

Automobile Emission Control Systems

A REPORT FROM THE SAE INTERNATIONAL CONGRESS

The papers presented at the 1989 SAE International Congress, held in Detroit, Michigan, U.S.A., from 27th February to 3rd March, reflected the continuing high interest both in the extension of current technologies and in the development of new applications for the platinum group metals in automobile emission control systems. The topics ranged from a historical review of catalyst formulations, through current issues such as the control of hydrogen sulphide emissions from three-way catalyst systems, to new and novel approaches to emission control catalysis. In addition, several papers dealt with the issue of diesel particulate control using catalyst systems.

In a special session dealing with the history of the automobile and the environment, P. J. Willson, M. L. Church and B. J. Cooper of Johnson Matthey presented a historical review of the evolution of the catalytic converter, covering the development of the automotive substrate, the design requirements for catalysts using noble metals and improvements in the canning systems used to contain the ceramic substrate (SAE 890815).

Catalyst Design and Durability

More recent work was reflected in three papers presented in other sessions dealing with issues of catalyst design, directed towards cost reduction and performance improvement. D. Chen and C. E. Cole of General Motors Corporation reported on a study of metal monoliths by a numerical simulation of conversion and thermal responses for a platinum-rhodium monolith. The investigation considered an oval converter with a metal monolith substrate, and the analysis accounted for transient inlet exhaust conditions and non-uniform inlet flow distributions (SAE 890798). Metal monolith converters are gradually finding increasing applications in the automotive industry, particularly where high performance engines can

take advantage of the lower pressure drop afforded by these substrate systems.

Recent interest in non-platinum three-way automotive emission control catalysts was highlighted in a paper by J. C. Summers, J. J. White and W. B. Williamson, of Allied Signal Automotive Products, in which palladium-only catalysts were compared to platinum + rhodium catalysts under a variety of operating conditions (SAE 890794). Vehicle evaluations covered the U.S. Federal Test Procedure, the Economic Commission for Europe (ECE) Procedure and the Japanese 10 Mode Test. Vehicle ageing studies were also conducted. Analysis of the results showed that the palladium catalysts were equivalent to the standard platinum + rhodium catalysts, with the exception of slight loss of control of nitrogen oxides. However it must be noted that the palladium catalysts were loaded at 3.5 times the concentration of the platinum-containing catalyst.

A third paper on catalyst design dealt with a novel approach which incorporated electrical resistance heating into the converter to improve catalyst cold-start performance. This work was reported by K. H. Hellman, R. I. Bruetsch, G. K. Piotrowski and W. D. Tallent of the U.S. Environmental Protection Agency, and was targeted towards improvements in emission control capability for proposed tighter emission regulation standards in the U.S.A. (SAE 890799). In addition, potential use in cold climate environments where additional heating of the catalyst substrate could prove beneficial in controlling emissions during cold-start was envisaged. The experiments were carried out using two different conductive materials; the first was an electrically conducting silicon carbide substrate system, the second an electrically conducting metal monolith system. Improvements of 54 to 79 per cent were achieved during cold-start operation by this approach.

The durability of catalytic converters was

addressed in two papers, the first dealt with the inter-relationship between catalyst coating and substrate properties while the second considered the impact of fuel additive on durability. S. T. Gulati of Corning Glass Works, J. C. Summers, D. G. Linden and J. J. White of Allied Signal Automotive Products compared two catalyst coatings on Corning EX20 substrate with respect to performance and impact on the physical integrity of the substrate system (SAE 890796). A current production catalyst was compared to an advanced high technology catalyst, in which the washcoat loading had been increased compared to that of the standard catalyst. A 10 per cent increase in carbon monoxide and nitrogen oxide conversion was demonstrated with the new catalyst system. In addition, the higher coating loading increased the mechanical strength of the substrate system. However, the coatings resulted in an increase in the expansion of the substrate system with a consequent reduction in thermal shock parameter (a measure of thermal shock resistance over that of the substrate itself). This paper indicated that substrate and coating properties may interact either positively (strength) or negatively (expansion), therefore catalyst and substrate designers have great scope for improving the integrity of future converter substrate coating combinations by cooperative work.

In the past methylcyclopentadienyl manganese tricarbonyl (MMT) has been used as a fuel additive for octane improvement, and its impact on modern catalyst systems was evaluated by R. G. Hurley, W. L. H. Watkins and R. C. Griffis of the Ford Motor Company (SAE 890582). A series of in-use catalysts covering 22,000 to 43,000 miles of operation were characterised to determine the effect of MMT. The results of this characterisation work showed the development of a 5 to 20 micrometres thick layer of Mn_3O_4 over the catalyst surface, sufficient to cause an increase in mass transfer resistance to reacting pollutants. Steady state and light-off measurements indicated that the catalyst efficiency was significantly reduced as exposure to MMT increased. The use of MMT in fuels is currently

prohibited in the U.S.A. by a 1978 ruling, but there is a possibility that the Environmental Protection Agency may be prepared to grant a waiver to this; hence the importance of work reported at this Congress.

Unregulated Emissions and Diesel Exhaust Control

In the area of unregulated emissions, papers were presented on the control of hydrogen sulphide emissions and the control of mutagenic exhaust emission compounds from passenger cars. E. Lox, B. Engler and E. Koberstein, of Degussa, reported on the development of scavenger-free three-way emission control catalysts which gave reduced hydrogen sulphide formation (SAE 890795). Current three-way catalysts with low hydrogen sulphide emissions utilise nickel oxide, which several countries, especially in Western Europe, do not recommend. It is therefore of interest to develop scavenger-free catalysts, and this work attempted to achieve this objective by minimising the storage of sulphur oxides, which lead to hydrogen sulphide in the catalyst system. The role of the catalyst age in the hydrogen sulphide formation mechanism was also discussed.

The catalytic control of mutagenic exhaust emissions from gasoline fuelled passenger cars was described in a paper by P. R. Shore of Ricardo Consulting Engineers and B. J. Cooper of Johnson Matthey (SAE 890494). In this study a vehicle equipped with a conventional U.S. style three-way catalyst and closed loop feedback control, and an advanced lean-burn engine vehicle were evaluated for the catalytic control of mutagenic polyaromatic and nitro polyaromatic hydrocarbons. The former vehicle was equipped with a platinum + rhodium three-way catalyst, and the latter with a platinum + palladium oxidation catalyst. Both vehicles showed over 90 per cent reduction of mutagenic exhaust emissions over the U.S. Federal Test Procedure, the ECE Test Procedure and the proposed European High Speed Cycle. In addition it was also shown that aldehyde emissions from these vehicles were also sufficiently reduced, including a large

reduction in carcinogenic formaldehyde emissions.

In the area of diesel exhaust control, B. J. Cooper and J. E. Thoss of Johnson Matthey demonstrated that excellent particulate trap regeneration could be achieved, below 300°C, by the use of a platinum-based diesel catalyst (SAE 890404). Furthermore, it was also proven that the catalyst did not have to be in direct contact with the diesel particulates for combustion of the particulates to be initiated. However, the disadvantage of this catalyst system was its tendency to produce high levels of sulphuric acid emission, due to the conversion of fuel sulphur to sulphuric acid over the catalyst. It was, therefore, recommended that significant reductions in diesel fuel sulphur should be made to take advantage of the particulate combustion capability of such a system.

Air : Fuel Ratio Sensors

The use of catalysts in wide-range air : fuel ratio sensors, to expand the detection range in the rich air : fuel region, was described by H. Tanaka, S. Nishimura, S. Suzuki, M. Miki, T. Harada, M. Kanamaru, N. Ichikawa and S. Ueno, of Hitachi Limited (SAE 890299). The paper concluded that the limiting cause of

detection in the rich air : fuel ratio region can be identified as insufficient combustion of carbon monoxide and hydrogen with oxygen on the electrode, thus preventing the realisation of a diffusion limited state which is necessary to detect the air : fuel ratio. This situation was corrected by applying an improved diffusion layer to decrease diffusion and increase combustion rate in an improved platinum electrode. It was demonstrated that the detection limit could be expanded to $\lambda=0.6$ whereas that of a conventional system is $\lambda=0.8$.

Conclusion

Overall, the papers presented at this Congress reflected the continuing high level of research and development involving the use of the platinum group metals for vehicular emission control. The developments in substrate technology, substrate coating interaction, new techniques for cold-start emission control, the use of catalysts and catalyst design for the control of currently unregulated emissions, the use of platinum catalysts for diesel emissions control, and the use of platinum catalysts for improved sensor performance all show that significant advances in catalytic devices continue to be made.

B.J.C., R.M.K.

Fuel Cell Developments and Future Potential

The nineteenth century invention and twentieth century development of fuel cell technology are admirably covered in a recent review (S. Srinivasan, *J. Electrochem. Soc.*, 1989, 136, (2), 41C-48C). The key feature of a fuel cell system is the electrochemical cell stack, and its components include the porous gas diffusion electrodes, the electrolyte and the bipolar plate, and these are determined largely by the primary fuel and by the temperature and pressure of the system. Unless very high operating temperatures are used the performance of the electrodes depends upon the characteristics of the electrocatalyst, and platinum or a platinum alloy is generally used.

The pioneering work of F. T. Bacon in the early 1930s served as the foundation for the fuel cells that successfully provided auxiliary power on the Apollo space vehicles. Fuel cells developed from these earlier models provide

the main electrical power supplies for the Orbiter space shuttles, and their success has led to a European programme to consider fuel cell generators for the Hermes reusable space craft.

The energy crisis of 1973 gave a significant boost to the development of fuel cells for terrestrial applications, and the continuing need to conserve petroleum fuels reinforced by the current interest in low pollution energy generation has helped to sustain major development programmes in America, Japan and Europe.

This useful review concludes by giving a most interesting prognosis of the economics and applications of fuel cell systems, and therefore at least in the short to medium term for platinum-containing electrocatalysts. It is suggested that lower manufacturing costs and higher fossil fuel prices make fuel cell systems most attractive for terrestrial use in the developing countries.