

# Automotive Catalytic Pollution Control

## THE FOURTH INTERNATIONAL CONGRESS – A SELECTIVE REPORT

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The Fourth International Congress on Catalysis and Automotive Pollution Control (CAPoC4) was held at the Université Libre de Bruxelles, Belgium, from 9th to 11th April 1997. Some 270 scientists from academia and industry attended for the presentation of 26 scientific papers, 43 posters and a small exhibition. The introductory session of the Congress was opened by Professor A. Frennet, founder of this series of meetings in September 1986, and featured invited speakers who set the scene for the technical sessions that were to follow.

Michael Walsh, International Consultant, discussed the explosive growth in the number of vehicles in the world from 50 million to 700 million vehicles in 50 years, despite energy crises, economic recessions and wars. Recent growth in Europe has resulted in the number of vehicles there exceeding those in North America. In Asia, the increase in vehicle numbers which began in Japan in 1970 has been followed by increases in Taiwan and Korea, and now Malaysia. In fact, growth rates for vehicles in these countries are presently greater than those for their populations.

Among items of note, Walsh reported on data from a model developed by the German Umweltbundesamt which showed that although annual distances covered on German roads had increased by 50 per cent since 1980, the advent of catalysts containing platinum metals in 1985 had resulted in a 50 per cent reduction in automobile exhaust emissions. China has recently announced a plan to introduce unleaded petrol by 2000.

Walsh also highlighted the need to control emissions, especially particulates from trucks and buses where few catalysts are fitted at present, although he expected significant levels of retrofitting to be undertaken by 2005. Motorcycles have not yet become a major catalyst market,

except in Taiwan, but Japan has now moved to curb emissions from 2-stroke motorcycles.

The contribution to air pollution made by the use of fossil fuels in Belgium since 1980 was reviewed by Walter Hecq of the Université Libre de Bruxelles. He highlighted concern in cities on health effects, the cost of cleaning buildings and other external social costs which are not generally included in transportation costs. Significant cuts in air pollution in Belgium have been made since 1980, with a 46.5 per cent fall in carbon monoxide levels in the period up to 1995, despite an increase of 44 per cent in carbon monoxide levels during this time from diesel vehicles. Similar results were found for the other key pollutants. The number of diesel cars in Belgium increased from 170,000 in 1980 to 1,180,000 in 1995, during which time diesel fuel consumption doubled. In 1995, vehicular traffic was responsible for 35 per cent of particulate emissions.

### Technologies Needed to Meet 2000 and 2005 Emission Standards

The problems facing the automobile and catalyst industry as it strives to meet the proposed emission standards for 2000 and 2005 were reviewed by Rob Searles of Automobile Emissions Control by Catalyst (AECC), the European catalyst industry association. He concentrated on the new technologies needed to be brought into production to achieve the emission requirements. These include further advances in technologies already in use, such as fast light-off, close coupled catalysts incorporating advanced platinum metals materials, improved washcoat formulations, higher cell densities, and thin wall substrates. New technologies, such as DeNOx catalysts (to reduce NO and NO<sub>2</sub> under oxygen rich conditions in lean-burn and diesel engines), adsorbers for

nitrogen oxides (NO<sub>x</sub>) and hydrocarbons, electrically heated catalysts and particulate traps with catalyst assisted regeneration, together constitute the biggest range of catalyst-based technologies that have ever been available to facilitate emission control from motor vehicles. The presentation highlighted the urgent need for improved fuel quality to assist the introduction of these new technologies; including the need for low sulfur diesel and gasoline fuels.

### **Strategies for Diesel Engine Emissions**

The restraints to diesel engine development, their emissions and parameters that affect NO<sub>x</sub> formation, were reviewed by Peter Herzog of AVL List GmbH, Austria. He considered ways of reducing particulate matter through increased fuel injection pressures and variable injector orifice areas, variable geometry turbochargers, intercooling and cooled exhaust gas recycling. He outlined three strategies to meet extremely stringent emission limits:

- improved engine technology
- new combustion technologies, such as homogeneous combustion
- and exhaust gas aftertreatment.

He concluded that, at present, aftertreatment was the most promising strategy, as he judged that twenty years of research and development work would be needed before the low levels of NO<sub>x</sub> and particulates required could be achieved solely by engine modification.

Oxidation catalysts were indispensable for the removal of carbon monoxide and hydrocarbons, including the soluble organic fraction of diesel particles. However, faced with the choice of either controlling particulates by engine modifications and NO<sub>x</sub> with a DeNO<sub>x</sub> catalyst or, alternatively, controlling NO<sub>x</sub> within the engine and then using a trap to control the particulate, Herzog strongly favoured the former on fuel economy grounds.

### **Platinum Metals Catalysis**

The main session after the plenary session featured papers on aspects of platinum metals catalysis and a selection of these are summarised.

The use of novel palladium-based three-way catalysts for high temperature operation in close coupled positions to produce a fast light-off were covered by R. van Yperen, D. Lindner, L. Mussmann, E. S. Lox and T. Kreuzer of Degussa, Germany. They investigated the effects of improved ceria stabilised washcoats, and of putting palladium in the lower layer, and rhodium in the top layer, of the washcoat. Using these techniques, they were able to lower platinum metals loadings by 25 per cent without sacrificing performance. However, both raw materials and deposition costs were higher.

The comparative behaviour of platinum, palladium and rhodium alone and as multimetallic mixtures was reported by J. R. González-Velasco, J. A. Botas, R. Ferret and M. A. Gutiérrez-Ortiz of the Universidad del País Vasco, Spain. They noted the interest in palladium because of its hydrocarbon activity and low cost, but in their presentation commented on concerns on the durability and alloying of multimetallic mixtures which include palladium. In evaluations of synthetic exhaust gas with perturbations, the main differences between the catalysts occurred for nitric oxide (NO) reduction, since all the catalysts completely oxidised hydrocarbon and carbon monoxide in the synthetic exhaust gas. For catalysts prepared by adsorption or coadsorption, platinum, platinum-rhodium and palladium-platinum-rhodium catalysts converted 90 per cent of the NO while palladium, rhodium, palladium-platinum and palladium-rhodium converted 70 to 75 per cent. However, physical mixtures of monometallic catalysts achieved 90 per cent NO conversion. The lowest light-off temperature for all three regulated pollutants was shown by a co-adsorbed platinum-rhodium catalyst.

The effect of alkaline addition on hydrocarbon oxidation for palladium three-way catalysts was discussed by H. Shinjoh, N. Isomura, H. Sobukawa and M. Sugiura of Toyota Central R&D Laboratories, Japan. Hydrocarbon oxidation activity is higher when alkaline earth metals are added to the palladium than when not, but the activity is decreased. They concluded that adding alkaline metals weakens

the adsorption strength of hydrocarbons on palladium and increases oxygen adsorption. The addition of alkaline earth metals suppresses the hydrocarbon chemisorption and allows a smooth reaction to take place.

The kinetics of NO reduction were discussed by R. Burch and T. Watling of Reading University who reviewed the options, including selective catalytic reduction and three-way catalysts. They concluded that lean-burn operation with catalytic NO<sub>x</sub> reduction was the main challenge and, since decomposition is not feasible, they looked at hydrocarbons as a reductant. High temperature oxide catalysts show moderate activity and selectivity but have a narrow temperature operating range and are affected by water and sulfur dioxide. This leads to a preference for low temperature catalysts incorporating the platinum metals; platinum is the most active.

Three mechanisms for NO<sub>x</sub> removal are suggested, two with hydrocarbon intermediates and the other with isocyanates. Burch and Watling proposed a mechanism involving NO decomposition to Pt-N and Pt-O species on the catalyst surface, which poison at low temperature and need high temperatures or an adsorbate with an affinity for oxygen to function successfully.

The model postulated allows up to 100 per cent NO<sub>x</sub> removal, and the NO conversion versus temperature correlates with experimental data published by Johnson Matthey at CAPoC3. Sulfur can be used to check this postulation since sulfation suppresses DeNO<sub>x</sub> activity but enhances hydrocarbon oxidation. It was shown that different reactions occur with propene and propane. With propane sulfation suppresses DeNO<sub>x</sub> activity but with propene sulfation had no effect on catalyst activity. They questioned whether the use of a non sulfating support, such as silica, would be advantageous.

Nitrogen dioxide (NO<sub>2</sub>) and N<sub>2</sub>O formation during NO reduction on platinum metal catalysts were described by P. Bourges, G. Mabilon and S. Lunati of the Institut Français du Pétrole, France. They proposed three mechanisms for the formations, based on NO decomposition,

the formation of nitrogen containing organic species and NO reduction. They studied the latter mechanism to compare copper and the platinum metals (all except osmium) catalysts, and found that platinum was the only active catalyst for NO oxidation and reduction. They also studied different hydrocarbons and the selectivity for N<sub>2</sub>O formation.

The mechanism for the selective reduction of NO with propene on alumina supported platinum in the presence of oxygen using a TAP (Temporal Analysis of Products) reactor was investigated by S. Eckhoff and D. Hesse of the University of Hanover, and J. A. A. van den Tillaart, J. Leyrer and E. S. Lox of Degussa, Germany. NO adsorption, dissociation and adsorbed nitrogen atom recombination was found to be the reaction path for nitrogen formation on a reduced supported platinum catalyst.

The use of the IST (Isotope Transient Kinetics) technique in catalyst development for the simultaneous measurement of the number of active sites and their turnover frequency was reported by J. C. Frost, D. S. Lafyatis, S. R. Morris, R. R. Rajaram and A. P. Walker of Johnson Matthey. This has produced interesting information on thermal ageing and sulfur poisoning effects on autocatalysts, including, under model gas conditions, observations on the higher activity of palladium catalysts but with greater sensitivity to the sulfur in fuel.

A catalytic NO<sub>x</sub> management system for lean-burn engines was reviewed by R. J. Farrauto, J. Feeley, M. Deeba and J. Lampert of Engelhard. The NO<sub>x</sub> trap adsorbs NO<sub>x</sub> over the temperature range where a lean NO<sub>x</sub> catalyst is not active. Since lean-burn engines produce mostly NO, platinum incorporated into the washcoat of the trap converts it to NO<sub>2</sub> to enhance adsorption. NO<sub>x</sub> is then periodically released to the active lean NO<sub>x</sub> catalyst by desorption, using the heat produced from a small amount of injected hydrocarbon combusted on the trap washcoat. The system can be used with platinum and copper/ZSM-5 lean NO<sub>x</sub> catalysts. Unfortunately the trap is not sulfur-tolerant and is completely deactivated by 150 ppm sulfur.

Sulfur storage on platinum catalysts was compared on ceria, zirconia and mixed ceria-zirconia supports by P. Bazin, O. Saur and J. C. Lavalley from ISMRA-Université, and A. M. Le Govic and G. Blanchard of Rhône-Poulenc, France. The advantages of cerium-zirconium mixed oxides include higher oxygen storage capacity and better stability for the platinum, with the suggestion that better sulfate reduction could favour faster oxygen storage recovery.

In conclusion, CAPoC4 covered most of the

key areas that are important for meeting future exhaust emission standards. However, more papers on work to control diesel emissions would have better reflected its importance. The Proceedings of this Congress are expected to be published by Elsevier in their "Studies in Surface Science and Catalysis" series. The next CAPoC conference is planned to take place in 1999 and should cover progress made towards meeting the 2005 European Union emission standards, which will have been finalised by then.

## Platinum 1997

Monday 19th May saw the launch of "Platinum 1997", the latest annual survey, published by Johnson Matthey, of the supply, demand and applications of the platinum group metals during 1996.

Supplies of platinum fell by 2 per cent to 4.9 million oz during 1996 due to lower Russian exports and a slight decline in production from South Africa. The price of platinum in 1996 averaged \$397.32, compared to \$424.22 in the previous year. This was closely tied to the price of gold, reaching a peak of \$433 in February and then falling throughout the year to a low of \$367 in mid December, despite a temporary recovery in early August due to a series of disputes in South African mines.

Demand for platinum rose by 40,000 oz to reach a record of 4.88 million oz in 1996. The use of platinum in autocatalysts fell by 30,000 oz to 1.82 million oz due to some manufacturers switching to palladium-based technology on gasoline cars. Stricter controls on emissions, however, resulted in an increase in platinum demand for diesel vehicles, as only platinum technology is suitable for the extremely high air:fuel ratios of diesel engines. The introduction of direct-injection gasoline engines, operating under similar lean conditions, is expected to boost the demand for platinum in the future, as may the future commercialisation of fuel cells, for both automotive and stationary applications. Industrial consumption of platinum rose by 95,000 oz to 1.12 million oz with demand rising

for platinum coated hard disks installed in personal computers and for speciality glasses used in television screens and computer monitors, which are produced using platinum-based equipment. There was also strong demand from the petroleum sector for platinum catalysts used in the production of cleaner diesel and unleaded petroleum and for the dewaxing of engine lubricating oils. Sales of platinum to China reached a record 200,000 oz, most being to the jewellery sector, but investment in China's industrial infrastructure also required significant amounts of metal.

Demand for palladium rose by 30,000 oz to 6.15 million oz. Much of this was to the auto sector; around 60 per cent of European gasoline cars sold last year were equipped with palladium-based catalysts, as were those produced by Ford in the U.S.A. There was also increased use of palladium starter catalysts needed to meet the hydrocarbon limits imposed by Low Emission Vehicle legislation in the U.S.A. This demand is forecast to rise as emissions legislation is tightened further. Demand for ruthenium and iridium was greatly increased, mainly due to the development of processes using ruthenium and iridium to produce ammonia and acetic acid, respectively.

Readers of *Platinum Metals Review* who would like to receive a free copy of "Platinum 1997" can do so by writing to Alison Cowley, Johnson Matthey PLC, 78 Hatton Garden, London EC1N 8JP; Fax: 0171-269-8389.