the sulphur dioxide is regenerated and is reduced on the platinum group metal particles to form hydrogen sulphide. As the catalyst ages, the ability to form hydrogen sulphide sharply diminishes, while the ability of ceria to take up and release sulphur remains. The authors conclude that changes in the morphology of the platinum group metal particles are responsible for the lower hydrogen sulphide emissions in the aged catalysts.

Improving the stability of three-way catalysts to enable them to survive severe thermal age-

ing was also a topic of discussion, and covered the preparation of more thermally stable wash-coat and platinum group metal components. Researchers M. Pijolat, M. Prin, M. Soustelle, O. Touret and P. Nortier (Ecole Nationale Supérieure des Mines and Rhône Poulenc) described the stabilisation of ceria by the addition of specific cations, and R. W. McCabe, R. K. Usmen, G. W. Graham, W. L. H. Watkins and W. R. Rothschild of Ford Motor Company, showed that modifying the surface of the alumina with silica groups helped to prevent interactions between rhodium and alumina in high temperature oxidising environments. Reduction of the rhodium-alumina interaction enables the rhodium to remain in a reducible form. The benefit is seen particularly in the levels of nitric oxide conversion. Supporting the rhodium on a non-interactive support such as zirconia generates similar effects.

The effect of severe thermal ageing on the efficiency of hydrocarbon removal on a platinum/rhodium catalyst was reported by J. M. Bart, M. Prigent and A. Pentenero (Institut Français du Pétrole and University of Nancy), who related the changes in catalyst performance to morphological changes in the platinum group metal crystallites. The authors also concluded that the oxidation of hydrocarbons is structure sensitive, with the specific rate of reaction per unit area of surface increasing as the size of the crystallites increases.

### **Palladium Catalysts**

There is much interest in the possibility of using palladium in autocatalysts, either alone or in combination with platinum and/or rhodium. D. J. Ball and E. Jacque of A. C. Rochester demonstrated that a three-way catalyst with palladium only could be used on those vehicles with tight fuel control, to give significantly reduced hydrocarbon and carbon monoxide emissions, although the effect on nitrogen oxides was less dramatic. However, for many vehicles the better option was to use a palladium-only front brick followed by a platinum/rhodium rear brick. This combined the good hydrocarbon and carbon monoxide

light-off characteristics of the palladium catalyst with the better nitrogen oxides control provided by the platinum/rhodium system.

A two-layer palladium-only catalyst, in which the lower layer was designed to give efficient operation at low temperatures (less than 500°C), while the upper layer performed better at higher temperatures was described by J. Dettling and co-workers at Engelhard Corporation. The authors ascribe the differences to be due to variations in the level of interaction between palladium and ceria in the two layers.

The good performance of palladium catalysts for the removal of hydrocarbons was also emphasised in another paper by E. S. Lox and colleagues (Degussa A.G.). These authors characterised their catalysts by a number of techniques as well as by subjecting them to severe engine ageing. Their results demonstrated advantages of palladium and also palladium/rhodium systems over platinum/rhodium in certain vehicle applications aimed at future emission control standards.

### **Control of Nitrogen Oxides under Lean Conditions and Diesel Applications**

Since the last conference in 1990, much more emphasis has been placed on the pollution from diesel engines. Because diesel engines operate under very lean conditions, a conventional three-way catalyst does not convert any significant amount of nitrogen oxides. Accordingly much effort has been put into the development of special catalysts to convert nitrogen oxides under lean conditions. The first material to demonstrate significant lean nitrogen oxides activity under realistic conditions was copper on a zeolite support, ZSM-5. Some of the factors limiting the use of copper/ZSM-5 in diesel applications were highlighted in a paper by G. P. Ansell, S. E. Golunski, J. W. Hayes, A. P. Walker, R. Burch and P. J. Millington (Johnson Matthey and the University of Reading), who then went on to describe a system, based on platinum/alumina, which overcame some of these limitations. In addition, by carefully analysing the reaction by Temporal Analysis of Products (TAP) they were able to show that

the predominant mechanism for lean nitrogen oxides conversion over platinum catalysts was by a two-step mechanism: reduction of platinum sites by hydrocarbon species, followed by decomposition of nitric oxide (to nitrogen and adsorbed oxygen species) over the reduced platinum sites. Similar good performance in the conversion of nitrogen oxides under lean conditions by platinum catalysts was reported by B. H. Engler, J. Leyrer, E. S. Lox and K. Ostgathe of Degussa A.G., and K. C. C. Kharas, H. J. Robota, D. J. Liu and A. K. Datye (Allied Signal and University of New Mexico).

A range of platinum catalysts was examined by H. J. Stein, G. Huethwohl and G. Lepperhoff of Mercedes-Benz and FEV in order to identify the optimal engine/catalyst combination for one of their heavy duty engines in U.S. applications. They found light-off to be a function of platinum loading, and that conversion of the soluble oil fraction was very efficient. Sulphate formation was a limiting factor in particulate control, and on the U.S. transient cycle particulate levels were reduced by 20 to 35 per cent, whereas on the 13-mode cycle more sulphate was produced in the high power modes, leading to an eventual increase in particulate emissions.

The use of ethanol as an alternative fuel in diesel engines was described by L. J. Pettersson, S. G. Jaras, S. Andersson and P. Marsh (Royal Institute of Technology, Sweden, and Emissionsteknik A.B.). These authors showed that the selectivity of their platinum and palladium catalysts was important, since poorly selective catalysts could generate a number of side products, especially at low temperature. For this fuel, choice of the support for the active metal was a critical parameter.

Thus the conference covered a wide range of topics within the scope of control of pollution from automotive applications. Many good papers have, inevitably, not been included in this review. Hopefully this series of conferences will be continued long into the future. The Proceedings are expected to be published in the series "Studies in Surface Science and Catalysis" by Elsevier.

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