Exhaust Gas Pollution Control

Catalysis and Automotive Pollution Control, Studies in Surface Science and Catalysis

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The application of platinum group metal catalysts to control the emission of potentially harmful components in the exhaust gases of gasoline fuelled cars is now well established, particularly in the U.S.A.

In western Europe a growing awareness of the detrimental effects of pollution on the environment, fuelled by the acid rain debate, led to new standards being proposed by the EEC Commission in 1984. These were approved by the Ministers of the Environment the following year. The importance of catalysis to the achievement of the European standards was recognised at the First International Symposium on Catalysis and Automotive Pollution Control (CAPOC I) held in Brussels during September 1986. The proceedings of this symposium have now been published in the series Studies in Surface Science and Catalysis, a selection of the papers is reviewed here.

Possible effects of pollutants on health and on the environment, the viewpoints of the automotive and petroleum refining industries, and the complexities of the differing pollution control standards now established or proposed in various parts of the world are all examined in the first section, which consists of seven papers aimed at providing a general introduction to the problem of automotive exhaust gas pollution.

After reviewing the regulatory and test procedure situation in some detail, K. C. Taylor from the General Motors Corporation summarised the key features which enabled the use of catalytic converters to meet the requirements of the U.S. emission control limits from 1975 model year vehicles, pointing out that it is the only technology available for meeting the most stringent standards.

The principle components of modern exhaust emission control catalysts comprise [i] a ceramic based substrate, [ii] a high surface area washcoat, [iii] base metal additives acting as stabilisers and/or promoters, and [iv] the primary catalytic elements, usually platinum group metals either singly or in combination. The functional roles of these components and their interactions are very complex, but important in establishing the desirable performance and durability of the catalyst. The process for the manufacture of autocatalysts has to be developed with these factors firmly in view, and a paper by B. J. Cooper, W. D. J. Evans and B. Harrison of Johnson Matthey illustrated not only the intricacies arising from the interactions, but also the inevitable compromises required by the sometimes opposing requirements caused by the highly dynamic operating environment.

In the period since catalysts were first fitted to production vehicles substantial improvements have been achieved both in the performance of the catalysts and in our understanding of the relationship between the catalyst parameters and the duties they have to perform. This in turn reflects extensive investment in research and development, and the general improvement in the understanding of catalytic and surface science. Nevertheless the environment in which autocatalysts perform is one of the most complex that any catalyst experiences and much remains to be done to unravel the interactions involved. E. Koberstein and G. Wannemacher, Degussa A.G., reported on kinetic measurements, infrared surface investigations under reaction conditions, and model calculations for some of the reactions involving carbon monoxide, nitric oxide and oxygen on noble metal catalysts in an attempt to understand the factors determining the width of air:fuel ratio windows in three-way catalysts. At low temperatures they observed poisoning of the noble metal surface by adsorbed reactants. As the temperature increased regions corresponding to chemical reaction control, washcoat pore diffusion control and boundary layer diffusion control could also be seen

within the temperature range of normal autocatalyst operation.

The reaction of carbon monoxide with air and with nitric oxide on platinum and rhodium, respectively, was also report by G. B. Fischer (General Motors) and a team of academic and industrial colleagues. Although the measurements were made under ultra high vacuum, the authors show that from the data produced they could accurately predict results at higher pressures. W. C. Hecker and R. B. Breneman of Brigham Young University conclude that the low activation energy/high activity of silica supported catalysts with high rhodium loadings, contrasted to the higher activation energy/low activity observed with low rhodium loadings on the support, point to the reaction on this metal being structure sensitive. The complexity of this situation over rhodium is further demonstrated by C. Z. Wan and J. C. Dettling (Engelhard) who find that nitric oxide, carbon monoxide and propane conversions over rhodium oxide are structure insensitive, but that the same reactions over metal rhodates are structure sensitive. They relate this difference to the ease with which the rhodium species is reduced to the metallic form. H. Shinjoh, H. Muraki and Y. Fujitani of Toyota presented results on these and some of the other possible reactions involving known components of exhaust gas streams on alumina supported platinum, palladium and rhodium catalysts, using both static and cycling gas feedstreams to simulate engine exhaust gas conditions. They conclude that differences in reaction kinetics between the two regimes are a function of the adsorption of the reactants on the catalyst surface.

The nature of structure sensitive reactions was one of the subjects discussed in the paper by H. S. Gandhi and M. Shelef of the Ford Motor Company. These authors point out that certain reactions thought to be structure sensitive, for example the oxidation of saturated hydrocarbons, do not proceed so readily on highly dispersed platinum catalysts, whereas those reactions which are structure insensitive, for example the oxidation of carbon monoxide, proceed more readily as the dispersion (and hence the surface area) of the platinum increases. Thus additives deliberately included to, inter alia, stabilise the platinum dispersion and inhibit its agglomeration—ceria is perhaps the most common—may result in poorer activity for the oxidation of saturated hydrocarbons than with the "unstabilised" catalyst.

The Effect of Sulphur Oxides and Lead

Structural sensitivity may, however, be put to good use in inhibiting another unwanted reaction, that is the oxidation of sulphur dioxide to sulphur trioxide. In the U.S.A. the level of sulphur dioxide exhaust gas is typically 20 ppm; the situation in Europe may be more variable depending on the sulphur content of the fuel in individual countries. Sulphur oxides play an interesting role in the exhaust gas situation. Gandhi and Shelef and also J. W. A. Sachtler, I. Onal and R. E. Marinangeli of Allied-Signal presented evidence that the presence of sulphur dioxide was capable of causing enhanced activity in the oxidation of hydrocarbons on platinum. These authors also confirm that a further benefit of sulphur dioxide is to convert lead in the exhaust gas to lead sulphate when platinum is the catalyst, thus making platinum the least sensitive of the normally used noble metals to poisoning by lead. As with sulphur, the levels of lead in "lead free" fuel in Europe is likely to vary quite widely for some years. M. A. Kilpin, A. Deakin and Gandhi (Ford) provided evidence from laboratory, dynamometer and vehicle durability tests that, allowing for high temperature excursions, the maximum level of lead which could be tolerated without ultimate deleterious effect on a three-way catalyst was in the region of 5 mg/litre of fuel.

On the evidence of this symposium the complex catalysis which takes place in catalytic converters is gradually being unravelled. Much remains to be done and considerable effort is being put into the subject by both academia and industry. The organisers hope to hold CAPOC II, a similar symposium, in two to three years time. D.E.W.