

Vehicle Emissions Control Technologies

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The world's largest and most important automotive congress is held yearly in Detroit by the Society of Automotive Engineers (SAE), and regularly attracts over fifty thousand delegates. There are many technical sessions, with those devoted to describing advances in the control of exhaust gas pollutant emissions always being well attended (1). In this paper, key trends in catalyst emissions control systems which depend upon platinum group metal (pgm) catalysts are illustrated by research described in a small number of the papers presented at the 2002 World Congress (2). The reference numbers of the papers are cited in parentheses (3).

Three-Way Catalysts for Conventional Gasoline Engines

California is the home of the demanding legislation that is driving emissions control standards towards ever lower levels. The California Super Ultra Low Emissions Vehicle (SULEV) standards will reduce hydrocarbon (HC) emissions from cars in the American Federal Test Procedure (FTP) to 0.01 g/mile after 120,000 miles. The corresponding engineering targets required for series vehicle production are, of course, even lower than this. Such low levels can only be achieved with a combination of precise engine fuelling, efficient in-cylinder combustion and a highly efficient three-way catalyst (TWC) system.

To achieve the SULEV hydrocarbon levels, the catalytic conversion of HC in the catalyst system must be fully functioning within a few seconds of starting an engine. To facilitate rapid light-off a catalyst is mounted as close as possible to, or on, the exhaust manifold, but in this position it experiences higher operating temperatures than when located in the traditional underfloor location. Occasional engine malfunction could also expose this catalyst to very high temperatures because of its proximity to the engine. For example, engine misfires with concomitant substantial HC oxida-

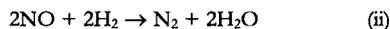
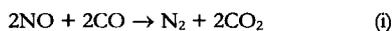
tion exotherms could take place over the catalyst. Therefore, when mounted on or near the manifold, catalyst longevity has often been a problem. Johnson Matthey and Ford have reported results (2002-01-0351) from a new generation of high performance TWCs of exceptionally high thermal durability which alleviate this problem. During evaluation of these catalysts the target catalyst ageing temperature was increased from the usual 960 to 1050°C in an ageing cycle that had occasional temperature excursions up to 1080°C. Even with this very harsh ageing both the new platinum/rhodium (Pt/Rh) and palladium/rhodium (Pd/Rh) catalysts, with pgm loadings less than a quarter of what was originally used, achieved European Stage IV emissions limits on a 1.6 litre engine.

The optimisation of pgm levels is a recurring theme for TWCs. For example, OMG have results (2002-01-0345) from a computer model calibrated using emissions data from catalyst on one car. The model was then applied to another vehicle equipped with front and underfloor catalysts. Increasing the catalyst cell-density to above 600 cpsi (cells per square inch) gave little improvement, and, when compared to the original manufacturer's system, the volume of the front catalyst could be reduced by some 40% without excessively increasing HC emissions. In addition, the pgm loading of the underfloor catalyst could be reduced by as much as 50%. This work highlights how effective new catalyst formulations are, and that the performance of the underfloor catalyst depends strongly on its interaction with the air/fuel control system (especially when there is rear sensor control) and on the response characteristics of the oxygen storage component in the catalyst.

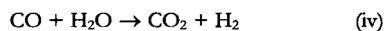
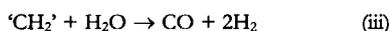
Catalytic Solutions (2002-01-0344) have been working on a sport utility vehicle (SUV) with a 4.6 litre V8 engine that has advanced LEV-II calibration, and also on a car equipped with a 2.4 litre four-cylinder engine having a SULEV calibration.

High cell-density, low thermal-mass ceramic substrates (900 cpsi for the SUV, 600 and 900 cpsi for the car) were used to facilitate fast light-off. California reformulated gasoline with a low sulfur content (40 ppm S) was used in the vehicle tests. The TWCs were aged at 950°C for the SUV, and at 900°C for the car, and not surprisingly LEV-II emissions standards were met on the SUV with less catalyst volume and less pgms than originally. The car with the SULEV calibration achieved ULEV-II limits with relatively low pgm loadings. There are benefits from having a short zone of relatively high pgm loading on the front part of a catalyst and such 'zoned' or 'striped' catalysts are already manufactured by other catalyst companies.

During hard accelerations and high-speed cruises nitrogen oxides (NO_x) are emitted at the highest levels. In cars having two catalyst systems, the larger underfloor catalyst is normally responsible for controlling NO_x emissions. N.E. ChemCat (2002-01-0348) have shown that metallic-state rhodium is the most effective active phase for reduction of NO_x to nitrogen (N₂), according to Equations (i) and (ii):



While NO_x can be reduced by carbon monoxide (CO), hydrogen (H₂) is particularly effective. Hydrogen can be obtained by HC steam reforming, and also from CO via the water gas shift reaction, see Equations (iii) and (iv), respectively, both being efficiently catalysed by rhodium:



An enhancement in the steam reforming reaction, which both removes HC and provides H₂ for facilitating NO_x reduction, appears to occur in advanced TWCs that have maximised rhodium function. Under appropriate conditions the catalyst described by N.E. ChemCat enabled some 50% reduction in pgm usage.

A zeolite-based catalysed hydrocarbon-trap (CHTTM) can help to control the initially formed HCs by retaining them until the catalyst light-off temperature is reached. The effectiveness of such a

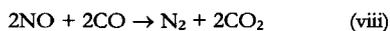
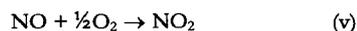
system depends on a number of often application-dependent factors, such as the nature of the zeolite used to retain the HC, and the types of HC involved at cold start. Older engines produce large amounts of unburned fuel-derived long chain HCs, whereas the cleaner engines in new cars produce lower levels of these HCs. Johnson Matthey (2002-01-0730) showed results obtained when the front catalyst on an SUV engine (that had both close-coupled and underfloor catalysts) was replaced by a CHTTM. In all cases the CHTTM improved the HC conversion. Such systems could be used in series production when HC absorbents, of the same high thermal durability as the advanced, exceptionally stable state-of-the-art TWCs, become available.

The advantages of combining advanced TWC formulations and ultra-thin-wall ceramic substrate have been explored by, for example, NGK, DaimlerChrysler and OMG (2002-01-0349). They have concluded that there is little to be gained from using cell densities higher than 900 cpsi. Catalyst canning concerns and pressure-drop considerations associated with high cell-density catalyst are seen as important and, in any case, the strategy for cold-start warm-up usually has more importance than catalyst cell-density effects.

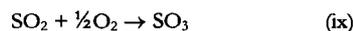
NO_x-Storing Catalysts for Lean-Burn Gasoline Engines

Operating a gasoline engine under lean conditions can improve fuel economy as fuel is burnt only when needed, particularly under part-load conditions, during idling and on low-speed cruises when full engine power is not required. Running the engine in this way is similar to the operation of a diesel engine, but it is more complex to obtain smooth combustion with gasoline spark-ignition engines, and optimal performance requires stratification of the air/fuel mixture in the cylinder. The most common technology being developed to achieve the stratification and thus optimal performance involves the direct injection (DI) of fuel into each cylinder. Normal TWCs are not good at removing NO_x from the exhaust of lean-burn engines, because NO_x cannot be efficiently reduced to nitrogen in the presence of excess

oxygen. Therefore, an alternative approach is being used which stores NO_x as nitrate phases under lean conditions, in a so-called 'NO_x-trap'. Periodically (every few minutes) the nitrate is converted to nitrogen by fuel-rich pulses in the exhaust gas; the pulses are produced by suitable adjustment of the engine management system. These reactions are illustrated by the idealised Equations (v)–(viii). Here, MO is a basic metal oxide, and under exhaust-gas operating conditions the stable species will be the carbonate rather than the oxide. Equations (v) and (vi) describe the NO_x-trapping process, and Equations (vii) and (viii) describe the regeneration process under rich conditions. Equation (v) is catalysed by Pt and Equation (viii) by Rh.



The nitrate phase in a NO_x-trap is usually derived from an alkaline earth compound (such as barium or strontium). These are basic and are gradually converted to very stable sulfates during prolonged use via reaction with sulfur dioxide (SO₂) in the exhaust gas. The SO₂ is derived from sulfur compounds originally present in the fuel, see Equations (ix) and (x). Oxidation of SO₂ to SO₃, Equation (ix), is catalysed by Pt.



As a result the capacity of the NO_x-trap decreases over time and so the fuel-rich regeneration pulses have to be made more frequently. This has a detrimental impact on fuel economy. Ideally it is desirable not to have any sulfur compounds in the fuel as, even with low sulfur fuel, sulfate will accumulate in the NO_x-trap. To overcome this problem it is necessary to periodically 'desulfate' the NO_x-trap by exposure to very high-temperature reducing conditions to recover the original NO_x-trapping capacity.

One means of achieving high catalyst temperature to desulfate the NO_x-trap has been described by Ford (2002-01-0733). They alternate the

air/fuel ratio so that the oxygen stored in the NO_x-trap during lean periods is used to oxidise HC, CO and H₂ in the high temperature, enriched periods. By continuing this process high desulfation temperatures can be achieved even during low-load operation. Ford have characterised the sulfate species present in the sulfated NO_x-traps by infrared spectroscopy, and have showed that surface sulfate species decompose more easily than the bulk compounds.

Ford have also (2002-01-0731) described an online method for estimating the sulfate levels in NO_x-traps. It involves closed loop NO_x-trap purging, with one heated exhaust gas oxygen (HEGO) sensor positioned before the NO_x-trap and one after, to provide information about the oxygen and NO_x storage capacities. If the oxygen storage capacity (OSC) does not change significantly over time the NO_x capacity changes can be seen in the observed values. This could form the basis of a control system for a desulfation strategy. It is possible that if the nitrate and OSC capacities have different chemical reactivities, they could be accessed under different temperature conditions.

Volkswagen and OMG (2002-01-0346) have described in detail the engine management and exhaust gas emissions control systems on the lean-burn FSI (fuel stratified injection) engine in the VW Lupo. Here a NO_x sensor (4), downstream of the NO_x-trap, is used to monitor NO_x-trap activity and to initiate regeneration. The system is adaptive and only undergoes rich regeneration when the trap is sufficiently full to warrant it. This feature further improves fuel economy. However, overall fuel economy depends on the sulfur content of the fuel since this determines how frequently the fuel-consuming desulfations take place. When the desulfation regeneration does take place there is a danger that hydrogen sulfide might form under the high-temperature rich conditions. This is eliminated by periodically switching between rich and lean conditions. As noted above this will also tend to maintain the high temperature because the oxygen stored in the NO_x-trap and on other catalysts in the system burns the combustible components in the rich gas.

OMG (2002-01-0057) are also working on the

dynamic chemical processes taking place in a NO_x-trap during NO_x absorption and subsequent regeneration. They have developed concepts relating to NO_x storage sites at the surface and in the bulk. The former are readily available, are initially occupied and readily regenerated, while access to the latter is diffusion limited and proceeds via a shrinking core-type process.

Toyota (2002-01-0732) have used potassium compounds to trap NO_x at temperatures higher than are possible with alkaline earth species, and their formulations contain materials such as titania and zirconia to provide improved sulfur tolerance. However, the very low sulfur-containing gasoline that is needed to obtain the required levels of fuel economy is not yet widely available.

Catalytic Particulate Control Systems for Diesel Engines

Soot or particulate matter (PM) from a diesel engine may be considered as a high-surface carbon core onto which are adsorbed a variety of HC species and other partially oxidised organic compounds, together with water and sulfuric and nitric acids. Controlling diesel exhaust gas PM emissions attracts attention because of potential adverse health effects, particularly in the urban environment.

Several kinds of filter could be used to trap the PM, but the trapped PM must be removed to prevent the build-up of an excess pressure drop across the filter that would prevent the engine functioning properly. The trapped PM has to be removed by oxidation to harmless CO₂ and water. The temperature at which diesel PM burns in air (typically > 550°C) is significantly higher than the normal temperature of the exhaust gas from a diesel engine. Several approaches have been used to remove PM and prevent a filled filter from causing excessive backpressure. These include fuel additives to lower the combustion temperature of the PM, and various heater devices to increase the gas temperature. In the past, the use of electrical heaters or burners resulted in serious problems as the temperature rise caused by the exothermic combustion above the ignition temperature had sometimes melted the filter material!

The most successful approach, however, has been to combust trapped PM with nitrogen dioxide (NO₂) rather than oxygen. The reaction with NO₂ takes place at relatively low temperatures, and can be achieved on a heavy-duty diesel engine, in a truck or bus, during most operating conditions. The required NO₂ is obtained by oxidation of the already present NO in the exhaust gas, by passing it over a Pt oxidation catalyst. Thus the device requires no attention during normal use. However, catalytic oxidation of NO is inhibited by the presence of SO₂ in the exhaust gas, so low sulfur fuel is necessary. This device, comprising an oxidation catalyst upstream of a particulate filter, can function continuously at appropriate temperatures. It is called a continuously regenerating trap (CRT™).

In California, a large collaborative programme involving ARCO, National Renewable Energy Laboratory, Johnson Matthey, West Virginia University, Engelhard, Battelle, and Abilene Christian University (2002-01-0433) has monitored heavy-duty diesel test fleets operating on low sulfur diesel fuel and retrofitted with either a CRT™ system or a catalysed particulate filter. The vehicles included grocery trucks, tanker trucks, refuse haulers, school buses and transit buses. After operating for a year the emissions were evaluated. The huge volume of results confirmed that retrofitted systems performed well, with little or no significant loss in their ability to reduce PM emissions – to over 90% in some instances after almost 200,000 miles.

Another field trial, this time with New York City buses fitted with a CRT™, has been reported by Johnson Matthey, Environment Canada, New York City Transit, New York State Department of Environmental Conservation, Equilon Enterprises, Corning and Sprague Energy (2002-01-0430). Again, after about a year in service, reductions in particulate emissions to more than 90% were found, demonstrating the long term durability of the CRT™ in appropriate applications.

Johnson Matthey have also developed (2002-01-0428) a modified CRT™ system which has a Pt-catalysed PM filter as well as an upstream oxidation catalyst – the CCRT™. Its performance has

been compared with that of a conventional CRT™ and with a catalysed filter. The regeneration efficiency of the CCRT™ has been found to be better than that of a CRT™, which in turn is significantly better than only a catalysed filter. The CCRT™ operates well in problematic situations where CRT™ performance is marginal. This is probably due to reoxidation in the filter of NO, formed from PM oxidation by NO₂. Each NO molecule is therefore used several times in PM oxidation via reaction with NO₂.

In situations where the exhaust gas temperature is too low for the PM/NO₂ reaction to be effective or where the NO_x:PM ratio is too low for the reaction involving NO₂ to remove all of the PM, it is necessary to provide a means of increasing the temperature to 550°C or higher to initiate PM combustion with oxygen. In cars with diesel engines this can be achieved by having a flexible fuelling system that enables injection of fuel into the cylinders during exhaust strokes, or perhaps injection of fuel directly into the exhaust gas. Partially burnt fuel in the exhaust gas is then oxidised over the Pt catalyst in front of the filter, and the exotherm produced is sufficient to raise the gas temperature to the point where the PM burns. However, it is important to control the rate of PM combustion in the filter to limit excessively high exotherm temperatures, particularly when the exhaust gas flow rate is low. Ford (2002-01-0427) have highlighted the practical control parameters that could be used to do this and have concluded that it is best to restrict the amount of oxygen present during combustion. This can be done reliably by combining exhaust gas recirculation (EGR) with an inlet air throttle. A strategy that can deal with transient response needs combined with as much forward control as possible is deemed to be necessary for overall successful operation.

Conclusions

Significant advances in the exhaust emissions control areas are taking place, and in many of them pgm-based catalysts play vital roles. Over recent months in Europe the demand for diesel powered cars has been growing. Some of the emissions control systems described here will help towards

achieving future emissions legislation requirements. If these systems show good in-field durability this could further increase the interest in diesel light-duty applications in North America, which would result in lower CO₂ emissions and significant fuel savings. At the next Detroit SAE World Congress we can confidently expect that further innovative and exciting developments in emissions control technology will be reported.

References

- 1 For a review of previous years' emissions control papers at the Detroit SAE see: *Platinum Metals Rev.*, 2001, 45, (2), 71; *ibid.*, 2000, 44, (2), 67
- 2 Cobo Center, Detroit, Michigan, 4–7th March, 2002
- 3 Most papers are available in electronic format on two CD-ROMs ('New Emission Technology from the SAE 2002 World Congress', SP-1703CD, and 'Direct Injection SI Engine Technology 2002', SP-1693CD). Copies of these and individual papers are available from: SAE, 400 Commonwealth Drive, Warrendale, PA 15096, U.S.A. See also www.sae.org
- 4 For a description of the principles of operation of the NO_x sensor see: M. V. Twigg, *Platinum Metals Rev.*, 1996, 40, (3), 111

The Author

Martyn Twigg is the European Technical Director of Johnson Matthey Catalytic Systems Division. 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".

Ruthenium Light-Switch Effects

Scientists at the University of North Carolina at Chapel Hill, U.S.A., report temperature-dependent excited-state lifetime measurements, in protic and aprotic solvents (MeOH, BuCN, MeCN) on [Ru(bpy)₂dppz]²⁺ which suggest that the light-switch effect is competitive (M. K. Brennaman, J. H. Alstrum-Acevedo, C. N. Fleming, P. Jang, T. J. Meyer and J. M. Papanikolas, *J. Am. Chem. Soc.*, 2002, 124, (50), 15094–15098).

The dppz ligand has bpy-like and phz-like states. The bpy is associated with the bright state and phz with the dark state. The bpy-like state is similar in size to the corresponding orbital in the ³MLCT state in [Ru(bpy)₃]²⁺; it is entropically favoured and populated at high temperatures. The dark state is lowest in energy and is populated at low temperatures. The switch effect results from competition between the energetic and entropic factors, not from state reversal.