

# Challenges in Emission Control Catalysis for the Next Decade

By B. J. Cooper

Johnson Matthey Catalytic Systems Division

*With new automobile emission standards going into effect in Europe, and even tougher standards ready for implementation in California and the rest of the United States, automotive emission control systems are required to perform even better, in the ongoing effort to reduce vehicle emissions. Catalyst manufacturers, in collaboration with vehicle producers, have spent several years on the research, design, development and testing of catalytic systems to meet the emission standards through to the end of this decade. This paper highlights key technical developments taking place in emission control catalyst technology.*

In 1994 an ambitious programme will begin in California which specifies emission standards for transitional low emission vehicles (TLEV), low emission vehicles (LEV) and ultra low emission vehicles (ULEV); this emission reduction programme will extend into the next century.

## Emission Standards

In the last few years several important changes in emission legislation have taken place which will define the requirements of the automotive industry for emission control technology. By far the most significant of them is the adoption, in California, of new, extremely stringent standards, see Table I. These standards call for reductions, from current levels, by the year 2000, of 90 per cent in the emission of hydrocarbons,

50 per cent in the emission of carbon monoxide and 80 per cent in the emission of nitrogen oxides. United States federal standards are taking a similar firm position on emissions, but with a longer time frame. Similar stringent emission standards have been introduced in Europe, and in 1992 the first widespread, mandated use of catalytic converters came into effect. The California Ultra Low Emission Vehicle (ULEV) standards are more than twice as severe as the possible future European standards, and currently represent the most stringent legislation worldwide for catalytic converter technology.

A second impact on the design of emission control systems is from legislation on the U.S. Corporate Average Fuel Economy standard, and also the proposed carbon dioxide standards

**Table I**  
**U.S. and California Emission Standards**

Year and standard	Pollutant, g/mile		
	Hydrocarbons	Carbon monoxide	Nitrogen oxides
1990 U.S.	0.41	3.4	1.0
1994 U.S.	0.25	3.4	0.40
1993 California	0.25	3.4	0.40
1994 (TLEV)	0.125	3.4	0.40
1997 (LEV)	0.075	3.4	0.20
1997-2003 (ULEV)	0.040	1.7	0.20

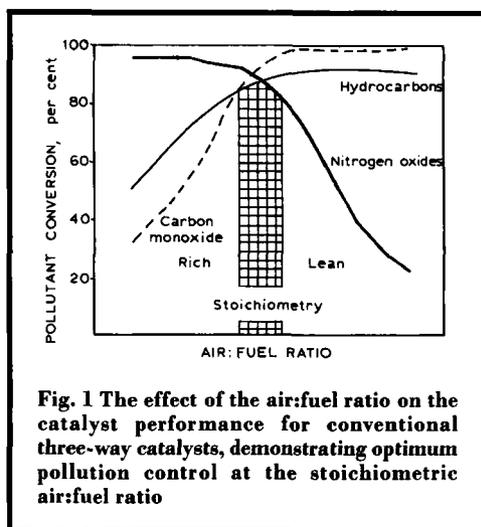
in Europe. From this perspective, the use of a leaner burning engine with significantly improved fuel economy is extremely desirable and has significant impact on the design of emission systems and catalytic converters. As a result, the leaner burn diesel engine is expected to continue as a serious contender in the European Market, and as such has its own specific catalyst requirements (1), and will be the subject of a future article in *Platinum Metals Review*. The lean burn gasoline engine, and the two-stroke engine are also likely to have some effect on emission control technologies towards the end of this decade.

### Engines, Emission Control and Catalysts

Since the early 1980s, the primary emission control system for four-stroke passenger car gasoline engines has consisted of the three-way catalytic converter, which is capable of simultaneously reducing hydrocarbons, carbon monoxide and nitrogen oxides emissions, see Figure 1. The three-way converter reaches maximum efficiency close to the stoichiometric air:fuel ratio. Therefore the engine has to function at around the stoichiometric air:fuel ratio, and is controlled by means of a feedback system containing an oxygen sensor placed in the exhaust system. In addition, mass air sensors together with electronic fuel injection systems, which allow much more precise air:fuel metering, are now common on modern emission controlled vehicles.

Lean burn versions of the four-stroke engine have been under development for some years. But because of the need to meet nitrogen oxides emission standards, a vehicle having an engine which operates at stoichiometry with a three-way catalytic converter is currently favoured. However, there is no doubt if an effective catalyst technology emerges, which could reduce nitrogen oxides under lean air:fuel ratios, that it would give a significant impetus to the development of the technology of lean burn four-stroke and two-stroke engines.

Advanced two-stroke gasoline engines, capable of meeting current emission control stan-



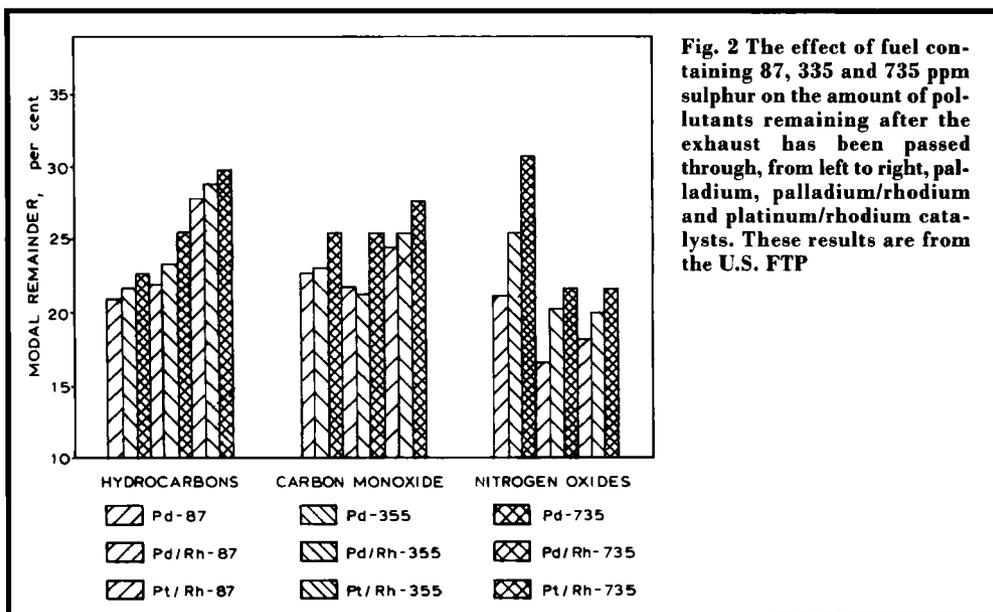
**Fig. 1** The effect of the air:fuel ratio on the catalyst performance for conventional three-way catalysts, demonstrating optimum pollution control at the stoichiometric air:fuel ratio

dards, are now under development. In contrast to the four-stroke engine, the two-stroke is a lean burn engine operating at air:fuel ratios between 20:1 to 40:1. It is clear that for these types of engines, the conventional three-way catalyst system would be incapable of reducing nitrogen oxides emissions, thus an alternate approach to control nitrogen oxides is required.

### Fuel Effects

In addition to the complexities of producing new types of engine, further complications are emerging due to the proposed use of reformulated gasolines. Those gasolines with reduced sulphur content offer advantages in meeting lower emission targets, due to the removal of the inhibition of the catalyst by sulphur. Figure 2 shows the emissions from a vehicle measured over the U.S. Federal Test Procedure (FTP) using gasoline containing three different fuel sulphur levels (87, 355 and 735 ppm). Tests were conducted over palladium, palladium/rhodium and platinum/rhodium catalyst systems.

In all cases the emissions increase as the fuel sulphur level increases. The greatest sensitivity to the fuel sulphur level is shown by the palladium-only catalyst for controlling nitrogen oxides. In contrast, the least sensitivity to fuel sulphur is also shown by palladium-only



catalysts, for hydrocarbon control. The hydrocarbon control capability of palladium-only catalysts is currently attracting attention as an aid to meeting the stringent California hydrocarbon emission limits.

### Systems Design

The most immediate need, both in Europe and the United States, is for catalysts that are more thermally durable. In the United States the achievement of the future emission standards is contingent upon increasing the efficiency of the catalytic converter system. The simplest approach to achieve that objective consists of mounting the catalyst close to the exhaust manifold so that the catalyst warms up faster. As a result, catalyst temperatures can be expected to be significantly higher, thus an improvement in the thermal durability of the catalyst is needed.

In Europe, a similar requirement has emerged due to the use of smaller capacity, high revolution engines, which are used at much higher vehicle speeds. This, together with aiming to achieve stoichiometric calibration at all engine speeds, is resulting in a significant rise in the temperature of the exhaust and catalyst system.

The requirement for a reduction in hydrocarbon emissions promulgated in the California standards has focused serious attention on controlling vehicle emissions during cold start. Under these conditions, large quantities of hydrocarbons can be emitted prior to the catalytic converter attaining its light-off temperature.

To overcome this problem, several alternate technologies are under development. Catalyst research has concentrated on developing fast light-off catalysts, which minimise the time before which the catalyst becomes active. Electrically heated substrates are also available which heat the catalyst to above its light-off temperature either prior to or immediately after starting the engine.

An alternate approach to controlling the hydrocarbon emissions produced during cold start is to use absorbent materials in the exhaust, which trap the hydrocarbon emissions before the catalyst becomes active and later release the emissions at higher temperatures. Due to limitations in the trapping materials used, these systems require complex arrangements of valves or heat exchangers in the exhaust system, and an extremely low light-off catalyst is required

downstream to combust the emissions desorbed from the hydrocarbon trap.

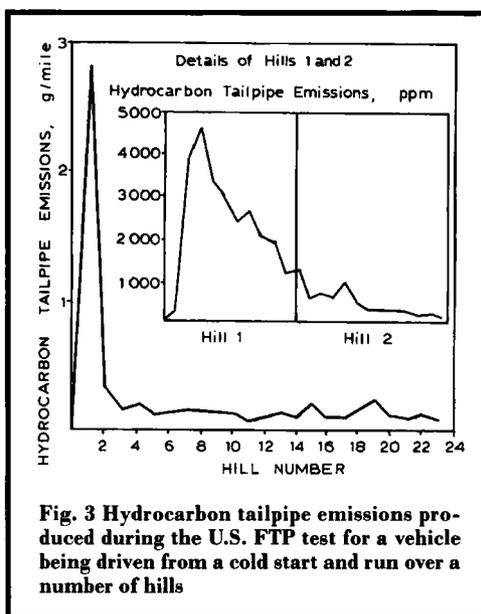
Thus, a broad picture emerges where the major thrust in catalyst development is towards producing catalysts capable of reacting extremely quickly after vehicle operation under cold start conditions. This results in an additional requirement for catalyst coatings of high thermal durability, for use in close coupled positions to the engine, and which can withstand harsh operating environments for up to 100,000 miles.

### Catalyst Substrate Designs

Virtually all emission control catalysts in use today are based on a monolith substrate design. The monolith may be either a ceramic or metallic construction, with cordierite being the preferred ceramic material, and ferritic steels being the preferred metallic material. The former is designed for low thermal expansion in order to maintain structural integrity and resistance to thermal shock. The latter is designed for oxidation resistance under high temperature conditions. Both substrates have a high surface area coating incorporating both base metals and noble metals to achieve the desired catalytic performance.

Moving a converter close to the manifold often produces space constraints within the vehicle, with the result that small converter shapes are being installed ahead of the main catalytic converter. The installation of small converters with smaller frontal areas produces flow constriction in the exhaust system and higher pressure drop. This results in power loss from the engine, which is often unacceptable to the automotive designer.

One approach to reduce the power loss is to develop thin walled substrate systems, which reduce the pressure drop. A significant increase in the intrinsic strength of the ceramic body is a necessary requirement for these thin walled substrates, so that they can withstand the canning pressures required during the insertion of the catalyst into the converter shell. This, in turn, requires a modification to the basic structure of the ceramic, especially with respect to its porosity, and also the development of adherent coatings for the new ceramic structure. All



**Fig. 3 Hydrocarbon tailpipe emissions produced during the U.S. FTP test for a vehicle being driven from a cold start and run over a number of hills**

this has been successfully achieved, so that the efficiency of a thin walled substrate catalyst is comparable to that of a conventional catalyst.

Early problems with the mechanical integrity of metal substrate systems have now been largely resolved, by improvements in fabrication technology. Metal substrates are now finding application, particularly on vehicles with small engines, where space is at a premium. The inherent benefit of using metal supports of thin walled structure has been in the lower pressure drop, and this has helped metal substrates to be accepted for such applications.

At present, attention is focused on developing metal substrates as electrically heated supports. These may be used to treat emissions during vehicle cold start, when hydrocarbon emissions are high, see Figure 3. Two principal types of metal support structures are under development.

The first consists of insulated layers of metal foil, and the second consists of an extruded powder metal support, in which the electrically conducting path is controlled through slots in the substrate. Both types of support systems have been evaluated as electrically heated catalysts (EHC), operating in conjunction with

<b>Table II</b>			
<b>Results Using Electrically Heated and Conventional Three-Way Catalysts</b>			
Metal support	U.S. FTP Emission results, g/mile		
	Non-methane hydrocarbons	Carbon monoxide	Nitrogen oxides
Extruded metal EHC	0.012	0.35	0.17
Foil EHC	0.024	0.31	0.17
California ULEV standards	0.04	1.7	0.2

Reproduced with the kind permission of Corning Glass Works and Camet Company

conventional three-way catalytic converters. Emission levels at or below those required for the California ULEV standards have been achieved on prototype systems, as Table II shows, and the durability of the systems are currently being evaluated. Future developments in this area are concentrating on reducing the power consumption required for electrical heating and on optimising battery and alternator systems.

### Advances in Catalyst Design

The most prominent three-way catalyst system in use today typically consists of platinum and rhodium as the active catalyst ingredients supported on a stabilised alumina coating containing cerium oxide as an oxygen storage component. Nickel oxide can also be added to suppress the formation of hydrogen sulphide, which is produced from sulphur in the exhaust under rich air:fuel ratio conditions. It should be noted, however, that the use of nickel oxide in catalyst systems is generally avoided in the European market due to concerns over health hazards associated with nickel. In contrast, nickel oxide is used extensively in the U.S. market, as there is no evidence to support a loss of nickel from emission control catalysts.

### Thermally Stable Catalysts

As previously mentioned a major challenge, for future catalyst systems, is to develop more thermally stable catalyst materials. This is due to the sintering of catalyst materials being significantly enhanced under typical close coupled

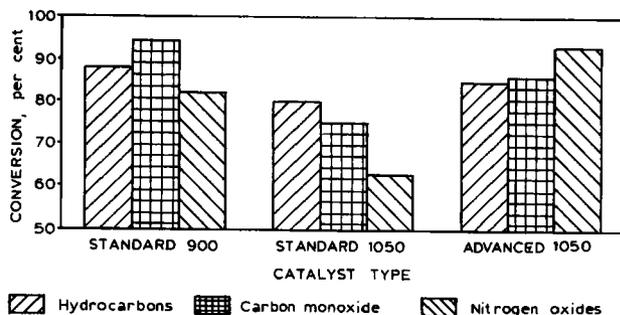
operating conditions. In the design of future emission systems it is desirable that the maximum operating temperature of the catalyst system is increased to around 950°C. Under such conditions it is expected that there will be significant loss of surface area and some crystallite growth. Thus, extensive research and development is being undertaken into methods of dispersing and stabilising the key catalytic materials for operation at higher temperatures. Incorporating these materials into new catalyst systems has given a significant improvement in high temperature durability when the system is aged at temperatures up to 1050°C, as is shown in Figure 4.

### Palladium Catalysts

In general the techniques described above, for enhancing the thermal durability of a catalyst, are most beneficial in improving the efficiency of platinum/rhodium three-way catalysts for controlling emissions of carbon monoxide and nitrogen oxides after high temperature ageing. Although the platinum/rhodium catalyst generally retains good efficiency for hydrocarbon control, it is desirable to enhance it because of the future severe standards for hydrocarbons.

Developments in palladium catalyst technology have resulted in a significant improvement in hydrocarbon control, see Figure 5. Palladium catalysts will see application in close coupled converter systems, either as a single palladium catalyst, or as a palladium catalyst in combination with a platinum/rhodium catalyst. Table

**Fig. 4 Conversion of hydrocarbons, carbon monoxide and nitrogen oxides at the stoichiometric air:fuel ratio by a standard platinum/rhodium three-way catalyst, aged at 900 and 1050°C, and by an advanced platinum/rhodium catalyst aged at 1050°C, showing that the advanced catalyst has much greater high temperature stability**



III shows a comparison of the relative performance of several converter combinations in two vehicles, employing palladium only and platinum/rhodium catalysts in close coupled and underfloor converters. The optimum converter system design on these test vehicles appears to be a combination of palladium-only and platinum/rhodium converters, to take advantage of the superior hydrocarbon control capability of palladium and the superior control of nitrogen oxides by platinum/rhodium, Figure 5.

### Low Light-off Catalysts

In the absence of further enhancements to the thermal durability of catalyst systems, the second option is to design catalysts that are much more effective under low temperature exhaust conditions. In this case the emission system designer would then have the option of locating the converter in an exhaust position which is

more remote from the engine, thus avoiding excessively high exhaust temperatures. Substantial enhancements in catalyst light-off must also be achieved to produce a significant effect during the emission test.

New catalyst formulations under development in the Johnson Matthey laboratories have demonstrated a potential for significantly lowering the light-off temperature, when compared to a conventional platinum/rhodium three-way catalyst. In Figure 6 the improvement in light-off achieved with a new catalyst formulation is shown, when measured in a laboratory reactor operating at a gas hourly space velocity of 90,000. Installation of this catalyst on a vehicle has shown promising advantages for cold start control of emissions of hydrocarbons and carbon monoxide.

As a result of such new formulations, other options have emerged, for instance low light-off

**Fig. 5 Comparison of the pollutant conversions by palladium/rhodium and palladium-only three-way catalysts from U.S. FTP results for a 4.6 l vehicle, showing the superior performance of palladium for hydrocarbon control, and platinum/rhodium for nitrogen oxides control. In all cases the advanced catalyst gives superior results**

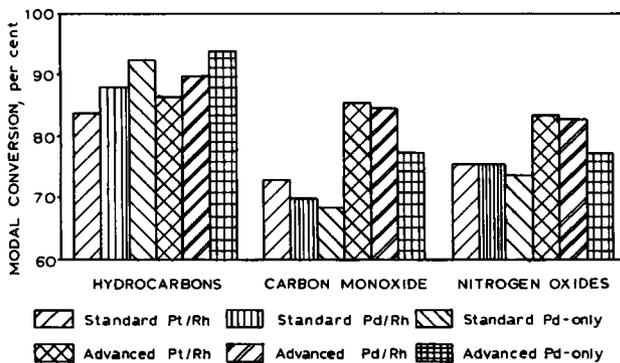


Table III Comparison of Palladium-only and Platinum/Rhodium Catalyst Efficiencies in Underfloor and Close-Coupled Positions							
Pollutant	Catalyst positions	U.S. FTP 2.2 l vehicle			U.S. FTP 2.5 l vehicle		
		Underfloor					
Hydrocarbons	Close-coupled	Catalyst	Pd-only	Pt/Rh	Catalyst	Pd-only	Pt/Rh
		Pd-only	90.1	87.8	Pd-only	90.5	89.0
		Pt/Rh	89.2	87.7	Pt/Rh	85.1	80.4
Carbon monoxide		Pd-only	91.1	91.0	Pd-only	92.8	93.3
		Pt/Rh	90.9	91.1	Pt/Rh	91.9	89.6
Nitrogen oxides		Pd-only	84.5	86.9	Pd-only	91.4	95.0
	Pt/Rh	93.0	93.5	Pt/Rh	94.2	93.7	

catalysts could be used to improve the effectiveness of converters under the low speed portion of the European driving cycle, or could be utilised to improve the effectiveness of converters in meeting TLEV and LEV standards in California. They might also be used in conjunction with electrically heated catalysts or hydrocarbon traps to meet the ULEV standards in California, which are due for implementation at the end of the decade.

### Non-Regulated Emissions of Hydrogen Sulphide

The decision to eliminate the use of nickel in catalyst formulations for the European market has presented a difficult technical challenge to the catalyst designer, who must maximise the reduction of nitrogen oxides to nitrogen while minimising the reduction of sulphur dioxide to hydrogen sulphide. Tackling this selectivity problem has generally resulted in some lowering in catalyst performance for nitrogen oxides reduction, as hydrogen sulphide formation is suppressed.

The advantage which nickel oxide provided was its ability to absorb hydrogen sulphide and release the stored sulphur as sulphur dioxide in

oxidising conditions. This allowed the catalyst designer to formulate a catalyst composition to achieve maximum activity for the reduction of nitrogen oxides.

However, it is necessary to find an effective substitute for nickel, to suppress hydrogen sulphide emissions, for the European market. The progressive improvements in catalyst technology, which have been achieved by research and development in the Johnson Matthey laboratories over the past five years, for hydrogen sulphide suppression are shown in Figure 7. The formulations that have currently been developed

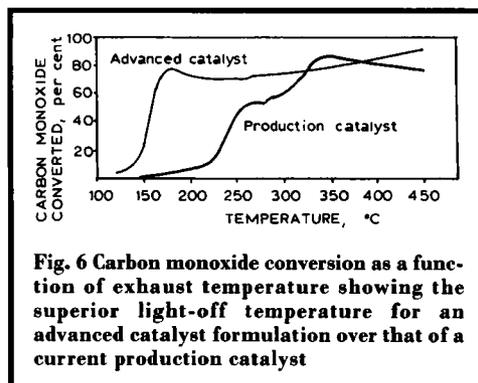
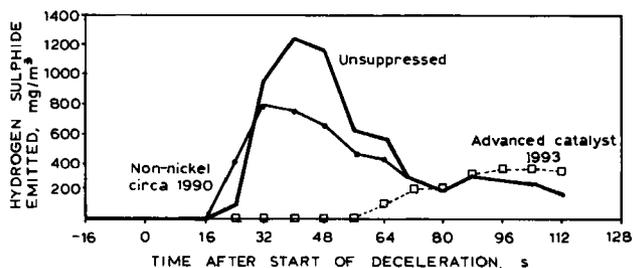


Fig. 6 Carbon monoxide conversion as a function of exhaust temperature showing the superior light-off temperature for an advanced catalyst formulation over that of a current production catalyst

**Fig. 7 Hydrogen sulphide emissions from an unsuppressed three-way catalyst, and two suppressed catalysts produced in 1990, and 1993 demonstrating the progressive reduction in hydrogen sulphide emissions in non-nickel three-way catalysts**



are effective in suppressing emissions of hydrogen sulphide, while still maintaining a high converter efficiency.

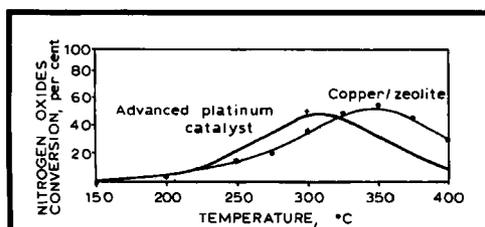
### Catalysts to Control Nitrogen Oxides under Lean Conditions

Emerging engine technologies have designs that operate at air:fuel ratios leaner than stoichiometric, giving benefits in fuel economy and a reduction in emissions of carbon dioxide, which is considered to be a serious contributor to global warming. In addition to lean burn four-stroke gasoline engines, diesel and two-stroke engines also operate at air:fuel ratios greater than 20:1. Conventional three-way catalysts can control the carbon monoxide and hydrocarbon emissions at these air:fuel ratios, but there is little ability to control emissions of nitrogen oxides. As a result, there is a tremendous interest in catalyst systems that can reduce nitrogen oxide emissions at lean calibrations.

A new range of catalyst materials has been

developed which shows activity for removal of nitrogen oxides under lean operating conditions. The new "Lean NO<sub>x</sub>" catalysts are based on zeolites containing active metals exchanged within the zeolite structure. One of the most active materials evaluated to date is copper-exchanged ZSM-5 zeolite, but this material has shown limited durability. More active and durable materials – including the platinum group metals – are being sought as catalysts for nitrogen oxide control under lean conditions, see Figure 8.

Current "Lean NO<sub>x</sub>" catalyst systems are ineffective for controlling carbon monoxide and hydrocarbons and, therefore, future systems utilising such catalysts would have to operate in conjunction with a platinum group metal catalyst to control the carbon monoxide and hydrocarbons. Measurable reductions in nitrogen oxides have been demonstrated by lean burn gasoline, diesel, and two-stroke engines using the new "Lean NO<sub>x</sub>" catalyst systems. This suggests that there will be a new approach to catalytic emission control towards the latter half of the decade, once issues of durability are solved.



**Fig. 8 Nitrogen oxides conversion by an advanced platinum catalyst compared to a copper/zeolite catalyst under lean exhaust conditions, as a function of the exhaust temperature**

### Conclusions

Significant progress is being made in the development of emission control catalysts to meet the challenges arising from tightening emission legislation. These challenges will lead to new developments in emission control catalysts throughout the rest of this decade.

Advances are being made with new substrate designs, including the advent of electrically heated substrates, for catalyst systems. The thermal

durability of catalysts is improving and enhancements in light-off temperature are being achieved with new catalyst formulations. It is likely that platinum and rhodium will continue to be the primary ingredients for controlling carbon monoxide and nitrogen oxides and that palladium will continue to emerge as an important contributor to control hydrocarbon emissions.

New horizons are now being opened for controlling nitrogen oxides under lean operating conditions, and it is felt that the most likely mar-

ket for such catalyst systems will be the lean burn diesel engine, and possibly the lean burn two-stroke engine. Both copper and platinum catalysts are under development, but problems with the durability of such catalyst systems remain to be resolved. However, this area gives the most challenging and intriguing possibilities for the design of future emission systems.

#### References

- 1 B. J. Cooper and S. A. Roth, *Platinum Metals Rev.*, 1991, 35, (4), 178-187

## Nitric Oxide Catalysis as Applied to Vehicles

A recent review paper by Kathleen C. Taylor of General Motors covers the technical literature on nitrogen oxides automotive emission control published during the period 1982-1991 (*Catal. Rev.-Sci. Eng.*, 1993, 35, (4), 457-481). The paper concentrates on three-way catalysts applied on gasoline engine vehicles, but a brief summary is also presented of recent work on lean nitrogen oxides catalysts for lean burn engine vehicles. The requirement for further reduction in nitrogen oxides emissions from vehicles is highlighted by reference to the recent tightening of standards in the United States; as outlined in the above *Platinum Metals Review* article. The paper considers the fundamentals of three-way catalyst operation and describes rhodium as the preferred metal for nitrogen oxides control, due to its high activity for their reduction and high selectivity to form nitrogen rather than ammonia.

The paper states that wide adoption of rhodium replacements such as palladium or copper appears unlikely at this stage due to the stricter control standards coming into force. It references the use of platinum in three-way catalysts together with ceria, and describes basic work on the role of ceria and its operation in conjunction with platinum and rhodium. Ceria is shown to be capable of extending the time for nitric oxide decomposition over platinum/rhodium/ceria catalysts due to the fact that the ceria absorbs oxygen from nitric oxide decomposition. Thus, ceria prevents the noble metal catalyst becoming deactivated by the accumulation of surface oxygen. Ceria is also claimed to alter favourably the reaction kinetics of carbon monoxide oxidation and nitric oxide reduction, and to decrease the apparent activation energy of the carbon monoxide/nitric oxide reaction, so favouring high conversion at low temperatures. Lower ceria particle size enhances the reduction of nitric oxide over platinum/ceria catalysts and this is attributed

to the increased platinum-ceria interaction.

The paper addresses the recent interest in the substitution of palladium for rhodium as a cost reduction move. It describes palladium as having a narrower air:fuel operating range for the control of nitrogen oxides emissions compared to platinum/rhodium, particularly under rich air:fuel conditions. This has been ascribed to poisoning of palladium sites by hydrocarbons in the exhaust, which can be alleviated by the addition of lanthanum and other additives.

The reduction mechanism for nitrogen oxides removal is described as a nitric oxide decomposition process over the noble metals, followed by the removal of oxygen from the noble metal surface via reaction with a reducing agent. Surface chemistry studies of reactions over rhodium surfaces have clearly identified the elementary steps necessary to complete the reaction process. Rhodium is found to be structure sensitive with particle size having a major effect, but crystallographic orientation only a moderate effect, on sensitivity.

The recent Auto/Oil Quality Improvement Research Program has clearly shown that fuel sulphur level can have a dramatic impact on nitrogen oxides emissions from a vehicle. During this study an increase of fuel sulphur from 49 ppm to 466 ppm showed a 9 per cent increase in the emissions with the higher sulphur content fuel. Laboratory studies have confirmed these results. Platinum and rhodium show rapid reversibility when the fuel sulphur level is lowered back to 49 ppm; however, palladium is slower to recover. The presence of ceria in the catalyst prolongs the recovery process due to sulphur adsorbed on the ceria surface.

The review is a useful compendium of the literature published during the period, particularly with respect to the mechanism and reaction of nitric oxide removal over rhodium based three-way catalyst systems.

B.J.C.