

# Automotive Exhaust Emissions Control

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The technical sessions on emissions control at the Society of Automotive Engineers' (SAE) 2003 World Congress, held in Detroit earlier this year were well attended and covered systems for conventional gasoline engines, lean-burn gasoline and diesel engines (1). Sessions on emissions from diesel engines attracted strong interest and more attendees than there were seats! This reflects the wide acceptance in Europe that modern diesel cars have gained due to improvements in recent years. Driving characteristics of modern diesel cars are now excellent with engine noise and smell virtually eliminated while high 'bottom-end torque' and good fuel economy are maintained. This raises the possibility of using modern diesel engines in North American 'pick-up trucks' and popular sport utility vehicles (SUVs) to achieve major fuel savings and reduced carbon dioxide (CO<sub>2</sub>) emissions. However, there are major challenges in meeting ultra low emissions requirements for particulate matter (PM) and nitrogen oxides (NO<sub>x</sub>).

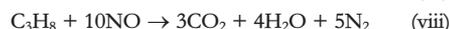
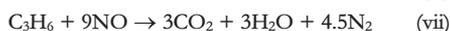
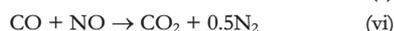
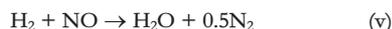
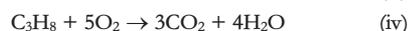
In this article a selection of technical papers highlighting the roles of platinum group metals (pgms) in catalytic emissions control systems are reviewed. The reference numbers of the papers are given in parentheses: most are available in SAE Special Publications of selected papers (2). Two of these, dealing with diesel emissions, are available on a CD-ROM ('Diesel Emission Measurement, Modeling, and Control', SP-1754CD) (3). Here, emissions control systems for conventional gasoline engines are considered first, then lean-burn gasoline and lastly diesel engine technologies.

## Conventional Gasoline Engine Catalysts

The most stringent car emissions requirements are the Californian *Super Ultra Low Emissions Vehicle* (SULEV) standards that demand hydrocarbon (HC) emissions over the American *Federal Test Procedure* (FTP) to be 0.01 g mile<sup>-1</sup> after 120,000

miles, and the even more demanding *Partial Zero Emissions Vehicle* (PZEV) standards requiring SULEV emissions levels for 150,000 miles. These emissions are so low that measuring them (engineering targets ~ 0.008 g mile<sup>-1</sup>) requires state-of-the-art analytical equipment. Such emissions can only be achieved by combining a highly efficient catalyst system with precise engine fuelling and efficient in-cylinder combustion. In fact, the catalytic conversion of HC must take place within a few seconds of engine start-up, therefore mounting the three-way catalyst (TWC) close to the exhaust manifold is essential. The use of TWCs (based on metallic substrates with different cell densities) in this close-coupled position was described in a paper by Emitec, Johnson Matthey and South West Research Institute (2003-01-0819). As expected, higher cell density catalysts improved the light-off characteristics, but key are the engine start-up strategy and the rate of temperature increase provided by the hot exhaust gas. The practical optimal catalyst cell density depends on the actual application.

The University of Stuttgart and Volkswagen (2003-01-1001) reported results from a mathematical model of a TWC operating in a high conversion SULEV system based on the following reactions:



The oxidation Reactions (i)–(iv), the reduction Reactions (v)–(viii), and the catalyst's uptake and release of oxygen Reaction (ix) describe the overall

chemistry taking place. A model in which the mechanisms involved in oxygen storage and release were combined in a single rate expression gave an acceptable mathematical description when tested against emissions from a SULEV car. The validating car had a rich start-up strategy with air injected into the exhaust gas to ensure very rapid heating of the underfloor catalyst following a cold start. There was good agreement between measured and simulated temperatures in the catalyst, and small differences were attributed to difficulties of temperature measurement. There was also good agreement between simulated and measured cold-start emissions. Special attention was given to transient behaviour and in general good agreement with the simulation was obtained. The model helped in understanding the observed overall behaviour.

The theme of advanced TWC formulations requiring less pgms than current technologies – developed at last year's Congress (4) – was continued by Honda (2003-01-0814). Honda described TWCs containing perovskite and other mixed metal oxides. Previously, perovskites lacked the stability for successful operation in modern TWCs, due, for example, to the formation of inactive aluminates and silicates. Honda's test vehicle was a 2001 SULEV car with a 2.3 litre four cylinder engine, a rapid warm-up strategy and a precisely controlled air/fuel ratio. The car had two under-floor catalysts: a 0.7 litre and a 1.0 litre on 600 cell  $\text{inch}^{-2}$  and 4.3 mil (1 mil = 0.001 inch) wall substrates; the washcoat had  $33 \text{ g ft}^{-3}$  pgm containing platinum (Pt), palladium (Pd) and rhodium (Rh) (4:25:4). After ageing to the equivalent of 120,000 miles the car was still able to meet LEV-II LEV standards for all three pollutants.

### Catalysed Hydrocarbon Trap

The use of a zeolite-based catalysed hydrocarbon trap (CHT<sup>TM</sup>) to control initially-formed HCs by retaining them until catalyst light-off is reached was discussed last year (4), and continued this year. The effectiveness of such a system depends on the zeolite used to retain the HCs, and on factors such as the types of HCs involved (older engines, for instance, produce more unburned long-chain HCs

than newer cleaner engines), and on the initial rate of exhaust gas temperature increase.

Nissan (2003-01-0816) described improvements made in emissions from the first car certified for PZEV credits. Engine-out emissions had been reduced, and a more compact catalyst system was achieved by using ultra-thin-wall ceramic substrate (1.8 mil) of reduced thermal mass. Two CHT<sup>TM</sup> stages had also been incorporated, the first placed in the close-coupled converter, behind the TWC, and the second in an underfloor position. The second CHT<sup>TM</sup> had a new cerium-based oxygen storage component incorporated into its TWC layer that improved aged HC conversion. As a result catalyst volume was reduced from 3.9 to 1.8 litres, and the amount of pgm was lowered while still maintaining the PZEV requirements.

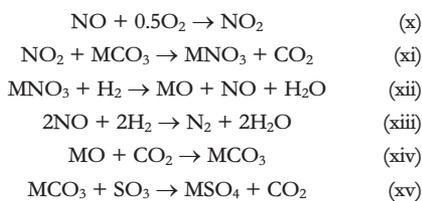
Hitachi (2003-01-0815) described eleven different transition metal- and alkaline earth metal-exchanged zeolites for enhanced HC retention. Silver-exchanged zeolite containing a few per cent silver (Ag) was found to retain *n*-pentane to about 100°C higher temperatures than pure zeolite. In practice the low oxygen level in a car's exhaust gas when operating around stoichiometry means the released HC cannot be combusted, so an oxygen storage component ( $\text{CeO}_2$ ) was incorporated into the catalyst to aid combustion. Tests were made on a V6 engine that originally had a close-coupled TWC on each bank and also an underfloor TWC. The latter was replaced by the Ag-containing CHT<sup>TM</sup>. Tail-pipe HC emissions were significantly improved, but the sensitivity of Ag catalysts to thermal sintering and poisoning by, for example sulfur compounds, may seriously restrict actual use. Nevertheless, in the light of recent reports on the effectiveness of Ag-containing lean-NOx diesel catalysts (5), it is interesting to see Ag markedly influencing the performance of CHTs.

During driving, the on-board diagnostic (OBD) system measures oxygen storage capacity (OSC) of a catalyst with two oxygen sensors, one upstream of it and one downstream. The catalyst selected for testing is usually the one nearest the engine as legislative emissions requirements will not be met if this catalyst does not function correctly.

However, taking OSC measurements of very low emissions systems can be difficult. Volvo and Emitec (2003-01-0818) reported an approach that might help. They placed the first control oxygen sensor in the front catalyst, rather than in the open exhaust gas. This protects the sensor from the effects of liquid water during cold starts, so the early heating and functioning of the sensor are no longer concerns.

## NO<sub>x</sub>-Trapping Catalysts for Lean-Burn Gasoline Engines

A lean-burn gasoline engine is not as fuel efficient as a diesel engine, but they are being developed because of their perceived advantages over diesel engines. The emissions control systems being developed typically involve a TWC mounted close to the exhaust manifold to control emissions during stoichiometric start-up and high speed driving, and an underfloor NO<sub>x</sub>-trap to store NO<sub>x</sub> during lean operation when a TWC is ineffective for NO<sub>x</sub> removal. The chemistry involved is shown in Reactions (x)–(xv).



NO<sub>x</sub> is retained in the NO<sub>x</sub>-trap as a nitrate usually derived from an alkaline earth compound (such as barium or strontium) or an alkali metal compound (such as potassium), Reactions (x) and (xi). Periodically the trap is exposed to short rich excursions to reduce stored NO<sub>x</sub> to nitrogen and regenerate the trap, Reactions (xii) to (xiv). The basic materials are gradually converted to stable sulfates during prolonged use via reaction with sulfur trioxide (SO<sub>3</sub>) derived from sulfur compounds in the fuel, Reaction (xv). Thus the NO<sub>x</sub>-trap capacity decreases over time, and rich regenerating pulses must be made more frequently. This has a detrimental effect on fuel economy. To recover maximum NO<sub>x</sub> capacity the trap must be occasionally ‘desulfated’, essentially the reverse of Reaction (xv), by treatment at higher reducing

temperatures than used to reduce stored NO<sub>x</sub>. The oxidation Reaction (x) is catalysed by Pt which is also important for Reaction (xi) and for the nitrate decomposition, Reaction (xii). Rhodium is normally the catalyst for the NO<sub>x</sub> reduction Reaction (xiii), and Pd may be incorporated to help oxidise HCs that inhibit Reaction (x).

Ford (2003-01-1162) described a rapid engine-based sulfation procedure in which sulfur dioxide (SO<sub>2</sub>) is injected upstream of the NO<sub>x</sub>-trap. When compared with NO<sub>x</sub>-traps sulfated over an extended period of normal use, the amount of sulfur absorbed was found to depend on total sulfur exposure, and both sulfated catalysts had similar desulfation characteristics. Temperature is the most important factor once desulfation is thermodynamically allowed, and although the ratio of SO<sub>2</sub>/H<sub>2</sub>S formed changes with richness, the desulfation rate follows a simple Arrhenius relationship.

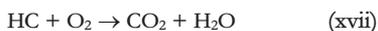
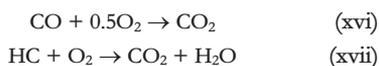
Ford (2003-01-1159) also examined NO<sub>x</sub> release from NO<sub>x</sub>-traps during regeneration. The main cause for the appearance of NO<sub>x</sub> is insufficient reductant, particularly under hot conditions. The regeneration process itself increases temperature which destabilises the nitrate; the consumption of reductant by other oxidised species exacerbates this and increases temperature. In a joint contribution Ford and Mazda (2003-01-1160) examined these factors in more detail. They found that increasing the amount of ceria-containing mixed oxide in a NO<sub>x</sub>-trap increased the time for regeneration, as did the amount of NO<sub>x</sub> released during this process. Although the presence of ceria introduces additional OSC, it also facilitates hydrogen formation via the water gas shift reaction – so there should be an optimum level of cerium.

DaimlerChrysler and OMG (2003-01-1161) described the emissions control system for a new lean-burn supercharged direct injection engine that has a close-coupled TWC and a dual flow system with a cooling section and a bypass to the underfloor NO<sub>x</sub>-trap. Active switching of gas between the main cooled section and the bypass enables the NO<sub>x</sub>-trap to operate in an optimal temperature range over a wide range of vehicle running conditions. Moreover, restricting its exposure to high temperatures ensures long life for the

NO<sub>x</sub>-trap. A NO<sub>x</sub> sensor behind the NO<sub>x</sub>-trap is used to initiate and stop the regeneration process. Emissions well below Stage IV levels were reported.

## Diesel Emissions Control

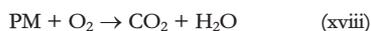
Progress made in reducing diesel emissions last year was reviewed by Corning (2003-01-0039) in what has become a traditional presentation by Tim Johnson. He indicated that tightening regulations over the next few years will force the introduction of combined technologies for NO<sub>x</sub> and PM. Diesel engines operate very lean, and when required, Pt-based oxidation catalysts achieve control of CO and HC emissions according to Reactions (xvi) and (xvii).



Modern Pt catalysts for diesel cars have been formulated to cope with both the low-temperature operation resulting from the good fuel economy of diesel engines and, to some extent, with the effects of sulfur oxides derived from sulfur compounds in the diesel fuel. The major future challenges are to reduce NO<sub>x</sub> emissions and PM (soot).

## Catalytic Particulate Control Systems

Diesel engine PM is aggregated carbon particles with a variety of adsorbed HCs and partially oxidised organic compounds, together with water, and sulfuric and nitric acids. Controlling PM is important due to their adverse health effects. Tremendous improvements have been made in recent years to reduce the amount of PM produced, but concern remains, particularly over nanoparticles. Several kinds of filter can trap PM, but then the problem lies in removing the trapped PM – by oxidation to harmless CO<sub>2</sub> and water – to prevent excess pressure drop building-up across the filter. Diesel PM burns in air above about 550°C (Reaction (xviii)), a significantly higher temperature than that of normal diesel exhaust gas.



Several approaches have been used to remove the collected PM, such as using fuel additives to

lower the combustion temperature, and including devices to increase the gas temperature. Heating devices have not been totally successful because the temperature rise from the exothermic PM combustion, if not controlled, can push the temperature in the filter to above its melting point.

One successful approach has been to combust the trapped PM with nitrogen dioxide (NO<sub>2</sub>). The combustion occurs at temperatures as low as 250°C, a temperature available during diesel truck or bus operation. The NO<sub>2</sub> is obtained by oxidising NO present in the exhaust gas over a Pt oxidation catalyst, Reaction (xix). The reaction is inhibited by SO<sub>2</sub>, so low sulfur fuel is needed for efficient operation. Under appropriate conditions such a device – an oxidation catalyst upstream of a particulate filter – can function continuously. This is called a continuously regenerating trap (CRT<sup>®</sup>).

For some heavy-duty applications NO<sub>x</sub> emissions can be reduced by applying exhaust gas recirculation (EGR) to the engine, while also controlling PM emissions and any additional PM produced by EGR with a CRT<sup>®</sup> system. Johnson Matthey and STT Emtec (2003-01-0048) reviewed the performance of over one thousand EGR-CRT<sup>®</sup> systems installed on urban buses and other heavy-duty vehicles in Europe during the last four years. Typically the EGR-CRT<sup>®</sup> system is as efficient as a CRT<sup>®</sup> for HC, CO and PM reduction, and additionally lowers NO<sub>x</sub> by 46–58%.

Future legislation requires lower NO<sub>x</sub> emissions, but a lower NO<sub>x</sub>/PM ratio will be less favourable for the ‘CRT effect-with-NO<sub>2</sub>’ to operate. One potential solution is to recycle NO<sub>x</sub> so it is used several times to oxidise PM. Delft University (2003-01-0379) described a Pt-catalysed ceramic foam filter in which the trapped PM is partially removed by reaction with NO<sub>2</sub>. If this filter is placed upstream of a monolithic wall-flow filter, sufficient NO<sub>2</sub> is available here to remove the trapped PM. Delft only gave laboratory results. One constraint may be pressure-drop limitations.

Another potential solution is to use a catalysed particulate filter with an upstream oxidation catalyst, referred to as a CCRT<sup>™</sup> (described by Johnson Matthey (2002-01-0428) last year (4)). In field trials on problematical applications the

CCRT™ could be regenerated better than a CRT®, which in turn was much better than a catalysed filter. Indeed, a CCRT™ can operate well in situations where a CRT® performance is marginal.

This year Michigan Technological University (2003-01-0049) tested a low loaded ( $5 \text{ g ft}^{-3}$ ) Pt-catalysed filter on a 1995 turbocharged 10.8 litre engine, and found good conversions for HCs, aldehydes and CO, as well as some lean-NOx under favourable conditions. The oxidation reactions were less efficient than for a conventional oxidation catalyst; PM sulfate-derived emissions were significantly increased because high sulfur-content fuel was used.

Corning and Donaldson (2003-01-0843) studied pressure-drop variations of Pt-catalysed filters loaded with PM, and highlighted the complexities. The way the filter is catalysed has a major impact on its PM loading characteristics.

While the conditions referred to above are typical of heavy-duty, large, diesel engines, they are less typical of small-engined cars where additional ways to combust PM have to be considered. For instance, Ford (2003-01-0047) reported preliminary results for a 2.5 litre turbocharged engine with a system having two active lean-NOx catalysts (with fuel injection) followed by a Pt-catalysed filter ( $50 \text{ g ft}^{-3}$ ). Ford used normal diesel and ultra low sulfur fuel. The filter was effective at removing PM; the less-than-one-percent PM that was not trapped had a size distribution similar to that of the raw gas. Filter regeneration was achieved by increasing the exhaust fuel injection rate and duration to give filter temperatures high enough for PM combustion. This worked well, with smooth regeneration taking place between 500–600°C. During regeneration when using high sulfur fuel, high PM emissions occurred because the stored sulfate was released, again highlighting the need for ultra low sulfur diesel fuel. Information about the active lean-NOx performance was not provided.

### Catalytic NOx Control Systems

Moderate NOx conversions are possible – using active lean-NOx catalysts – when HC reacts with NOx in the narrow temperature range, ~

200–250°C for Pt, defined by the catalyst activity and the temperature at which complete HC oxidation takes place. Formulations with copper work at higher temperatures (~ 350–400°C); and there is current interest in Ag formulations (see above). Iridium (Ir) has been used on a production lean-burn gasoline engine, and Industrial Power Alliance (2003-01-0044) examined its use on diesel engines.

In their paper, Industrial Power Alliance reported that an Ir-based active lean-NOx catalyst reduced NOx emissions on a Tier 1 ( $6 \text{ g kWh}^{-1}$ ) stationary heavy-duty diesel engine to Tier 3 levels ( $4 \text{ g kWh}^{-1}$ ), but the fuel economy penalty of 15% was excessive. They improved fuel economy by changing the fuel injection point and by operating the catalyst in the optimum temperature range (by masking its central portion). On applying EGR the raw NOx was reduced and the lower oxygen content improved catalyst performance. However, at low NOx levels Ir catalysts appear inefficient, and so this approach is unsuitable for more demanding standards where NOx-trapping and SCR systems are better suited.

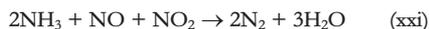
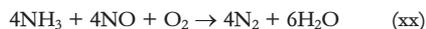
Johnson Matthey (2003-01-0045) described the optimisation of NOx-trapping catalysts for heavy-duty diesel applications by choosing suitable nitrate-forming phases to give improved high temperature performance. The low-temperature NOx-trapping characteristics have also been improved and so provide a wider operating temperature window. The improvements include an upstream Pt oxidation catalyst that removes HCs and oxidises NO to NO<sub>2</sub>.

The U.S. Environmental Protection Agency (EPA) has a programme to define the capabilities of NOx-traps for heavy-duty applications. Their previous work has demonstrated that high NOx conversions (> 90%) are possible with large catalyst volumes in a dual system with flow control valves to reduce the fuel needed to achieve rich regenerating conditions (6). The EPA (2003-01-0042) now reported an investigation of thermal ageing in high temperature (510°C) exhaust gas that is typical of high-load high-speed operation. The actual catalyst temperature was higher during reductive regeneration and, even when sulfur was

not present, the NO<sub>x</sub> conversion could significantly degrade over prolonged time. This effect depends on the catalyst formulation; the most recent formulation examined suffered only slight deterioration. The work did not examine the impact of periodic high-temperature excursions for catalyst desulfation, and this will be the basis of future work.

AVL (2003-01-0043) equipped two diesel cars with common rail fuelling and new control systems capable of providing rich exhaust-gas pulses via post injections to regenerate a NO<sub>x</sub>-trap placed in front of a catalysed PM filter. The simultaneous reduction of about 90% PM and conversion of more than 50% NO<sub>x</sub> was recorded, indicating the potential of this approach. However, a number of practical problems will require solving; for example oil dilution resulting from frequent post injections could result in serious engine deterioration.

Selective catalytic reduction (SCR) of NO<sub>x</sub> by ammonia (NH<sub>3</sub>) over a suitable catalyst can be an efficient means to reduce NO<sub>x</sub>, for example see Reaction (xx):



In a joint presentation Johnson Matthey, Volvo Powertrain, Eminox and Robert Bosch (2003-01-0778) described the design and performance of a system incorporating a SCR unit for NO<sub>x</sub> control combined with a CRT<sup>®</sup> for PM control in an extremely small package. The SCR catalyst is annular and placed around the CRT<sup>®</sup>. The four-way emissions control system is designated a SCRT<sup>™</sup>. The exhaust gas from the engine passes through the Pt oxidation catalyst of the CRT<sup>®</sup> and PM filter; urea solution is then injected into the gas flow before it passes through the annular SCR catalyst. Residual NO<sub>2</sub> not consumed in the PM combustion promotes low-temperature SCR activity, according to Reaction (xxi), and helps to provide the excellent overall performance of the compact SCRT<sup>™</sup>.

On a state-of-the-art 12 litre diesel engine with an NH<sub>3</sub>/NO<sub>x</sub> ratio of 0.95 (maximum possible NO<sub>x</sub> conversion is 95%), conversions of up to 92% in the *European Stationary Cycle* test procedure

were reported. As expected, the retention of PM and the conversions of HC and CO were also very high. A number of compact SCRT<sup>™</sup> systems are in service on vehicles, and their in-field performance will be reported later.

## Conclusions

Major advances are being made with pgm-based catalytic exhaust emissions control systems, and these are enabling stringent standards to be achieved. The overall efficiency of TWCs on gasoline cars is now extremely high, and the amounts of pgm used to achieve ultra low standards are being lowered as more advanced technologies are introduced. In comparison, control of exhaust emissions from diesel engines is at a relatively early stage of development, progress is rapid and more exciting new results may be expected at the next Detroit SAE World Congress (7).

## References

- 1 Cobo Center, Detroit, Michigan, 3rd–6th March, 2003
- 2 ‘Advanced Catalysts for Emission Controls’, SP-1756; ‘Emission Measurement and Testing 2003’, SP-1757; ‘General Emissions’, SP-1758; ‘Lean Engine NO<sub>x</sub> Control’, SP-1759; ‘Diesel Exhaust Emission Control’, SP-1754; ‘Diesel Emission Measurement and Modeling’, SP-1755. Papers in the last two publications are available on the CD-ROM SP-1754CD (‘Diesel Emission Measurement, Modeling, and Control’). The following contain related papers of interest: ‘In-Cylinder Diesel Particulate and NO<sub>x</sub> Control 2003’, SP-1738; ‘Homogeneous Charge Compression Ignition (HCCI) Combustion 2003’, SP-1742
- 3 Copies of the CD-ROM and individual papers are available from: SAE, 400 Commonwealth Drive, Warrendale, PA 15096, U.S.A.; see [www.sae.org](http://www.sae.org)
- 4 M. V. Twigg, *Platinum Metals Rev.*, 2003, 47, (1), 15
- 5 See for example: S. Satokawa, J. Shibata, K. Shimizu, A. Satsuma and T. Hattori, *Appl. Catal. B: Environ.*, 2003, 42, (2), 179 and references therein
- 6 SAE Technical Papers: 2001-01-1351; 2001-01-3619; 2002-01-2871
- 7 SAE 2004 World Congress, Cobo Center, Detroit, Michigan, 8–11th March, 2004; see [www.sae.org](http://www.sae.org)

## The Author

Martyn Twigg is the European Technology Director of Environmental Catalysts and Technologies, Johnson Matthey Catalysts. His main interests are in applying advanced chemical concepts to highly efficient emissions control systems. He is the author of numerous research papers in this area and is the editor of the book series “Fundamental and Applied Catalysis”.