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Throughout his long and distinguished career with the Ford Motor Company Haren Gandhi was concerned with controlling tailpipe pollutants from cars, and through his work this article reviews the huge amount of progress made during his four-decade career. His early work with gasoline engines embraced all of the major developments ranging from the first platinum-based oxidation catalysts through nitrogen oxides (NOx) reduction using platinum-rhodium catalysts and the later introduction of palladium into three-way catalysts (TWCs) via ‘trimetal’, palladium-rhodium and palladium-only formulations. Gandhi’s other work included the interactions of poisons with catalysts as part of maintaining their in-use performance, the potential for using ruthenium in NOx control in gasoline TWCs and NOx adsorbing catalysts (NACs) for lean-burn engines, and the use of zeolite-based selective catalytic reduction (SCR) catalysts for effective diesel engine NOx control. Gandhi received many awards and honours in recognition of his technical achievements and a selection is mentioned here. Haren Gandhi is remembered with tremendous fondness and respect throughout the automotive industry concerned with exhaust gas emissions control and his technical contributions towards improving the quality of the air we breathe will continue to benefit us all.

Haren Gandhi: An Appreciation
Harendra Sakarlal Gandhi (Haren, as he was known) (Figure 1), was born into a large family in Calcutta, India, on 2nd May 1941 and raised in Bombay (Mumbai), the capital of the State of Maharashtra and then the most populous city in the world. He obtained a first class honours degree from the Department of Chemical Technology at the University of Bombay in 1963. Later he moved to the USA where he attended
the University of Detroit, and on 15th February 1967 he joined the Ford Motor Company in Dearborn, Michigan, as a Research Engineer while still studying. In the same year he was awarded a Master of Science degree, and in 1971 he gained a doctorate in Chemical Engineering with a thesis entitled “Adsorption of Nitric Oxide on Transition Metal Oxides”. By the time Gandhi had completed his doctoral research, the US 1970 Clean Air Act had been signed. This required a 90% reduction of carbon monoxide (CO) and hydrocarbon (HC) emissions from 1970 model year levels by 1975, and a 90% reduction of nitric oxide (NO) emissions from 1971 model year levels by 1976. These requirements were major challenges to the car industry, and Gandhi joined a research team dedicated to achieving them.

Haren Gandhi spent his working life with Ford, first as a research engineer and, after a number of engineering and scientific positions in the area of automotive catalysis and emissions control, as a Henry Ford Technical Fellow overseeing Ford’s worldwide emissions control projects. He had a keen awareness of the social benefits that result from improved urban air quality delivered by emissions control catalysts, and he wished to extend these benefits around the world and especially to developing countries. He began early in the catalytic control of exhaust pollutants, and his successes were driven by a love and enthusiasm for his work that was supported by always having a creative research group of excellent scientists and engineers at Dearborn, coupled with the strong technical links that he developed with leading scientists from global catalyst manufacturers. He was a visionary leader with openness to new ideas and an ability to translate science and research into innovative products that went to series production. He worked closely with US government organisations such as the Environmental Protection Agency (EPA) and the California Air Resources Board (CARB), as well as national laboratories and universities. Haren Gandhi is shown in Figure 1 when, on one of his regular European visits, he was invited to the UK House of Lords to help clarify the detrimental effects sulfur from fuel has on the performance of autocatalyst systems.

Gandhi was always a most honourable person with a strong professional appreciation of the ethics associated with commercial dealings. Through his successes he raised the profile of all those who innovate and are responsible for introducing new technologies, especially those associated with transportation. Haren Gandhi passed away on 23rd January 2010 and he will be deeply missed by his many friends around the world, although his technical contributions towards improving the quality of the air we breathe will continue to benefit us all. Above all Haren Gandhi was a family man, and many technical meetings with him started with talk about his most recent family holiday or how his grandchildren were developing; he leaves his wife Yellow, his daughter Sangeeta and his son Anand.

Recognition and Awards
Apart from his earliest research, almost all of Gandhi’s work involved the application of platinum group metals (pgms), and his successes were largely based on the tremendous catalytic activity these metals can have in optimally formulated practical catalysts. Gandhi was keenly aware of the unique roles pgms have in controlling tailpipe emissions. He often recalled the experience of visiting a pgm mine and

Fig. 1. Dr Haren Gandhi photographed on 18th July 1996 prior to attending a meeting accompanied by the present author in the House of Lords with Lord Porter and Lord Lewis, to discuss the impact of fuel sulfur levels on catalytic emissions control systems
seeing for himself the very low levels of these metals in the ore that necessitate extensive concentrating and refining to provide pure salts of the metals for the manufacture of catalysts.

One of the earliest awards Gandhi received was the Chemical Engineer of the Year Award from the Detroit Section of the American Institute of Chemical Engineers (1984). This was followed by others including the UK Institution of Mechanical Engineers (IMechE) Crompton Lanchester Medal (1987), the Society of Automotive Engineers (SAE) Ralph R. Teetor Industrial Lectureship Award (1988–1989), the Technological Innovation Award by Discover Magazine (1990), the Award for Excellence in Catalysis by Exxon (1992) and his election to the US National Academy of Engineers (1999). He heads the list for the number of Henry Ford Technological Awards, with the last, in 2009, being for the development and integration of virtual design and optimisation of global diesel after-treatment systems. But his chief award, and most prized by him, was the US National Medal of Technology for research, development and commercialisation of automotive exhaust catalyst technology and precious metal utilisation that he received from President George W. Bush in 2002.

Contributions to Catalytic Emissions Control Systems

Oxidation Catalysts

In anticipation of the 1975 implementation of the 1970 Clean Air Act several approaches were investigated to meet the demanding HC and CO tailpipe reduction targets. These included non-catalytic means such as running gasoline engines lean and having post-engine thermal combustion devices. But it became appreciated that the initial requirements could be met by using an oxidation catalyst in conjunction with an air pump to ensure that the exhaust was sufficiently lean (containing excess oxygen) for the oxidation of residual HC and CO to small amounts of carbon dioxide (CO₂) and water (H₂O), Equations (i) and (ii), to take place.

\[
\begin{align*}
2\text{CO} + \text{O}_2 & \rightarrow 2\text{CO}_2 \quad (i) \\
2\text{CO}_m\text{H}_n + (2m + \frac{1}{2}n)\text{O}_2 & \rightarrow 2m\text{CO}_2 + n\text{H}_2\text{O} \quad (ii)
\end{align*}
\]

Base metal catalysts were inadequate in terms of long-term activity and poison resistance (1) while platinum-based ones performed well, and once sufficient durability was demonstrated catalytic oxidation was successfully introduced into production. At this time a profound decision of lasting importance was to use coated monolithic ceramic honeycomb catalyst structures, rather than traditional catalyst pellets initially employed by some other companies which lacked long-term physical durability. The addition of a second pgm to oxidation formulations was used by catalyst manufacturers to provide improved durability, by inhibiting sintering of the very small catalytically-active platinum crystallites under lean conditions. This could be done with either palladium or rhodium and for technical reasons Johnson Matthey used small amounts of rhodium. Later this took on special significance when NOx emissions also had to be controlled – NOx refers to the combined NO and nitrogen dioxide (NO₂) emissions. The control of tailpipe emissions with just an oxidation catalyst only lasted a short time because the need to reduce NOx emissions by 1976 required implementation of more complex catalyst systems.

NOx Reduction

It was apparent that engine measures alone, such as exhaust gas recycle (EGR) used to moderate the formation of NOx in an engine by reducing the levels of oxygen present during combustion, would not be sufficient to meet the NOx emissions limits by 1976. It would be necessary to convert NOx to inert nitrogen (N₂) to meet the demanding legislation, and a huge amount of research was directed to understanding how this difficult transformation could be achieved. At Dearborn, Ford was in the thick of NOx reduction research. A key scientist there, who became very important, was Mordecai Shelef with whom Haren Gandhi worked (2, 3). The possibility of using base metal catalysts had appeal and this approach was thoroughly explored; indeed Gandhi’s doctoral work was concerned with some of the relevant fundamental chemistry. Although dissociation of NO into its elements is thermodynamically favoured, under practical lean conditions this could not be done. The most active surfaces for NO dissociation are metallic, and dissociative adsorption of NO, Equation (iii), can be followed by rapid desorption of N₂, Equation (iv). However, oxygen atoms remain strongly adsorbed on the catalyst surface, and soon coverage by oxygen is complete and this prevents further adsorption of NO so its dissociation is halted. Effectively the surface is poisoned by adsorbed oxygen atoms, and under the prevailing conditions they can only be removed through reaction with a reductant, for example with...
hydrogen, as illustrated in Equation (v), or with CO as in Equation (vi), to provide a clean active surface for further NO dissociation.

\[
\begin{align*}
2\text{NO} & \rightarrow 2\text{N}_{\text{ads}} + 2\text{O}_{\text{ads}} \\
\text{N}_{\text{ads}} + \text{N}_{\text{ads}} & \rightarrow \text{N}_2 \\
\text{O}_{\text{ads}} + \text{H}_2 & \rightarrow \text{H}_2\text{O} \\
\text{O}_{\text{ads}} + \text{CO} & \rightarrow \text{CO}_2
\end{align*}
\]

These equations do not imply intimate mechanistic detail, but rather highlight the key role that surface oxygen plays in inhibiting NO dissociation. Consequently, at that time NO emissions could only be controlled by reduction to N\textsubscript{2} in the absence of oxygen. It was found that the most catalytically active metals for this process were rhodium and ruthenium, and Gandhi explored the use of both. The reduction of NO became a theme that ran throughout his career.

**Reduction/Oxidation Systems**

The first practical system to control all three pollutants from cars used two separated pgm-based catalysts (4), the first reduced NO\textsubscript{x} to N\textsubscript{2} and the second oxidised HC and CO to CO\textsubscript{2} and H\textsubscript{2}O. The upstream catalyst operated under rich conditions and, after addition of excess oxygen from an air pump, HC and CO were oxidised over the downstream catalyst. However, chemical complexities including over-reduction of NO\textsubscript{x} to ammonia (NH\textsubscript{3}) by the first catalyst took place with some formulations, with remarkably high selectivity and high conversion (5–7). NH\textsubscript{3} emissions are undesirable, although any NH\textsubscript{3} formed in this way would almost certainly be oxidised back to NO\textsubscript{x} over the downstream oxidation catalyst, causing significant overall NO\textsubscript{x} conversion inefficiency. To combat this, catalyst selectivity was improved and operating conditions were kept not too rich. Such two-catalyst systems for controlling HC, CO and NO\textsubscript{x} emissions were effective, but the catalyst and ancillary equipment cost was high.

**Three-Way Catalysts (TWCs)**

Fundamental work on conversion of the three pollutants HC, CO and NO\textsubscript{x} as a function of air to fuel ratio showed that if a gasoline engine is operated around the stoichiometric point (an air to fuel ratio of about 14.7) a single platinum-rhodium catalyst could remove the three pollutants simultaneously, and this concept was christened the three-way catalyst (TWC) (8, 9) (Figure 2). There was a strong drive for the introduction of TWCs because of improved cost and efficiency, but well-controlled stoichiometric engine operation required implementation of three new key technologies:

(a) An oxygen sensor to determine whether the exhaust gas is on the lean or rich side of the stoichiometric point;

(b) An electronic fuel injection (EFI) system to permit metering precise amounts of fuel into the engine to maintain stoichiometric operation;

(c) A microprocessor for closed-loop feedback control of the overall system.

By the late 1970s all these features had become available, and TWCs came into production in the early

---

Fig. 2. Photograph of a cut-away three-way catalyst (TWC) converter of a type much used by Ford in Europe in the early 1990s. For a long time two separate TWCs were contained in one can, perhaps reflecting the time when two separated catalysts were used with different functions.
1980s as the technology of choice for controlling all three legislated pollutants (10). Subsequent addition of components such as air mass flow meters, better oxygen sensors, substantial microprocessor and software improvements and major catalyst improvements enabled TWCs to be integrated into the engine management system with remarkable results. Today TWCs can achieve almost complete removal of the three legislated pollutants, while an onboard diagnostics (OBD) system monitors their performance via measurement of oxygen storage capacity with two oxygen sensors. Table I illustrates trends in Californian emissions limits set by CARB since 1993 (11) that for several years guided the direction of Gandhi’s work. The SULEV hydrocarbon limit after 120,000 miles’ driving (0.010 g mile\(^{-1}\), and significantly less than this when the vehicle is new) can be compared with the 15 g mile\(^{-1}\) of a typical mid-1960s US car to provide a direct indication of the progress made in controlling emissions over three and a half decades. Indeed, tailpipe emissions of regulated pollutants from gasoline cars can now be less than levels in ambient air, so it could be said that during Gandhi’s career the situation moved from these emissions being a major

<table>
<thead>
<tr>
<th>Year</th>
<th>Category</th>
<th>Emissions (g mile(^{-1}), FTP Test)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HC</td>
</tr>
<tr>
<td>1993</td>
<td>–</td>
<td>0.25(^a)</td>
</tr>
<tr>
<td>1994</td>
<td>Tier 1</td>
<td>0.25(^b)</td>
</tr>
<tr>
<td>2003</td>
<td>Tier 1</td>
<td>0.25(^c)</td>
</tr>
<tr>
<td>2004</td>
<td>TLEV(_1)^d</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>LEV(_2)^e, f</td>
<td>0.075</td>
</tr>
<tr>
<td>2005</td>
<td>LEV(_1)^d</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>ULEV(_2)^g</td>
<td>0.040</td>
</tr>
<tr>
<td>2006</td>
<td>ULEV(_1)^d</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>SULEV(_2)^e, f, g</td>
<td>0.010</td>
</tr>
<tr>
<td>2007</td>
<td>ZEV(_1)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>ZEV(_2)</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)NMHC = non-methane hydrocarbons, i.e., all hydrocarbons excluding methane
\(^b\)NMOG = non-methane organic gases, i.e., all hydrocarbons and reactive oxygenated hydrocarbon species such as aldehydes, but excluding methane. Formaldehyde limits (not shown) are legislated separately
\(^c\)FAN MOG = fleet average NMOG reduced progressively from 1994–2003
\(^d\)LEV\(_1\) type emissions categories phased out 2004–2007
\(^e\)LEV\(_2\) type emissions limits phased in 2004 onwards
\(^f\)LEV\(_2\) standards have same emission limits for passenger cars and trucks <8500 lb gross weight
\(^g\)SULEVs onwards 120,000 miles durability mandated

Note: TLEV = transitional low emission vehicle, LEV = low emission vehicle, ULEV = ultra low emission vehicle, SULEV = super ultra low emission vehicle, ZEV = zero emission vehicle,
CARB = California Air Resources Board, FTP = Federal Test Procedure
contributor to atmospheric pollution to one in which car use could help to reduce their levels in the air! And this was achieved with no more pgm per car than originally employed (Figure 3), thanks to the tireless efforts of Gandhi and other catalyst scientists in the automotive industry.

**Ruthenium Catalysts**

Although platinum-rhodium-based catalysts were discovered to be effective in NOx reduction, during the search for NOx reduction catalysts it was found that ruthenium was particularly effective and had the advantage of being cheaper than rhodium. However, the major problem encountered with ruthenium (and also to a lesser extent with iridium) catalysts is metal loss via volatile higher oxidation state oxides. Gandhi with his colleagues undertook research aimed at stabilising ruthenium catalysts against metal loss by forming stable ruthenates, and this was the subject of some of Gandhi’s first patents (12–16). There was some success (17–19), although real-world performance and durability proved insufficient to displace rhodium from platinum-rhodium TWC formulations.

**Palladium Catalysts**

The pgms have outstanding catalytic activity and ruthenium was one of the cheapest for NOx reduction, but because of durability concerns it was inappropriate for autocatalyst applications. The next most cost-effective metal was palladium, but it is very sensitive to poisoning by lead and sulfur. Unleaded gasoline was introduced to allow the use of catalysts, and when fuel sulfur levels were reduced in the early 1990s, it became feasible to incorporate palladium into platinum-rhodium catalysts to form commercially successful ‘trimetal’ TWCs (20). These still contained a high proportion of platinum. Palladium-rhodium formulations were later developed that actually outperformed the older, more costly platinum-rhodium TWCs. Gandhi became a strong advocate for the development of ‘palladium-only’ formulations that provided very good HC control and sufficient NOx control to meet the legislative requirements of the time. Gandhi pushed catalyst manufacturers to develop palladium-only TWC formulations with exceptional thermal durability and this was achieved, allowing durable palladium-only products to enter series production in the mid-1990s (21). The increased demand for palladium caused its price to increase and this, together with more demanding legislation that required tighter NOx control, took rhodium back into TWC formulations (see Table 1). However, the experience and knowledge obtained in the development of palladium-only catalysts was...
transferred by catalyst manufacturers to developing advanced palladium-rhodium formulations (22) that led to remarkable TWCs for super ultra low emission vehicles (SULEVs) with astonishing performance and durability using relatively low pgm loadings (23).

Sources and Effects of Catalyst Poisons
Throughout his career Gandhi was involved with understanding the effects of poisons on automotive catalysts. In fact, the introduction of catalytic control of exhaust pollutants was only possible once unleaded gasoline was made available (for many years significant levels of toxic tetraethyl lead (TEL) were used to enhance the octane rating of gasoline). Lead is a powerful catalyst poison that blocks surface active sites and forms inactive alloy phases with pgms (24). Sulfur, a common catalyst poison, originates from gasoline and also lubrication oil (25). Other poisons derived from lubrication oil include calcium, zinc and phosphorus compounds. Phosphorus can form glassy surface layers on the catalyst that prevent gases reaching the active components (26) as well as being responsible for other problems (27, 28). Some TWCs are also susceptible to forming redox-inert cerium phosphate that degrades washcoat structure and depletes its vital oxygen storage capacity (29). Addressing these problems, which forms part of ensuring that in-use catalyst activity is maintained, concerned Gandhi. In this area he was also much troubled by the use of the lead-substitute octane enhancer methycyclopentadienyl manganese tricarbonyl, because manganese oxide deposits which form from it degrade engine performance by fouling the spark plugs and engine internals (30). In the exhaust system these deposits can inhibit the behaviour of the oxygen sensors which are instrumental in the proper running of the engine and OBD measurements. Catalyst performance can also be impaired through a surface coverage/blocking process (31–37). Recently the manganese fuel additive was reported to form ultra-fine nanoparticle tailpipe emissions (38, 39) that may themselves give rise to health concerns (40).

Lean-Burn Gasoline Engines
Over the last decade or so there has been growing interest in the reduction of greenhouse gas emissions. Widespread use of lean-burn engines, especially diesel engines (see below), with improved fuel economy could make significant contributions to lowering emissions of the main greenhouse gas, CO₂, and starting in the mid-1990s lean-burn gasoline engines had a revival for this reason. The possibility of operating gasoline engines under lean conditions with direct injection of fuel into the cylinder has a number of attractions, including increased power and fast response as well as some fuel economy benefits. Several lean-burn direct injection gasoline engines in cars followed Mitsubishi’s 4G93 1.8 litre engine which was first used in Japan and came to Europe in the Mitsubishi Carisma model in 1995. The fuel mixture is stratified in the cylinder of these engines so that it can be ignited by the spark plug, and progressively the mixture is leaner further away from the ignition point, so overall the combustion is lean. Thus the main emissions challenge was to control NOx emissions under lean conditions. Because of these considerations, controlling pollutants from lean-burn engines became the focus of some of Gandhi’s latest work at Ford.

The typical catalytic emissions control system for a direct injection lean-burn gasoline engine, illustrated
in Figure 4, has in practice a close-coupled TWC for use when the engine runs stoichiometrically (usually when starting and during acceleration) and an oxidation catalyst to control HC and CO emissions when the engine runs lean (41). NOx is then removed by a cooler downstream NOx absorbing catalyst (NAC) (also known as a lean NOx trap (LNT)) through a process involving oxidation to NO2 over a platinum component followed by its reaction with an alkaline component to form a nitrate phase, as illustrated in Equations (vii) and (viii). Before the absorbing catalyst is saturated with nitrate the exhaust is enriched, causing the nitrate to destabilise and decompose, Equation (ix), liberating NO that is reduced to N2 over a rhodium component in much the same way as in a TWC. Under operating conditions the alkaline component (M), usually the alkaline earth metal barium, when not nitrated is present as a carbonate, Equation (x). The overall process is called ‘regeneration’ and typically takes place every minute or so, with enrichment lasting around a second (Figure 5) (42).

\[
\begin{align*}
    \text{NO} + \frac{1}{2} \text{O}_2 &\rightarrow \text{NO}_2 \quad \text{(vii)} \\
    \text{MCO}_3 + \text{NO}_2 &\rightarrow \text{MNO}_3 + \text{CO}_2 \quad \text{(viii)} \\
    \text{MNO}_3 &\rightarrow \text{MO} + \text{NO} + \frac{1}{2} \text{O}_2 \quad \text{(ix)} \\
    \text{MO} + \text{CO}_2 &\rightarrow \text{MCO}_3 \quad \text{(x)}
\end{align*}
\]

In a typical Gandhi way he embraced these concepts with energy and vigour (43–45), and even returned to his desire to use ruthenium-based catalysts – one of his recent patents uniquely uses ruthenium in NAC formulations (46). He considered lean operation of gasoline engines under a variety of situations, including when idling, as a way to help improve real-world fuel economy. However, none of these approaches have yet gained widespread acceptance, perhaps because of technical complexity and the cost of direct injection. However, the combination of an upstream NAC over which NH3 can be formed during regeneration if the exhaust is sufficiently rich, followed by an SCR catalyst (see the section on Diesel Engines) that uses this NH3 to reduce residual NOx, may well gain acceptance in diesel engine NOx control (47) as evidenced by several recent publications (48–51).

**Diesel Engines**

The ultimate lean-burn concept is the diesel engine, and during the last decade Gandhi gave attention to the control of diesel engine emissions, especially NOx (52). In the 1990s major diesel engine developments took place in Europe. The bottom-end torque and driving characteristics of new turbocharged direct injection diesel-powered vehicles, coupled with their outstanding fuel economy (low CO2 emissions) resulted in them becoming very popular. Around half of all new passenger cars in Europe are currently diesels. The two most difficult to control diesel engine emissions are particulate matter (PM) or soot, and NOx. By 2000 diesel particulate filters in combination with fuel-borne catalyst (to enhance periodic burning of PM retained in the filter) were introduced on some European cars (53, 54). This was followed by the introduction of catalysed particulate filters that do not need the fuel-borne catalyst and its associated equipment. By 2005, small compact catalysed filters had been developed that fit directly on the engine's turbocharger and perform all the catalytic and filtration functions necessary to control HC, CO and PM (55).

Diesel NOx control has all the problems associated...
with lean-burn direct injection gasoline engines, exacerbated by lower-temperature operation. Formulation modifications enabled NACs to be used on diesel engines (56), but Gandhi generally favoured selective catalytic reduction (SCR) of NOx with NH₃ derived from hydrolysis of urea supplied as an aqueous solution, Equation (xi). NO and NO₂ react differently with NH₃, Equation (xii) and Equation (xiii), and equal amounts of both react faster than either individually, so the SCR catalyst is usually located downstream of an oxidation catalyst to adjust the NO:NO₂ ratio for optimum NOx control performance.

\[
\begin{align*}
\text{(NH}_2\text{)}_2\text{CO} + \text{H}_2\text{O} & \rightarrow 2\text{NH}_3 + \text{CO}_2 \\
4\text{NH}_3 + 4\text{NO} + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}
\] (xii) (xiii)

Since the 1970s SCR technology has been used to remove NOx from the flue gas of power stations and the off-gases from industrial processes such as the manufacture of nitric acid (HNO₃) from NH₃. Here the catalyst is vanadium-based and requires quite high temperatures, close to those available on heavy-duty trucks, and over recent years these catalysts have been increasingly used in these mobile applications. However, the lower temperatures on cars mean that catalysts of much higher activity are required to be effective. Gandhi over several years pushed catalyst manufacturers to achieve this remarkably difficult target through the use of new zeolite-based SCR catalysts whose performance is remarkable in the light of previous technologies, and they are being introduced into series production (57).

**Conclusions**

Throughout his entire career Haren Gandhi was deeply engaged in the technical aspects of emissions control, and he led the catalyst manufacturers to continually produce technically better products to meet increasingly demanding legislative requirements. He saw car tailpipe emissions go from being relatively out of control (compared to today) and a cause of major environmental problems, to being well controlled by innovative catalytic technologies. However, and as he appreciated, there are always new challenges and demands in this area, as evidenced by the recent growth of advanced diesel engines in cars in Europe with their unique emissions control requirements, and the growing need to reduce CO₂ emissions.

Unlike most in the automotive industry, Gandhi remained in his specific chosen area, and saw a series of major objectives achieved. Because of his wide experience and depth of knowledge he became known as a practical emissions control guru. In many ways Gandhi was unique in the industry and all of those who knew and worked with him mourn the loss of a very special friend.

**Acknowledgements**

The author gratefully acknowledges and thanks the many people who helped to complement his own recollections of working with Haren Gandhi for almost two decades, by sharing recent and more distant memories of collaborations with him, some that stretched over almost four decades. There are too many people to thank individually, although particular special thanks are due to Barry Cooper and to Barb Rutkowski, who was for many years Gandhi’s personal assistant.

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US Patent 5,750,082; 1998

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Martyn Twigg was the Chief Scientist of Johnson Matthey PLC and before that the Technology Director for the Environmental Catalysts and Technologies Division. He has authored or co-authored many original research papers, holds many patents, has written numerous chapters in encyclopedic works, and edited and contributed to several books. He edits the book series Fundamental and Applied Catalysis, and has academic positions at several universities.
In the ‘bad old days’, when diesel lorries produced clouds of black smoke as they accelerated or climbed hills, a diesel engine in a car was a rarity, but during the last few years Western Europe has seen a huge increase in the production of diesel passenger cars. Today more than 50% of all new European cars have a diesel engine (1). This increased demand results from the introduction of the powerful turbocharged high-speed diesel engine that provides excellent driving characteristics with high torque at low speed, and very good fuel economy. Modern passenger car diesel engines produce much less soot or PM than did their older counterparts, because of improved fuelling and enhanced combustion characteristics. For instance, fuel pumps operating at very high pressure enable injection into several very fine nozzles into the cylinder and these injection systems permit multiple injections of fuel. In spite of the improvements in PM emissions from diesel powered vehicles, there are still concerns about the environmental consequences of these emissions. Legislation is being introduced that will demand fitment of PM filters to all diesel car models sold in Western Europe, with the implementation of the European Stage 5 emissions requirements (2) starting in 2009. In fact a growing number of new diesel passenger cars have PM filters, even though they may not be necessary to meet current legislative requirements.

The Origin of Particulate Matter

The operation of a diesel engine involves compressing air in the cylinder producing heat via the Joule-Thomson effect, and then injecting finely ‘atomised’ fuel under very high pressure (up to 2000 bar) directly into the hot gas that causes it to explosively combust. The exact details of the combustion process are the subject of active research, and it is clear that the atomised fuel droplets evaporate and burn in a fuel-rich region limited by ingress of oxygen into the burning flame front. In
the fuel-rich zone, carbon forms from reactive intermediates. Subsequently when excess oxygen is present the carbon that has formed may be burnt, and if this is not completed when the combusted mixture is discharged from the cylinder through the exhaust ports, a residue of fine carbon cores remains in the exhaust gas. As the gas cools during passage into the exhaust manifold, turbocharger and the associated pipework, the carbon particles agglomerate forming high surface area material onto which uncombusted and partially combusted products adsorb, as well as sulfur oxides and nitrogen oxides (NOx) formed during the high temperature combustion in the cylinder.

When inhaled the scale of some of the smallest nanosized particles enables them to pass almost unheeded into the lungs and then even into the bloodstream. It is this mobility, coupled with the composition of the cocktail of adsorbed species, which gives rise to environmental health concerns. Figure 1 illustrates schematically the nature of diesel PM, and Figure 2 shows a chromatograph trace that indicates the very large number of different species that are adsorbed on typical diesel car PM.

The amount of exhaust PM that European diesel cars are permitted to emit has decreased considerably over the last couple of decades, and this is illustrated graphically in Figure 3. The European PM emissions limits have decreased by more than an order of magnitude since 1983. Although the test conditions for each of the emission levels are not exactly the same, the overall downward trend is clear. The very low passenger car PM emissions limits for the European Stage 5 legislation, due to be phased in during 2009, can only be achieved through the fitment of filters, and legislation in other parts of the world will mean that filters will also be fitted to diesel cars elsewhere in the future.

**Diesel Particulate Filter Types**

Several types of ceramic and sintered metal diesel particulate filters (DPFs) have been developed. The most successful and the most commonly used commercially, are porous ceramic wall-flow filters, as shown schematically in Figure 4. Refractory materials used to make them include cordierite, silicon carbide and aluminium titanate. Alternate channels are plugged, so the exhaust gas is forced through the channel walls. The exhaust gases pass through the walls but the PM does not and it is trapped in the filter. As PM accumulates in the filter, the backpressure across it increases, and if this continues it will become excessive, and significantly degrade engine performance.

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**Fig. 1** Schematic representation of diesel particulate matter (PM) formed during combustion of atomised fuel droplets. The resulting carbon cores agglomerate and adsorb species from the gas phase.
performance – ultimately the engine will stop! It is therefore essential that the backpressure across the filter is not allowed to rise above a predetermined limit, so PM must periodically be removed from the filter to prevent this from happening. The best way of removing PM from the filter is to oxidise it to carbon dioxide (CO2) and water.

Filter Regeneration

The process of oxidising retained PM in a diesel filter is called regeneration (3, 4). The temperature of diesel passenger car exhaust gas rarely exceeds 250°C during urban driving, so the use of nitrogen dioxide (NO2) as shown in Equations (i) and (ii) for combustion of trapped PM (written as “CH”) that takes place at temperatures in the range 250 to 400°C can only remove some of the accumulated soot when suitable temperature conditions are achieved:

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad (i)
\]

\[
5\text{NO}_2 + 2\text{“CH”} \rightarrow 5\text{NO} + 2\text{CO}_2 + \text{H}_2\text{O} \quad (ii)
\]

In contrast, heavy-duty trucks and buses operate at higher temperatures and therefore the regeneration with NO2 is very effective and continuously cleans the filter. Whilst the exhaust gas temperature for cars is too low for this regeneration method when driving in urban conditions, at speeds of around 100 km h\(^{-1}\), the exhaust gas temperature can be sufficiently high for nitric oxide (NO) in the exhaust gas to be oxidised over a platinum catalyst, producing NO2 which can in turn oxidise retained PM in the filter, as in Equation (ii). This type of regeneration is called
'passive regeneration'. But to provide a regeneration method for all driving conditions, an 'active' form of regeneration must be employed that periodically increases the exhaust gas temperature to burn PM in the filter with oxygen (typically 550 to 600ºC) every 400 to 2000 km, depending on the actual driving conditions. Three commercial filter systems developed for cars using active periodic oxygen regeneration are illustrated in Figure 5. 'Generation 1' employs one or two platinum-based oxidation catalysts in front of the filter to control hydrocarbons (HCs) and carbon monoxide (CO) emissions. The catalyst also oxidises extra partially burnt fuel when it is injected into the engine, to raise the exhaust temperature for active PM combustion with oxygen (5). This system was introduced in 1999 (6) and uses a base metal fuel additive to lower the temperature for PM combustion with oxygen. The first fuel additive was based on ceria, and others now in use contain base metals such as iron or strontium, and one based on platinum has been described. These multicomponent systems work well, although they are costly and fuel additive residues are retained in the filter as inorganic ash (see below), and this contributes to a higher back-pressure across the filter than would be the case if no fuel additive were used.
'Generation 2' has the advantage of using no fuel additive. As well as one or two upstream oxidation catalysts, the filter has catalyst in the walls to promote PM combustion, and today many cars use this configuration. The more recently introduced (2005) 'Generation 3' by Johnson Matthey requires neither a fuel additive nor an upstream catalyst. It comprises a single catalysed filter, incorporating all of the oxidation catalyst functionality to oxidise HC and CO during normal driving, and to periodically oxidise extra partially burnt fuel to raise the temperature sufficiently to combust PM with oxygen during active regenerations. Under some conditions, the catalyst might also oxidise some NO to NO₂ to provide some passive PM removal during high-speed driving. This system is thermally the most efficient, because during active regeneration there is only the filter to heat, which is mounted actually on the engine turbocharger so as to minimise heat losses. The oxidation reactions used to boost the temperature actually take place in the filter, in the same location as the retained PM (7, 8). In contrast, systems with a separate upstream catalyst lose some of the heat provided during regenerations to the surroundings via the pipework between the turbocharger and the filter and so are less thermally efficient.

**Particulate Matter Nanoparticles**

Figure 6 shows the range of particle sizes typically present in diesel exhaust gas. Filters can remove the larger, coarse, micron-sized PM and 'accumulation mode' particles above 100 nm in size that together account for almost all of the PM mass. Very small nanoparticles, about 10 nm and even smaller in size, are now being addressed because when they are inhaled they can pass through the bronchial tissue into the bloodstream. Although collectively they have very little mass, they can be present in huge numbers. Recent research (9) indicates that most of this ‘nucleation mode’ PM comes from volatile organic or inorganic precursors that are formed as the exhaust gas cools. Laboratory and on-road studies on heavy-duty diesel engines show that when hot, the platinum oxidation catalyst can effectively remove all the HCs in the exhaust gas. Then, most of the nucleation mode PM is inorganic ‘sulfate’,
probably as sulfuric acid, ammonium sulfate \((\text{NH}_4\text{SO}_4)\) or ammonium hydrogen sulfate \((\text{NH}_4\text{HSO}_4)\) derived from sulfur compounds originally present in the diesel fuel and lubrication oil and traces of ammonia \((\text{NH}_3)\) present in the air. The lifetime of this PM is expected to be short, because such very fine particles coalesce and undergo other processes that take them out of the air (10). As expected, they are not formed if the sulfur concentration in the fuel and oil is reduced to below a critical level. Research in this area is very active, and more work is needed to obtain a full understanding of the nature and reactivity of nanoparticles from diesel exhaust gas. However, recently it was shown that careful chemical design of catalytic filter systems can control emissions of nanoparticles, as well as the coarser types of PM (11), and work in this area is continuing.

**Inorganic Ash**

Inorganic compounds are added to lubrication oils as viscosity modifiers and to provide antitrust and antioxidant properties, and to keep solid matter, especially soot, in suspension. The more commonly used compounds contain elements such as phosphorus, calcium, zinc, magnesium and sulfur (12, 13). These elements can be present in the exhaust gas, having originated from the small amounts of oil burnt in the cylinder, and they are retained as stable compounds in the filter. Similarly, inorganic species derived from the fuel are also trapped in the filter. As mentioned above, PM combustion aids are used as fuel additives in the first generation of filters on passenger cars, and these can include compounds of elements such as cerium, iron or strontium.

Because of the very high temperatures during combustion in the engine, the nature of the species present in the exhaust gas is determined by their thermodynamics (14), as is the composition of the ultimate deposit in the filter. Typically, zinc phosphate and calcium sulfate, together with material resulting from engine wear, are found in filters after a car has travelled large distances. Although the rate of ash accumulation in the filter is gradual, its presence does cause the backpressure across the filter with no PM present to increase over the lifetime of the vehicle. The gradual backpressure increase caused by accumulating inorganic ash can be minimised in three main ways: using a larger filter, using lubrication oils with reduced concentrations of inorganic additives ("ashless oil"), and using filters with asymmetric channel structures that provide a larger inlet volume compared to that in the outlet side. The last approach may result in slightly higher backpressure for an asymmetric filter than for a symmetrical one, when fresh, but this relative difference decreases as ash accumulates in the filter and the asymmetric structure then has the lower backpressure (15). The advantage of asymmetric channels in the long term is significant, and filters of this type are likely to be used increasingly in the future. During the development of modern emissions control systems, it is essential that the performance be maintained over very many miles of use. Durability is tested both by real-world driving trials and by laboratory work, as illustrated in Figure 7.

Fig. 7 Durability testing of a compact diesel particulate filter on a vehicle. The robot (upper right insert) ‘drives’ the car in simulated service, and the emissions are measured periodically over the European test cycle to confirm that the emissions control system is working correctly.
Future Filter Systems

Fitment of filters to diesel engines is environmentally important, and future legislation will demand their use in Europe and elsewhere around the world to reduce PM emissions. The overall trend in diesel emissions control systems is one of increasing complexity. Initially, platinum-based oxidation catalysts were used on diesel cars to control HC and CO emissions (16). More recently, PM filters were introduced, and the types used have evolved so that now all of the catalytic oxidation and filtration functions can be incorporated in a single relatively small filter. In the future, additional control of NOx emissions from passenger car diesel engines will be done by one of two processes. In the first, NOx is converted to nitrate species within a catalyst and they are periodically reduced to nitrogen (N₂) by pulses of enriched exhaust gas obtained by late injection of fuel into the engine. This approach has the advantage that the reductant for converting NOx to N₂ (diesel fuel) is already available on the vehicle. The second method uses ammonia as the reductant, which is derived from an aqueous urea (\text{(NH}_2\text{)}_2\text{CO}) solution that is injected into the hot exhaust gas. Over a special catalyst, the ammonia selectively reduces NOx to N₂ (a process known as selective catalytic reduction (SCR)). To be cost- and space-effective, some of these functions will be combined in single components. So SCR or NOx-trapping components are likely to be incorporated into future designs of filters fitted to diesel passenger cars. When CO, HC, PM and NOx emissions are controlled by a single unit, the systems will be known as ‘four-way catalysts’ (FWCs) (17).

Conclusions

Sophisticated emissions control systems are being developed for fuel-efficient (lower CO₂) modern diesel engines in passenger cars. For several years platinum-based catalysts have been fitted to diesel engine exhausts to oxidise CO and HCs, and the spotlight is now on preventing PM from entering into the atmosphere. This is done with wall-flow filters, and periodically it is necessary to combust the PM retained in the filter to prevent build-up of PM. This is done by catalytically oxidising with platinum-based catalysts extra fuel that is partially burnt in the engine to achieve the temperatures needed to burn PM with oxygen. Catalytic filter systems are capable of eliminating coarse and accumulation mode PM from diesel exhaust, and the latest and most efficient of these used on cars is mounted directly on the turbocharger in the small space in the engine compartment. The small filter contains all of the catalytic functionality to oxidise CO and HCs during normal driving, as well as to oxidise additional CO and HCs to provide sufficient temperature for regenerations with oxygen. Nanoparticles from diesel engines are the subject of much research, and ways of controlling them are understood. In the future, NOx reduction systems will be needed to meet legislative requirements, and will involve NOx-trapping technology or SCR using ammonia derived from an aqueous solution of urea. Once these approaches have been fully developed, it is likely that multifunction four-way catalyst systems will be developed, analogously to the use of three-way catalyst systems on traditional gasoline passenger cars.

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Critical Topics in Exhaust Gas Aftertreatment

By Martyn V. Twigg
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No combustion process is completely efficient. The exhaust gas from an internal combustion engine, besides containing water (H₂O) and carbon dioxide (CO₂) - the main products of combustion - also contains some unburned and various partially-oxidised hydrocarbons (HCs), and carbon monoxide (CO). During combustion the flame front temperature is so high (1600°C or even higher) that the endothermic equilibrium between nitrogen (N₂) and oxygen (O₂) to form nitric oxide (NO) is established. Subsequent rapid cooling and ejection of combusted gas into the exhaust system freezes this equilibrium, so exhaust gas also contains significant levels of NO.

Vehicle exhaust emissions are undesirable and can cause serious pollution via a series of complex photo-initiated free-radical reactions. In bright sunlight, reactions between NO, HC and O₂ result in low but significant levels of ozone (O₃). This is a bronchial irritant, and the main oxidising species in the photochemical smog that has plagued many major cities. Other undesirable chemicals, including the powerful lachrymator peroxycetal nitrate, can also be formed. CO can participate as a reductant in related photochemical reactions, but these reactions are much less important than those involving HCs. Therefore, controlling HC and nitrogen oxides (NOx) emissions from vehicles can have a direct impact on restricting the formation of urban photochemical smog.

Autocatalyst Development

The key step in controlling car exhaust emissions was the introduction of ‘autocatalysts’ some twenty-five years ago. Initially a platinum-based (Pt) oxidation catalyst was used with an air pump which provided excess air in the exhaust gas to oxidise HC and CO to less harmful CO₂ and H₂O. A few years later, legislation demanded lower NOx levels. Initially, NOx was reduced to N₂ by HC or CO, by passing O₂-deficient (‘rich’) exhaust gas over a Pt/Rh (rhodium) catalyst before the addition of air. After air addition, a Pt-based catalyst oxidised the remaining HC and CO. Thus, with two catalysts operating under different conditions, all three legislated tail-pipe emissions were controlled.

By the early 1980s it had been discovered that CO and HC could be oxidised and NOx reduced simultaneously over a single ‘three-way catalyst’ (TWC) containing Pt and Rh. The exhaust gas had to contain chemically equivalent (stoichiometric) amounts of reductant (HC and CO) and O₂. This condition was maintained through a combination of technologies: ‘electronic fuel injectors’ operated by a microprocessor fed with signals from an exhaust gas O₂ sensor (a solid stabilised zirconia electrolyte with Pt electrodes). Since that time combustion engineering, electronic engine management and catalyst technology have advanced greatly, and now extremely low emissions can be achieved from gasoline engines equipped with TWCs. Indeed, ambient air may now contain higher levels of some pollutants than tail-pipe exhaust gas! When catalyst is designed for a particular vehicle, the required performance is that it meets the legal emissions when aged. In U.S. legislation, this is now 150,000 miles for the most demanding PZEV (partial zero emission vehicle) limits.

Gasoline Engines

Three-Way Catalysts (TWCs)

The continuous measurement of O₂ levels in exhaust gas is a key part of the emissions control system on gasoline engines. Once the operating temperature is reached, a modern TWC is remarkably efficient in removing pollutants: over 99 per cent conversion efficiencies are possible. In recent years, effort has gone into minimising the time taken for a TWC to reach operating temperature after engine start-up. As a result of engine management techniques, such as ‘spark retard’ (causing combustion to burn in the exhaust manifold) the time before the TWC operates can now be only a few seconds, rather than the several minutes of a
few years ago. Placing the catalyst close to the exhaust manifold can further reduce the time, but it may experience very high temperatures. Johnson Matthey developed special heat-durable Pd/Rh and Pt/Rh formulations for this duty. These have very stable components, including some that store and release O2 as the exhaust gas composition oscillates from slightly lean to slightly rich, respectively. Catalyst formulations, that trap HC's formed during the initial low temperature engine cranking and release them when the temperature is high enough for their oxidation, have also been developed.

Lean-Burn Gasoline NOx-Traps

Increasing fuel prices and a desire to reduce CO2 emissions are two reasons to improve fuel efficiency. Improvements toward this can be obtained with spark ignition gasoline engines having direct injection of fuel into the cylinder under overall lean conditions. This technology is gradually being introduced. However, when running lean, NOx removal is difficult since the only practical process involves reduction to N2. This problem has been solved by 'NOx-traps' which contain Pt and Rh to trap NOx as nitrate (NO3-) when the engine is running lean. This stored NO3- is reduced to N2 by periodic short rich excursions. Thus the overall process involves a Pt-based catalyst oxidising NO to NO2 which is subsequently converted to NO3-. During the rich excursions the storage process is reversed and released NOx is reduced to N2 over a Rh-based catalyst.

Poisoning by sulfur is a concern here as sulfur dioxide (SO2) present in the exhaust gas is oxidised to sulfur trioxide (SO3) and then to sulfate (SO4^2-) in the NOx-trap. SO4^2- is more stable than NO3- and therefore the NOx capacity of the trap gradually deteriorates. To restore the original NOx capacity, SO4^2- can be removed from the trap by high temperature (600-700°C) treatment under reducing conditions.

Diesel Engine Exhaust

Particulate Matter

The traditional characteristic component of diesel engine exhaust is soot, although modern diesel engines produce very much less soot or particulate matter (PM) than even a few years ago. In a diesel engine, the compression-ignition process involves combustion of fuel droplets rather than ignition of the almost-homogeneous gas mixture characteristic of a gasoline engine. Diesel PM emissions can be controlled by trapping them in several different kinds of diesel particulate filter (DPF), and the practical problem is then to prevent PM build-up in the filter as this causes high back-pressure which could prevent proper functioning of the engine.

The exhaust gas temperature of a diesel engine is usually insufficient to burn PM in a DPF, and burners and electrical heaters have been used to increase the temperature to initiate PM combustion. However, once PM in a full DPF starts to burn, at around 550°C in air, excessively high temperatures may result that could cause major problems, such as melting the filter. Catalyst (e.g. Pt) within the DPF can mediate combustion, but the most effective method of removing PM from a DPF involves oxidation at lower temperature, with nitrogen dioxide produced by the catalytic oxidation of NO over a Pt catalyst upstream of the DPF. On large diesel vehicles (trucks or buses) this reaction takes place most of the time, so this system is called a continuously regenerating trap (CRT).

Carbon Monoxide and Hydrocarbons

With diesel engines, Pt oxidation catalysts are used for removal of HC, CO and partially-oxidised species, such as aldehydes, which cause the characteristic odour of diesel exhaust. Sulfur compounds present in the fuel burn to SO2 in the engine. Modern oxidation catalysts are efficient, but SO2 is a catalyst poison that can significantly impair performance. Johnson Matthey have developed diesel oxidation catalysts that are more tolerant to these effects, and therefore have improved performance.

At higher temperatures SO2 is oxidised to SO3 over the Pt catalyst, and the SO3 is hydrated to sulfuric acid mist, which contributes to the measured amount of tail-pipe PM. This problem is not as significant as it once was because fuel sulfur levels have been markedly reduced. When diesel fuel contained high sulfur levels, the catalyst selectivity

* B. J. Cooper et al., SAE Technical Paper, 1989, 890404
was tailored by modifying the formulation to control the amount of SO₂ produced at higher temperatures.

Removal of NOₓ

In contrast to the high efficiency of TWCs operating around stoichiometric conditions, NOₓ removal from lean diesel engine exhaust gas is difficult. Under ideal conditions, almost 50 per cent NOₓ reduction is possible over a Pt catalyst, by small amounts of added HC, with overall exhaust gas staying lean. In practice this is not a solution, as it is only effective over a restricted temperature range. Fuel combustion over a catalyst increases its temperature, and this must also be noted to stay operating in the optimum temperature window.

Two other ways of dealing with the 'lean-NOₓ' problem are in development. The first is selective catalytic reduction (SCR) with ammonia (NH₃). NH₃ SCR is now used to control NOₓ from large power and chemical plants, and from some stationary diesel engines. NH₃ can be conveniently obtained in situ from aqueous urea solutions [(NH₄)₂(CO), but for small vehicles there are practical problems associated with SCR, such as maintaining adequate temperature and preventing NH₃ tailpipe emissions.

The second approach involves Pt/Rh NOₓ-traps similar to those used on lean-burn gasoline engines to store NOₓ as NO₃⁻ under lean conditions. NO₃⁻ is periodically reduced to N₂ by having the engine run rich. There are technical problems to be overcome before NOₓ-traps can be widely used on diesel cars. As with SCR, low temperatures are a problem. Another concern is sulfur accumulation in a NOₓ-trap. This progressively lowers the NOₓ storage capacity, but can be overcome by sporadic rich high temperature treatment. Providing rich exhaust gas to reduce stored NO₃⁻ and achieving higher temperatures for desulfation are adverse to fuel economy. It may, however, be expected that efficient NOₓ removal systems for diesel cars will become available.

Monitoring and Control Systems

In-use monitoring of catalyst performance is now a legal requirement, and is referred to as on-board diagnostics (OBD). This covers emissions and a dozen other distinct parameters. Catalyst malfunction is defined in terms of HC conversion efficiency, and should this fall below a threshold value (which depends on the model year) a malfunction indicator lamp (MIL) alerts the driver that it is necessary to have the car checked.

The most widely reported diagnostic method is the determination of the catalyst O₂-storage capacity. This can be measured by applying perturbations to the air/fuel ratio and finding the time taken by the catalyst to return to its normal operating condition, using O₂ sensors before and after the catalyst. The dual O₂ sensor method is used because reliable and more direct approaches are not yet available. NOₓ sensors will be used in applications, such as lean-burn gasoline and diesel engines equipped with NOₓ-traps, and NH₃ sensors in SCR systems. It is clear that sensors will be increasingly important in the future for control and monitoring of emissions systems.

Conclusions

Platinum group metals based catalysts are critical in controlling exhaust emissions, and their range is widening. As well as TWCs and oxidation catalysts, NOₓ-traps are used on gasoline lean-burn engines and may be used on diesel engines. Platinum group metals can enable control of diesel PM emissions, and they are also used in sensors that provide signals for overall computer control. It is therefore clear that the important use of platinum group metals in the vehicle emissions area will continue well into the future.

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Twenty-Five Years of Autocatalysts

By Martyn V. Twigg
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A quarter of a century ago the first autocatalysts were manufactured on a commercial scale by Johnson Matthey at Royston, near Cambridge, in England. This article looks at the background to this major contribution towards cleaning urban air and briefly traces the progress of car catalyst technology since the work of the early autocatalyst pioneers.

As early as the 1940s, some large cities had begun to experience problems of atmospheric pollution. The Los Angeles’ basin in the U.S.A. was particularly affected, experiencing frequent natural ambient temperature inversions, which trap and recycle polluted air. Mass production of cars, powered by the internal combustion engine, was then giving tremendous personal mobility, but the very large numbers in cities were understood to be a major source of the man-made urban emissions (1).

Photochemical interactions between hydrocarbons and nitrogen oxides from car exhaust and oxygen occur in the lower atmosphere, forming ozone-containing “photochemical smog”, Equation (i), identified as an important contributory factor to the pollution. The oxidation of fuel to carbon dioxide and water in engines, Equation (ii), was far from completely efficient. Unburned hydrocarbons and partially combusted products, particularly carbon monoxide (CO) and to a smaller extent oxygenates, such as aldehydes, were present in the exhaust gases*. Relatively high levels of CO were formed, Equation (iii), and, under the forcing conditions in the engine, nitrogen (N₂) and oxygen (O₂) reacted to establish a partial equilibrium with nitric oxide (NO), Equation (iv). Appreciable amounts of NO and its oxidised form, nitrogen dioxide (NO₂) (together referred to as NOx) can be present in exhaust gas.

The three major pollutants in exhaust gas are therefore HC, NOx and CO. Subsequent photoinduced reactions of the first two pollutants with oxygen forms ozone, which is a strong irritant, as well as low levels of other compounds, notably peroxyacetyl nitrate, which is a very strong lachrymator irritant (3).

\[
\begin{align*}
\text{HC} + \text{NOx} + \text{hv} & \rightarrow \text{O}_1 + \text{other products} \\
4 \text{H}_2\text{C}_x + (m+4n)\text{O}_2 & \rightarrow 2\text{mH}_2\text{O} + 4n\text{CO}_2 \\
4 \text{H}_2\text{C}_x + (m+2n)\text{O}_2 & \rightarrow 2\text{mH}_2\text{O} + 4n\text{NO} \\
\text{N}_2 + \text{O}_2 & \rightarrow 2\text{NO}
\end{align*}
\]

\[(i)\]  \[(ii)\]  \[(iii)\]  \[(iv)\]

**Johnson Matthey Targets Research**

In the late 1960s, in the U.K., Johnson Matthey was developing catalyst technology to control the gaseous pollutants from industrial applications, such as the reduction of NOx in “tail gas” from nitric acid plants, and the destructive oxidation of odours from food processing facilities. These used catalysts based on platinum group metals (PGM); for instance, the reduction of NOx in tail-gas by methane (CH₄) was achieved particularly effectively over a rhodium (Rh) promoted platinum catalyst.

In the U.S.A. the 1970 Clean Air Amendments Act was the driving force to reduce emissions from cars. Political pressures from the environmental lobby had resulted in Senator Edmund Muskie announcing a plan to reduce emissions from cars by 90 per cent and highlighted the need to develop specific technology for automotive pollution control. The clean air legislation was also to apply to manufacturers exporting cars to the U.S.A. It was appreciated that engine modifications could provide improvements to emissions, but that additional measures would be needed after model year 1975 to comply with more stringent Federal and Californian limits. Catalytic converters became the chosen route after Johnson Matthey successfully demonstrated the positive benefits of

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* Unburned hydrocarbons and oxygenated species are referred to as “hydrocarbons” and designated HC (2).

platinum-containing catalyst to clean up car exhaust (4). This resulted in demand by car manufacturers for samples of catalysts for test programmes, and by Johnson Matthey for their own projects.

The first work done by Johnson Matthey was in England at the Research Laboratories, at Wembley, in west London. But at the end of 1971 sample manufacture was transferred to the new Catalyst Development Laboratory at Royston and the Wembley research scientists concentrated on developing new catalyst technologies.

Catalyst Structures

Initially two catalyst structures were tested: pellets catalysts, similar to those used in chemical industries, and “monoliths”. In a monolith, the catalyst volume is a single structure with many small open channels running along its length, like a honeycomb. Johnson Matthey concentrated on “monolithic” catalysts, through which the hot exhaust gas from the engine would pass for conversion of pollutants to harmless species. This structure caused only a small drop in exhaust gas pressure, and its low heat capacity caused it to become hot quickly in use. Additional benefits of monoliths were that they did not suffer the attrition/erosion problems of pellets. Today, monoliths are the basis of all autocatalysts, and typically they have 400 cells inch\(^{-2}\). Later Johnson Matthey developed some novel metal-based versions and experimented in making ceramic monoliths, but early monoliths were supplied mainly by Corning Glass and 3M-American Lava in the U.S.A.

Corning monoliths were prepared by an extrusion method which is now the standard route. In England, Imperial Chemical Industries (ICI) were also working in this area and invented some key processing methods which facilitated full-scale production (5).

The 3M company used a paper laying technique, with alternate layers of flat and corrugated sheets, which were impregnated with a suspension of ceramic oxide powders before firing to remove the paper and give a rigid monolith. These two processes gave products with different properties, but neither type of monolith had catalytic activity itself. Cordierite (2MgO.2Al\(_2\)O\(_3\).5SiO\(_2\)) which has a low coefficient of expansion, made it the material of choice for ceramic monoliths, and is still used today.

Catalyst Formulation Developments

Initially, catalysts containing nickel, copper, cobalt or iron, similar to those used in the production of methanol and ammonia (6) had been assessed as autocatalysts, but had insufficient activity, especially at low temperatures. Moreover, they were very susceptible to poisons derived from the fuel. The catalysts eventually chosen were based on the highly active PGMs (7).

Although PGMs are more poison resistant than base metal catalysts, sulfur and lead did affect their performance, lead being the worst, as it forms an inactive alloy with the active catalyst metallic phases (8). These had already been recognised in the U.S.A. as harmful, and “cleaner” gasoline was being introduced. Unleaded gasoline is needed for catalysts to control automotive emissions, and this was introduced first in the U.S.A. and later, increasingly, around the world. The environmental benefits from this in itself are very significant.

Depositing PGM directly on the monolith channels gave poor catalyst performance: because there was little to prevent small metal crystallites from migrating and coalescing to large crystallites with low surface area. Therefore, the Wembley research group developed technology to increase the surface area available to the PGM by providing the monolith with a higher surface area material. This was based on alumina (Al\(_2\)O\(_3\)) with stabilising additives and a process was developed to coat monoliths with a high surface area “washcoat”. The washcoat had to be even, and not block the channels, while adhering strongly to the substrate. The washcoat rheology was critical during coating. Expertise was soon developed, and high performance catalysts were manufactured and employed on cars (9).

For a few years, the emissions limits could be met by oxidation of HC and CO and exhaust gas recycle (EGR), as in Equations (ii) and (v).
However, legislation tightened and it became necessary to control NOx emissions. The only way to do this was to reduce it catalytically to nitrogen (N₂), as in Equations (vi) and (vii):

\[ \begin{align*}
2\text{CO} + \text{O}_2 & \rightarrow 2\text{CO}_2 \\
(8n+2m)\text{NO} + 4\text{H}_2\text{C}_n & \rightarrow \\
(4n+m)\text{N}_2 + 2m\text{H}_2\text{O} + 4n\text{CO}_2 & (vi) \\
2\text{NO} + 2\text{CO} & \rightarrow \text{N}_2 + 2\text{CO}_2 & (vii)
\end{align*} \]

Early concepts used two catalysts: the engine was run slightly rich to enable reduction of NOx over a Pt/Rh catalyst, then air was introduced between the catalysts to enable the second one to oxidise remaining CO and HC. It was important that the first catalyst reduced NOx to N₂ with high selectivity, because if ammonia (NH₃) was formed, it would be oxidised over the second catalyst to NOx according to Equation (viii).

\[ 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \quad (viii) \]

**Development of Three-Way Catalysts**

From earlier experience with catalytic NOx reduction with CH₄, Johnson Matthey had developed low light-off Pt/Rh oxidation catalysts which were used by some European car manufacturers (10). With them, if the engine was operated close to the stoichiometric point (the air:fuel ratio corresponding to complete combustion), some NOx control was obtained via reduction, even though oxidation reactions were taking place. Suitable catalyst formulations were important in optimising this behaviour (11).

By 1979, oxygen sensors had been developed and placed in the gas close to the exhaust manifold to provide feedback control to the fuelling, so conditions could be maintained around the stoichiometric point using electronic control. This enabled good consistent catalytic performance, and the use of Pt/Rh catalysts to simultaneously control HC, CO and NOx became the preferred system. Because all three pollutants were controlled with one catalyst, the concept was named the “Three-Way Catalyst”, TWC.

Early TWCs had a narrow operating air:fuel range over which all three pollutants were removed, and from about 1980 they were almost universally fitted to cars sold in the U.S.A. Since then effort has been directed towards improving catalyst performance: enhancing activity, thermal durability, selectivity and widening the air:fuel ratio operating window. Catalyst improvement went with increasingly sophisticated fuel management systems; carburettors gave way to single point fuel injection and then multi-point injection into the inlet manifold, and latterly direct injection into the cylinder.

**Expansion at Royston**

During the early 1970s washcoating processes were intensively investigated and developed, later to be transferred to Johnson Matthey plants around the world. At first, development activities and plant design phases ran in parallel. The rate of the initial process development and implementation was frantic and complicated by the Royston manufacturing area being too small for the anticipated increasing demand. An adjacent building, previously used for developing equipment for army tanks, had to be purchased.

In late 1973, construction of the first catalyst production line at Royston was completed. Contracts had been signed to produce catalysts for Volkswagen cars exported to the U.S.A., and negotiations were well advanced with Rolls Royce and British Leyland in the U.K. and with the Ford Motor Company in the U.S.A. The large number of catalysts needed in the U.S.A. required a big plant to be constructed there. Before this was done, a proving run was undertaken at Royston to demonstrate process viability. This was achieved in spite of the “threeday working week” resulting from the national miners’ strike in December 1973. Electricity allocated to the Royston site was limited, so catalyst production was given all the available power: no other heating and lighting was permitted, and the run was very successful.

Shortly afterwards construction of a very large plant began at Wayne, Pennsylvania, to supply the U.S. market. The Royston plant was officially opened in February 1974, and by the end of April the world’s first autocatalyst production pieces were being made for Volkswagen. Subsequently, other companies were supplied, and as production numbers increased, a second
line was installed at Royston. Development and introduction of new catalyst formulations then followed rapidly.

**Global Growth**

At an early stage Johnson Matthey invested extensively in test facilities in the U.K. and U.S.A. for evaluating autocatalysts on engines and cars. Initially work was done at Ricardo Consulting Engineers in Sussex, although a small test facility had been installed at Wembley. As demand for testing increased, an enlarged facility was built at Royston: four static engine cells, and a “rolling road” for making measurements on cars, all then state-of-the-art. Over the years, these underwent numerous improvements, until a major expansion to provide a modern “European Technology Centre” was opened in February 1995. This ongoing investment in R&D reflects the importance placed by Johnson Matthey on technical developments in this area. Indeed, Johnson Matthey now has Autocatalyst Technology Centres at Royston, in Pennsylvania (U.S.A.), Kitsuregawa (Japan), Gothenburg (Sweden) and at Curitiba (Brazil). In addition fundamental scientific aspects are worked on at the Corporate Technology Centre, near Reading, England, to where the original Wembley Research Laboratories moved in 1975.

The importance of Royston as Johnson Matthey’s main European production unit diminished in the early 1990s after a much larger facility was built in Brussels and opened in 1991, to serve the growing European market. This followed a plant in Sydney, Australia, opened in 1985, and the world’s largest plant, in Wayne (Pennsylvania, U.S.A.) which began production in 1974. Since the Belgium plant was built, further plants have been established in South Africa, Mexico, Malaysia, Argentina and India.

**Recognition of the Pioneering Work**

The importance of the technology developed by Johnson Matthey was recognised in 1976 by a “Queen’s Award” for Technological Achievement. In 1980, five of the original autocatalyst team received the Fellowship of Engineering’s MacRobert Award (12) and in 1992 two “Queen’s Awards” were granted: for Environmental Achievement and for Export Achievement.

**Conclusions**

The development of autocatalysts has enabled major reductions in emissions from automobiles. Over a quarter of a century, many millions of tons of pollutants have not been released into the atmosphere. This has improved urban air quality, with many associated environmental benefits. Research and development continues to be pursued at the highest levels: new aftertreatment systems are being developed for lean-burn gasoline, diesel engines, and engines burning a range of alternative fuels, being some examples. It can be said that pioneering work still continues today on many environmental fronts, with the intention of bringing about yet further social benefits.

**References**

2. In Europe total hydrocarbons (THC), including the most difficult to oxidise methane, are measured, partially oxidised oxygenates are not. In the U.S.A. methane is excluded, but oxygenates are included in “non-methane organic gases” (NMOG)
12. The recipients were Gary Acres, Brian Cooper, Barry Cooper, David Evans and Dennis Webster.
“Catalytic Air Pollution Control: Commercial Technology”, 3rd Edition

By R. M. Heck (RMH Consulting, USA) and R. K. Farrauto (BASF Catalysts, USA) with S. T. Gulati (Consultant to Science and Technology Division, Corning Inc, USA), John Wiley & Sons, Inc, New Jersey, USA, 2009, 522 pages, ISBN: 978-0-470-27503-0, £73.00, €84.60, US$110.00


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Introduction
Thirty-five years ago the use of catalytic systems for controlling tailpipe pollutants from vehicles was virtually non-existent, yet now every new car in the major countries of the world is equipped with one or more emissions control catalysts. Over this time the autocatalyst industry has grown to become a multi-billion dollar worldwide business, and underpinning this success is the extremely high catalytic activity of the platinum group metals (pgms), especially rhodium and palladium as well as platinum itself.

On a vehicle, operating conditions are not smooth and steady as they are on a large single-stream methanol or ammonia plant (1). Low-temperature catalyst activity is vital during ‘cold-starts’ and very high temperatures (1000°C) can result from occasional engine misfires so very good catalyst thermal durability is a prerequisite. Conditions are highly transient – the gas flow rate changes often and it pulses as exhaust gas is discharged from each cylinder in turn. The exhaust gas flow can be very high and the corresponding space velocity much higher than in a chemical plant, and there can be detrimental catalyst poisons such as sulfur and phosphorus species in the exhaust gas, as well as continuous physical vibration etc.

The primary pollutants from combustion of petrol, diesel and other hydrocarbon fuels such as liquefied petroleum gas (LPG) and compressed natural gas (CNG) are unburnt or partially oxidised hydrocarbons (HCs) and carbon monoxide (CO). Nitric oxide (NO) is also present, being formed from oxygen and nitrogen combining at the high-temperature flame front during combustion. Once in the air HCs and NO can undergo a series of photochemical reactions that lead to even more noxious secondary oxidising pollutants such as ozone (O₃) and organic compounds like peroxyacetyl nitrate (PAN) that are powerful and
very unpleasant lachrymators. So while cars and other vehicles with internal combustion engines have given society previously undreamt of mobility, they have also contributed to major undesirable environmental consequences (2, 3). The approach for solving this problem has been to deal with the primary pollutants at their source and prevent them from entering the environment by catalytically oxidising HCs and CO, and catalytically reducing NO to small amounts of water (H2O), carbon dioxide (CO2) and nitrogen (N2). And in the case of three-way catalysts (TWCs) these three reactions are done simultaneously.

Catalytic Air Pollution Control

Since their introduction the importance of catalytic control technologies has grown, and the first edition of the book "Catalytic Air Pollution Control" by Ronald Heck and Robert Farrauto (then with Engelhard Corporation), published in 1995 as a relatively slim volume with a little more than 200 pages, was a particularly significant contribution (4). Its appearance was timely and it provided a valuable easy-to-read reference for those working in the area of environmental control, and especially the catalytic control of tailpipe emissions from passenger cars. Seven years later there followed an enlarged second edition (5) with almost twice the number of pages. Suresh Gulti, formerly with Corning Incorporated, joined the two original authors and his contributions provided additional coverage of the ‘chemical engineering’ aspects of conventional flow-through monolithic catalysts, design and sizing of ceramic diesel particulate filters and other related substrate details. The latest, third edition has 522 pages, and is again an enlargement and update over the previous edition and covers the recent developments.

The Third Edition

The present book is divided into four main sections: the first deals with ‘Fundamentals’ and is followed by sections entitled ‘Mobile Sources’, ‘Stationary Sources’, and ‘New and Emerging Technologies’. The ‘Fundamentals’ section has been expanded to give more detailed background on kinetics of catalytic reactions, characterisation of catalysts and their modes of deactivation. In this section there are chapters on catalyst fundamentals, preparation of the components of monolithic-based catalysts, catalyst characterisation, the chemical engineering of catalysts, including the chemical kinetics of catalytic reactions, heat and mass transfer considerations, and pressure drop characteristics. The last chapter in this section deals with the various modes of catalyst deactivation including: thermally induced modes such as sintering; poisoning by, for example, sulfur species and lubrication additives such as calcium, zinc and phosphorus; and washcoat loss. Importantly it also covers the diagnostics used to identify the mode of deactivation in practical situations.

The second section deals with ‘Mobile Sources’ and forms the heart of the book, with some 270 pages and more than 500 cited references concerned with automotive catalysts and the substrates used to produce them (see Figure 1). The introduction of emissions control catalysts on cars is classified chronologically into different generations, and the most important
areas of TWCs for controlling emissions from stoichiometric gasoline engines and oxidation catalysts and particulate filters for diesel engines (see Figure 2) are well covered. The control of NOx emissions under the lean conditions of a diesel engine is not straightforward and the technologies being implemented are NOx-trapping with a basic catalyst component such as an alkaline earth with periodic exhaust gas enrichments to convert stored nitrate to nitrogen, and selective catalytic reduction (SCR) with ammonia derived from an aqueous urea solution. Both approaches are now in series production. Some of the legislative emissions requirements are touched on in this chapter, and details of the test cycles used in different regions of the world are provided. However, the focus is mainly on chemical and catalytic technical aspects such as the stabilisation of alumina surface area, and details of engine-based cycles used to accelerate the ageing of catalysts during development work – an aspect that often has slight attention paid to it in academic studies, but is vital when developing practical catalysts. The stabilisation of alumina surface area, and details of engine-based cycles used to accelerate the ageing of catalysts during development work – an aspect that often has slight attention paid to it in academic studies, but is vital when developing practical catalysts that have to maintain high performance over 120,000 (or more) miles of use! Another technology that is often overlooked is the retaining of ceramic monolithic catalyst in a stainless steel can – here it is covered in considerable detail. The section concludes with a relatively short (17 pages) chapter on the catalytic decomposition of ozone in high-flying aircraft.

The next section deals with the control of pollutants from 'Stationary Sources', and is a third of the size of the previous one on mobile sources. It has four chapters concerned with 'Volatile Organic Compounds' (VOCs), 'Reduction of NOx', 'Carbon Monoxide and Hydrocarbon Abatement from Gas Turbines' and 'Small Engines'. The first chapter here includes emissions from sources such as catalytic incineration and wood burning stoves. Interestingly this is one of the few areas where deactivated catalysts are regenerated routinely. With modern pgm-based VOC oxidation catalysts sintering is not a problem and deactivation usually takes place through fouling or masking of the surface by material present in the flue gas. The most commonly used regeneration technique is to chemically wash the catalyst to dissolve the offending material without disrupting the structure of the underlying catalyst. Treatments often make use of mild acids and chelating agents, and if properly done catalyst lives may be extended to between five and ten years. However, in general the overall economics of catalyst regeneration mean that in some situations it might be more appropriate to replace old catalyst with new, depending on the time it takes to carry
out the regeneration procedure and the economic penalty of not having the catalyst operating.

The final section on ‘New and Emerging Technologies’ is relatively small (49 pages) and includes on-vehicle ambient ozone decomposition by catalytic coatings on radiators. At first a platinum catalyst was suggested and later a particular form of manganese dioxide containing the complex anion called cryptomelane, \((\text{Mn(IV)}_6\text{Mn(II)}_2\text{O}_{16})^-\), which is more cost effective than platinum, went into series production on some cars. However, this technology has not been as widely adopted as was thought would be the case. A larger chapter then considers fuel cells and the generation of on-board hydrogen for mobile applications such as fuel cells. First, types of fuel cells are discussed, and the authors concentrate on the low-temperature proton exchange membrane (PEM) fuel cells that use pgms as electrocatalysts. Then routes to hydrogen are detailed. In the chemical industry this is done via steam reforming of hydrocarbons, especially natural gas, to form a mixture of hydrogen and carbon oxides (mainly CO) called synthesis gas, or syngas, that is used in large single-stream plants to manufacture ammonia and methanol (1). For mobile on-vehicle use methanol is a very convenient ‘fuel’ for hydrogen production via low-temperature steam reforming over copper-based catalysts (6). It will be interesting to see if these electrically-based power systems will have sufficient advantages to replace the highly refined ultra low emission internal combustion engines in the future.

**Commercial Catalytic Systems**

This book is unlike most textbooks on catalysis. The authors are industrial researchers who have been deeply involved in the development and application of innovative commercial catalytic emissions control systems for vehicles. They were responsible for many successful innovations that have benefited society, and in some ways their book gives a hint of the excitement of doing this. Throughout the book the emphasis is on the applied aspects and what is actually done industrially. Catalytic systems are included for both stationary and mobile sources and because the authors are from industry the topics are considered from a very practical point of view that is not found in standard textbooks. However, there are questions at the end of each chapter, rather in the form of a college textbook, and these would be of value to instructors using the book for specialist graduate courses. The cited references are collected together at the end of each chapter, and since there is no author index, tracking the work of a particular research group in different areas can be difficult. However, the titles of papers referred to are provided and this is helpful in identifying papers a reader might wish to pursue further. There is a subject index that usefully could be more exhaustive; it occupies only five pages.

**Concluding Remarks**

Overall this is a very good book that provides real technical insight into an important area of catalysis. Although there are occasionally some inaccuracies, for instance the mechanism of filtration with diesel particulate filters, this book will be of benefit to those working in the immediate area of catalytic pollution control, as well as those concerned with broader aspects of environmental chemistry both at the professional and student levels. Librarians are encouraged to ensure this volume is on their shelves.

**References**


**The Reviewer**

Martyn Twigg is the Chief Scientist of Johnson Matthey PLC and was previously Technical Director for the Environmental Catalysts and Technologies Division. Following work at the University of Toronto, Canada, and a fellowship at the University of Cambridge, UK, he joined ICI where he aided the development and production of heterogeneous catalysts used in the production of hydrogen, ammonia and methanol. Martyn has authored or co-authored many research papers, written numerous chapters in encyclopedic works, and edited and contributed to several books. He edits a book series on fundamental and applied catalysis.
Automotive Exhaust Emissions Control

By Martyn V. Twigg
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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 (CO₂) emissions. However, there are major challenges in meeting ultra low emissions requirements for particulate matter (PM) and nitrogen oxides (NOx).

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 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⁻¹ 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⁻¹) 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:

\[
\begin{align*}
H_2 + 0.5O_2 & \rightarrow H_2O \\
CO + 0.5O_2 & \rightarrow CO_2 \\
C_3H_8 + 4.5O_2 & \rightarrow 3CO_2 + 3H_2O \\
C_2H_6 + SO_2 & \rightarrow 2CO_2 + 4H_2O \\
H_2 + NO & \rightarrow H_2O + 0.5N_2 \\
CO + NO & \rightarrow CO_2 + 0.5N_2 \\
C_3H_8 + 9NO & \rightarrow 3CO_2 + 3H_2O + 4.5N_2 \\
C_3H_8 + 10NO & \rightarrow 3CO_2 + 4H_2O + SN_2 \\
C_2O_3 + 0.5O_2 & \rightarrow 2CO_2 \\
\end{align*}
\]

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 underfloor catalysts: a 0.7 litre and a 1.0 litre on 600 cell inch\(^{-2}\) and 4.3 mil (1 mil = 0.001 inch) wall substrates; the washcoat had 33 g ft\(^{-2}\) 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\(^{TM}\)) 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\(^{TM}\) 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\(^{TM}\) 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 (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\(^{TM}\). 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.

NOx-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 NOx-trap to store NOx during lean operation when a TWC is ineffective for NOx removal. The chemistry involved is shown in Reactions (x)–(xv).

\[
\begin{align*}
\text{NO} + 0.5\text{O}_2 & \rightarrow \text{NO}_2 \\
\text{NO}_2 + \text{MCO}_3 & \rightarrow \text{MNO}_3 + \text{CO}_2 \\
\text{MNO}_3 + \text{H}_2 & \rightarrow \text{MO} + \text{NO} + \text{H}_2\text{O} \\
2\text{NO} + 2\text{H}_2 & \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \\
\text{MO} + \text{CO}_2 & \rightarrow \text{MCO}_3 \\
\text{MCO}_3 + \text{SO}_3 & \rightarrow \text{MSO}_4 + \text{CO}_2
\end{align*}
\]

NOx is retained in the NOx-trap as a nitrato 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 NOx 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 (SO₃) derived from sulfur compounds in the fuel, Reaction (xv). Thus the NOx-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 NOx capacity the trap must be occasionally ‘desulfated’, essentially the reverse of Reaction (xv), by treatment at higher reducing temperatures than used to reduce stored NOx.

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 NOx 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 (SO₂) is injected upstream of the NOx-trap. When compared with NOx-traps saturated 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 SO₂/H₂S formed changes with richness, the desulfation rate follows a simple Arrhenius relationship.

Ford (2003-01-1159) also examined NOx release from NOx-traps during regeneration. The main cause for the appearance of NOx 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 NOx-trap increased the time for regeneration, as did the amount of NOx released during this process. Although the presence of ceria introduces additional OSC, it also facilitate 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 NOx-trap. Active switching of gas between the main cooled section and the bypass enables the NOx-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
NOx-trap. A NOx sensor behind the NOx-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 Coming (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 NOx 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).

\[
\begin{align*}
\text{CO} + 0.5\text{O}_2 & \rightarrow \text{CO}_2 \\
\text{HC} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

(xvi)  
(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 NOx 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 CO₂ 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.

\[
\begin{align*}
\text{PM} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{NO} + 0.5\text{O}_2 & \rightarrow \text{NO}_2
\end{align*}
\]

(xviii)  
(xix)

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 (NO₂). The combustion occurs at temperatures as low as 250°C, a temperature available during diesel truck or bus operation. The NO₂ is obtained by oxidising NO present in the exhaust gas over a Pt oxidation catalyst, Reaction (xix). The reaction is inhibited by SO₂, 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™).

For some heavy-duty applications NOx 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® system. Johnson Matthey and STT Emtec (2003-01-0048) reviewed the performance of over one thousand EGR-CRT® systems installed on urban buses and other heavy-duty vehicles in Europe during the last four years. Typically the EGR-CRT® system is as efficient as a CRT® for HC, CO and PM reduction, and additionally lowers NOx by 46–58%.

Future legislation requires lower NOx emissions, but a lower NOx/PM ratio will be less favourable for the ‘CRT effect-with-NO₂’ to operate. One potential solution is to recycle NOx 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 NO₂. If this filter is placed upstream of a monolithotic wall-flow filter, sufficient NO₂ 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® (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 g ft⁻¹) 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 combat 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 g ft⁻¹). 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 g kWh⁻¹) stationary heavy-duty diesel engine to Tier 3 levels (4 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 NO₂.

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 NOx 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 NOx-trap placed in front of a catalysed PM filter. The simultaneous reduction of about 90% PM and conversion of more than 50% NOx 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 NOx by ammonia (NH₃) over a suitable catalyst can be an efficient means to reduce NOx, for example see Reaction (xx):

$$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (xx)$$

$$2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad (xxi)$$

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 NOx control combined with a CRT® for PM control in an extremely small package. The SCR catalyst is annular and placed around the CRT®. The four-way emissions control system is designated a SCRT™. The exhaust gas from the engine passes through the Pt oxidation catalyst of the CRT® and PM filter; urea solution is then injected into the gas flow before it passes through the annular SCR catalyst. Residual NO₂ 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™.

On a state-of-the-art 12 litre diesel engine with an NH₃/NOx ratio of 0.95 (maximum possible NOx 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™ 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

7. SAE 2004 World Congress, Cobo Center, Detroit, Michigan, 8–11th March, 2004; see www.sae.org

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Platinum Metals Rev., 2003, 47, (4)
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 oxidation 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 cps (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 (NOx) are emitted at the highest levels. In cars having two catalyst systems, the larger underfloor catalyst is normally responsible for controlling NOx emissions. N.E. ChemCat (2002-01-0348) have shown that metallic state rhodium is the most effective active phase for reduction of NOx to nitrogen (N2), according to Equations (i) and (ii):

\[
\begin{align*}
2\text{NO} + \text{2CO} & \rightarrow \text{N}_2 + 2\text{CO}_2 \\
2\text{NO} + \text{2H}_2 & \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

(1) (2)

While NOx 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:

\[
\begin{align*}
\text{CH}_3\text{H}_2 + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{2H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

(iii) (iv)

An enhancement in the steam reforming reaction, which both removes HC and provides H2 for facilitating NOx 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 (CHT™) can help to control the initially formed HC's 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 HC's, whereas the cleaner engines in new cars produce lower levels of these HC's. 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 CHT™. In all cases the CHT™ 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.

NOx-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 NOx from the exhaust of lean-burn engines, because NOx cannot be efficiently reduced to nitrogen in the presence of excess.
oxygen. Therefore, an alternative approach is being used which stores NOx as nitrate phases under lean conditions, in a so-called 'NOx-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 NOx-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.

\[
\begin{align*}
\text{NO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{NO}_2 \quad \text{(v)} \\
\text{NO}_2 + \text{MO} & \rightarrow \text{MNO}_3 \quad \text{(vi)} \\
\text{MNO}_3 & \rightarrow \text{MO} + \frac{1}{2}\text{O}_2 + \text{NO} \quad \text{(vii)} \\
2\text{NO} + 2\text{CO} & \rightarrow \text{N}_2 + 2\text{CO}_2 \quad \text{(viii)}
\end{align*}
\]

The nitrate phase in a NOx-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 (SO\(_2\)) in the exhaust gas. The SO\(_2\) is derived from sulfur compounds originally present in the fuel, see Equations (ix) and (x). Oxidation of SO\(_2\) to SO\(_3\), Equation (ix), is catalysed by Pt.

\[
\begin{align*}
\text{SO}_2 + \frac{1}{2}\text{O}_2 & \rightarrow \text{SO}_3 \quad \text{(ix)} \\
\text{MO} + \text{SO}_3 & \rightarrow \text{MOSO}_4 \quad \text{(x)}
\end{align*}
\]

As a result the capacity of the NOx-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 NOx-trap. To overcome this problem it is necessary to periodically 'desulfate' the NOx-trap by exposure to very high-temperature reducing conditions to recover the original NOx-trapping capacity.

One means of achieving high catalyst temperature to desulfate the NOx-trap has been described by Ford (2002-01-0733). They alternate the air/fuel ratio so that the oxygen stored in the NOx-trap during lean periods is used to oxidise HC, CO and H\(_2\) 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 NOx-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 NOx-traps. It involves closed loop NOx-trap purging, with one heated exhaust gas oxygen (HEGO) sensor positioned before the NOx-trap and one after, to provide information about the oxygen and NOx storage capacities. If the oxygen storage capacity (OSC) does not change significantly over time the NOx 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 NOx sensor (4), downstream of the NOx-trap, is used to monitor NOx-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 NOx-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 NOx-trap during NOx absorption and subsequent regeneration. They have developed concepts relating to NOx 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 NOx 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\textsuperscript{TM}).

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\textsuperscript{TM} 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\textsuperscript{TM}, has been reported by Johnson Matthey, Environment Canada, New York City Transit, New York State Department of Environmental Conversation, Equilon Enterprises, Conning 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\textsuperscript{TM} in appropriate applications.

Johnson Matthey have also developed (2002-01-0428) a modified CRT\textsuperscript{TM} system which has a Pt-catalysed PM filter as well as an upstream oxidation catalyst – the CCRT\textsuperscript{TM}. 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 NOx: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 exothermic 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 exothermic 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, (1), 71; ibid, 2000, 44, (2), 67
2 Cobor 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-1095CD). 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 NOx sensor see: M. V. Twigg, Platinum Metals Rev., 1996, 40, (3), 111

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Ruthenium Light-Switch Effects


The dppz ligand has bpy-like and phen-like states. The bpy is associated with the bright state and phen with the dark state. The bpy-like state is similar in size to the corresponding orbital in the MLCT state in [Ru(bpy)3]+; 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.

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Exhaust Emissions Control Developments
A SELECTIVE REVIEW OF THE DETROIT 2001 SAE WORLD CONGRESS

The Society of Automotive Engineers' (SAE) Detroit World Congress in the Cobo Center (5th–8th March) was a great success, with some 50,000 delegates, and about 1300 technical presentations. There were many well-attended sessions on the control of engine exhaust emissions, and this selective review focuses on papers concerned with platinum group metal (pgm) catalysts. Platinum oxidation catalysts are used in selective catalytic reduction systems which use ammonia or urea, but these are not discussed here. The reference numbers of papers mentioned are given, most being available in SAE "Single Publications" (1).

Three-Way Catalysts
With conventional gasoline engines, the first objective in obtaining the very strict legislated hydrocarbon (HC) emissions requiring 99% conversion is to have the catalyst operating (light-off) within seconds of starting the engine. To achieve this a low-temperature light-off catalyst and an engine start-up procedure that rapidly heats the catalyst are required. It is essential to minimise heat losses, and computer models are used to understand the interplay between various components.

Volkswagen (2001-01-0940) described a simulation package for calculating gas/solid heat and mass transfer in exhaust systems. They studied the effects of conventional single-wall exhaust pipes, pipes with air-gap insulation, flanges, and flexible couplings. Their results indicated that conserving heat is essential for reducing catalyst light-off times and HC emissions during the crucial first seconds. Excess oxygen was beneficial with standard catalyst heating strategies (lean operation of the catalyst), and having oxygen stored in the catalyst was important.

Volvo (2001-01-1311) reported a new lean start-up strategy for five- and six-cylinder engines. They described how the 99% conversion/lambda window gradually decreased with time. Partial zero emission vehicles (PZEVs) require 150,000 miles durability. Heat losses and catalyst warm-up time are minimised by placing the catalyst close to the exhaust manifold. But in this 'close-coupled' position, it can be subjected to exhaust gas pulsation, poor mixing and high-temperature excursions which could be detrimental to performance.

Nissan (2001-01-0943) modelled the gas flow and heat transfer for a close-coupled catalyst configuration, and concluded that during low engine-load conditions, for example during catalyst warming, it is difficult to concentrate the gas flow in the centre of the catalyst and this can delay light-off. The difficulty in obtaining SULEV emissions was illustrated by projects that failed to achieve them (2001-01-1313, 2001-01-1314).

Threshold catalysts (deactivated so emissions are outside the legislative limits by a prescribed amount) are needed to calibrate on-board diagnostic (OBD) systems. The catalysts are often made by very high-temperature treatments that can degrade the substrate. Shell, DaimlerChrysler and Emitec (2001-01-0933) reported that a high-temperature vacuum treatment can achieve required activation without causing substrate deterioration.

The price of palladium (2) has been an incentive to develop high performance TWCs based on Pt/Rh rather than Pd/Rh. A paper by DaimlerChrysler and dmCI (2001-01-0927) described a durable two-layer Pt/Rh catalyst that at reduced pgm loadings could replace close-coupled and underfloor Pd/Rh catalysts on engines that rapidly warm the catalyst. On engines with less rapid heating strategies Pd-based catalysts were favoured in close-coupled positions due to a better HC performance. Probably for similar reasons, ASEC (2001-01-0923) in some two-catalyst configurations, favoured a Pd-only front catalyst followed by a Pt/Rh catalyst. Light-off of the front catalyst was improved if it did not contain ceria, and had only a small oxygen storage capacity (OSC).

Ford and the University of Precious Metals (2001-01-0225) confirmed that relatively low-loaded pgm TWCs containing appropriate oxygen storage components can be used for

emission control in emerging markets. If carbureted Chinese cars were retrofitted with catalysts, emissions could be significantly reduced.

NOx-Trapping Catalysts
Catalysts that store NOx as nitrate (NO₃⁻) under lean conditions, via nitric oxide (NO) oxidation over Pt to nitrogen dioxide (NO₂), and which are reacted with a pulse of reductant (CO and HCs) to give NO, are called NOx-traps or NOx-absorbing catalysts. These are being developed for use on lean-running gasoline and diesel engines. Temperatures below 550°C are required for efficient NOx removal, so NOx-traps are usually located underfloor.

Mitsubishi and ICT (2001-01-1300) discussed catalyst systems for direct injection gasoline engines, comprising a close-coupled TWC, an underfloor NOx-trap followed by a second TWC. The close-coupled TWC controls start-up HC (a Pd/Rh formulation was originally used). The OSC was minimal because stored oxygen increases the amount of fuel consumed during NOx-trap regeneration. Several Pt/Rh catalysts were evaluated in the close-coupled position. A single layer Pt/Rh catalyst had poorer HC oxidation performance under lean conditions than a Pd/Rh catalyst. Performance was substantially improved when the Pt and Rh components were in separate layers.

Toyota (2001-01-1297) modelled the duration of the rich pulse during NOx-trap regeneration. They confirmed that regeneration rate increases as the duration of the rich pulse increases, and that heat produced during regeneration (and by reduction of stored oxygen) heats the downstream part of the NOx-trap causing NOx to be released. These effects are taken into account when designing and sizing NOx-traps. NOx-traps react with sulfur dioxide (SO₂) in exhaust gas, storing it as sulfate (SO₄²⁻). This gradually decreases the NOx capacity of the trap. To overcome this a NOx-trap must be periodically desulfated under rich conditions at temperatures higher than needed to remove stored NOx. Mild desulfation gives SO₂, but rapid desulfation requires high temperatures and more strongly reducing conditions and may lead to undesirable H₂S formation.

Ford (2001-01-1299) addressed this problem and described two methodologies to minimise H₂S production; one used a ‘H₂S getter’, such as a nickel compound that forms a stable sulfide; the second involved the use of short lean pulses during high-temperature rich desulfation. This was sufficient to re-oxidise sulfide to SO₂. The combination of both methods should be interesting.

Alkali metals form stable nitrates, so could be used in NOx-traps. However, they are mobile at high temperatures in the presence of steam, and react with cordierite substrate causing loss of the NOx storage component, and deterioration of substrate properties. Mitsubishi, ICT and NGK (2001-01-1298) reported three approaches to overcome these problems. The first was to retain alkali in the washcoat by reaction with an acidic component: a zeolite was chosen. The second approach was to protect the substrate with a silica pre-coat, and the third was to minimise sulfur accumulation by incorporating titania in the washcoat. Combining all three modifications afforded a NOx-trap with improved overall thermal resistance.

Diesel NOx-Traps
Diesel NOx-traps have special demands: diesel engines operate at cool temperatures and are specifically designed to run lean, so obtaining rich regeneration conditions is a challenge. ASEC (2001-01-0508) described work confirming that NOx-traps can be desulfated at 650°C and at an air:fuel ratio ~ 13. A programme involving FVV, National Renewable Energy Laboratory, MEECA, Battelle, Ford, ASEC and Detroit Diesel examined desulfation of NOx-traps in diesel applications; finding NOx conversion efficiency could be restored. A NOx-trap aged for 250 hours running on 30 ppm sulfur fuel had its NOx conversion efficiency fully restored by a single desulfation. However, with repeated desulfations performance gradually decreased. The reason for this is unclear, but may be due to the regeneration procedure.

Diesel Particulate Filters
Diesel engines run lean and have excellent fuel economy, but removing particulate matter (PM) from the exhaust gas is difficult. Over recent years
the amount of soot has been lowered dramatically through higher injector pressures, better fuel atomisation, and by improved fuel management and combustion control. However, it is generally thought that ‘clean diesel’ requires a Diesel Particulate Filter (DPF), and the most common DPF is a ceramic wall flow filter.

Understanding the fluid dynamics of DPFs was extended by presentations from Michigan Technological University, CERTH/CPERI and Corning (2001-01-0908, 2001-01-0909, 2001-01-0911) describing three flow mechanisms which contribute to pressure drop: filtration inertia losses, channel inlet contraction and channel exit expansion losses. Exit losses are dominant, being about twice those at the filter inlet. The models estimate filter pressure-drop as a function of loading and agree well with observations. The influence of inlet radial non-uniformity can lead to partial regeneration near the periphery. The practical challenge is to burn trapped soot without high temperatures damaging the filter.

One successful approach used low-temperature oxidation of soot with NO at a Pt catalyst. In heavy-duty applications the temperature of the exhaust gas is usually high enough for this to occur. This system is known as the Continuously Regenerating Trap (CRT), or Continuously Regenerating Diesel Particulate Filter (CRDFF) and many thousands are installed on buses and trucks. Japanese/Finnish work (2001-01-1256) resulted in a procedure for increasing exhaust gas temperature at low engine speed for CRT operation without fuel penalty.

Experience with a test fleet of heavy-duty diesel vehicles fitted with CRTs in Southern California was reported by Johnson Matthey, National Renewable Energy Laboratory, BP and West Virginia University (2001-01-0512). The fleet included school buses, fuel trucks, and delivery and transit vehicles. The CRTs worked well and reduced PM, CO and HC in the exhaust by 90 to 99%. No measurable impact on fuel economy was noted. New York Environmental Conservation, Johnson Matthey, Environment Canada, Equilon Enterprises and Corning (2001-01-0511) reported the performance and durability of CRTs on diesel buses at New York City Transit. In this successful programme PM, CO and HC were reduced by over 90%, carbonyls by more than 99%, polyaromatic hydrocarbons (PAHs) by more than 80%, and nitro-PAHs by more than 90%.

NGK reported a computer simulation for high temperature regeneration of wall-flow filters, and performed 2D thermal stress analysis for different filter designs. Their results showed that the maximum temperature during soot combustion is moderated if the filter has high thermal mass and high thermal conductivity. These properties are larger for silicon carbide (SiC) than for cordierite, and explains why SiC is gaining popularity in potential light-duty diesel applications. Light-duty diesel vehicles have cooler exhaust gas than heavy-duty ones, and achieving high temperatures for DPF regeneration has an undesirable impact on fuel consumption, so the reaction of soot with NO; at moderate temperature is very beneficial. The regeneration of catalytic DPFs was discussed by Peugeot Citroën, dmc and the University of Siegen (2001-01-0907). They showed that having catalyst in the DPF can have a small benefit in reducing the soot combustion temperature.

Conclusions

The integration of new advanced pgm-based catalysts into total systems for emissions control is achieving extremely low tail-pipe emissions levels. Currently it appears that the role of platinum is becoming relatively more important. This trend could well continue.

M. V. TWIGG

References


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Advanced Exhaust Emissions Control
A SELECTIVE REVIEW OF THE DETROIT 2000 SAE WORLD CONGRESS

This selective review covers papers, involving platinum group metal (PGM) catalysts, presented at the Society of Automotive Engineers (SAE) annual Detroit World Congress, held from 6th to 9th March, 2000. The Congress attracts large numbers of attendees (49,249 this year from more than 80 countries), and there were some 1,300 exhibiting companies with a similar number of papers presented at the well-attended technical sessions. Almost all of the published papers referred to here are conveniently collected together in SAE "Single Publications" (1), and reference is given in parenthesis to each cited paper to enable those interested to easily access them.

Towards and Beyond SULEV
The effectiveness of PGMs in three-way catalysts (TWCs) has increased over recent years as more advanced washcoat formulations have been introduced. The distribution of PGMs in the catalyst is important, and ASEC (2000-01-0860) found that by having a palladium-only front catalyst followed by one containing platinum and rhodium was an effective solution in some LEV/ULEV applications because the palladium catalyst ensured optimal hydrocarbon light-off. The design of such low emissions systems has become relatively commonplace. The next major emissions target is the American SULEV (half ULEV levels) which seriously challenges all of the available technologies. Here advanced catalysts are incorporated into systems that push technology to the limits to give the lowest possible emissions for conventional gasoline engines.

High Cell Density Catalysts
Thin wall high cell density substrates provide high geometric surface area, that can be accompanied by low heat capacity which can shorten the time it takes for catalysts to light-off during the cold start of conventional gasoline engines – the key parameter in achieving very low emissions. This was an important theme at the last congress (2), and the trend continued this year. Denso (2000-01-0496) discussed ultra thin wall 3 or 2 mil (75, 50 μm) cordierite substrate, and highlighted material requirements of the front face, particularly when located close to the exhaust manifold. To increase strength, the walls of the outermost cells were made thicker than the inner ones. This could exacerbate radial maldistribution of gas across the catalyst, and the practical consequences of this have yet to be explored. NGK and Environex (2000-01-0494) developed computer models to predict performance of catalysts based on ultra thin wall high cell density substrates. Their results showed that reducing wall thickness to reduce thermal mass offers the greatest benefit in reducing light-off time. Higher cell density per se is however accompanied by extra thermal mass, and a cell density of around 1200 cpsi appeared to give optimum light-off. Johnson Matthey (2000-01-0502) also reported computer simulation of these effects, and gave extensive results for catalysts with cell densities up to 900 cpsi (2 mil walls) on laboratory engines and cars. Significant benefits were observed with palladium/rhodium and palladium-only formulations on high cell density substrates, but appropriate engine calibration is vital. There may be little benefit obtained from using high cell density catalysts if the engine calibration is poor: for example, a European Stage 2 car with a rich start-up strategy showed a nitrogen oxides (NOx) advantage with high cell density catalysts, but hydrocarbon (HC) and carbon monoxide (CO) advantages were swamped.

Another requirement for advanced substrates is that the catalyst formulation must have very good thermal durability, because high cell density catalysts will experience high temperatures caused by more intensive chemical exotherms.

Metallic Substrates
These can be made from very thin metal foil to achieve high cell densities; but disadvantages can include the higher thermal capacity of metals.
compared to porous ceramic materials. For several years Bosal (2000-01-0497) have been working with pre-coated metal foil, and they described how they produce a modular block design catalyst using 50 \( \mu \)m metal foil. These are assembled into V-shapes across the exhaust gas flow. This design offers the advantage of being able to use high cell density units without overly increasing pressure drop as the frontal area can be increased in proportion to the cell density, provided the necessary space is available.

In a joint paper AVL and Emetec (2000-01-0500) used computer simulation to probe the behaviour of normal high cell density catalyst designs in a cascade modular arrangement with an electrically heated catalyst. Tests were carried out on an ULEV production vehicle, and with the electrically heated catalyst operating for 25 seconds at 2.5 kW the light-off time shortened from 30 to 22 seconds, but SULEV HC levels were not achieved.

**Hydrocarbon Traps**

Trapping HCs formed during the cold start in a material such as a zeolite until the TWC has reached light-off temperature is a potential route to very low emissions. The University of Thessaly (2000-01-0655) developed a computer model for a system with a HC-trap in front of a main catalyst. With this configuration, desorption from the HC-trap, before the catalyst reaches operating temperature, is a major problem that is difficult to circumvent. Ford (2000-01-0654) modelled a catalysed HC-trap, that combines catalyst and HC-trap on a single substrate. Here the thermal problems associated with separate units were overcome, and the model predicted good performance on a vehicle. The computer model should permit design of optimised systems in the future. Nissan (2000-01-0892) presented results for systems comprising a closed-coupled TWC followed by underfloor two-layer catalysed hydrocarbon traps. These had a lower layer HC absorber, and a top TWC layer, and the overall system demonstrated potential for SULEV applications.

**Vehicle Demonstrations**

Volvo (2000-01-0894) discussed three SULEV approaches: hydrogen (H\(_2\)) injection onto the catalyst when starting, a rich start-up with rapid temperature rise and air injection, and storing start-up HCs in a canister until the catalyst is operating. Each has the potential of providing SULEV requirements, but the most attractive is the second, requiring least modification to current designs. By bringing together several different technologies on vehicles, emissions below the SULEV levels can be achieved. Nissan (2000-01-0890) described the combination of ultra thin wall (2 mil) substrate coated with low light-off catalyst, and a two-stage catalysed HC-trap, on an engine with tight air-fuel ratio control. The cold start HCs from the engine were minimised by incorporating an electronically actuated swirl control valve, and a high-speed starter. The resulting vehicle emissions were exceptionally low, as they also were from a car.
described by Honda (2000-01-0887). Honda used 1200 cps (2 mil walls) substrates made possible by a new canning method, which overcomes strength problems. However, to meet SULEV standards it was necessary to adjust the spark timing to decrease the time to reach catalyst light-off temperature, and to control intake air (early lean operation), and use an advanced secondary oxygen sensor feedback system. This identifies different catalyst models in real time and predicts the post-catalyst sensor output, so eliminating emissions that would be released while the control system adjusted to the actual secondary sensor signal.

NOx-Traps for Lean-Burn Gasoline Engines

The new generation of direct injection, lean-burn gasoline engines offers potential improved fuel economy, but requires NOx emissions to be trapped when running lean, and periodic regeneration under rich conditions to release the stored NOx as nitrogen (N2). This developing NOx-trap technology, which uses platinum and rhodium, suffers from sulfur poisoning, and NOx-traps need to be purged of sulfur periodically. Both regeneration conditions require careful engine management to achieve the desired effects without affecting driveability, but desulfation is the more difficult because of the higher temperatures involved.

Ford (2000-01-1200) described a novel way of sustaining high catalyst temperature by rapid air/fuel ratio fluctuations. The oxygen storage components in the NOx-trap respond to this and generate isotherms of around 300°C, without being overly rich. Toyota (2000-01-1196) investigated ways of restricting the amount of accumulated sulfur, and found that incorporating titania and zirconia into the formulation was beneficial. Honda (2000-01-1197) also reported formulation work, and found addition of "mixed metal oxides" of different types improved performance.

Diesel Aftertreatment

Control of Diesel Particulate Emissions

Diesel soot, formed by incomplete combustion of fuel, is a potential health hazard and it is desirable to minimise soot emissions into the environment (3). It comprises a high surface area carbon core with adsorbed HC, partially oxidised species like aldehydes, carboxylic acids, etc., with water, sulfur compounds (including sulfuric acid), and some nitric acid derived from nitrogen oxides. Over recent years improved fuelling, better combustion system characteristics, and enhanced engine management have contributed to a reduction of soot. However, the introduction of finer fuel spray from new injector nozzles, made possible by higher-pressure fuel systems, was probably the single most important advance (4). The development of the high performance modern high speed diesel engine also provided means of reducing exhaust pollutants, and additional benefits are now coming from use of increasingly-available ultra low sulfur fuel with low polyaromatic content which produces less soot than conventional diesel fuel (5).

Johnson Matthey (2000-01-0479) described a procedure to lower particulate emissions from older American diesel buses (built before 1994) by 25%, or to below 0.1 g bhp\(^{-1}\) h\(^{-1}\), by replacing some engine components, and fitting a platinum oxidation catalyst to provide additional particulate...
reduction. Platinum oxidation catalysts can remove some organic components from soot, but usually significant amounts of carbon are not oxidised.

Diesel Particulate Filters

Future legislation demands much lower particulate emissions than are made possible by engine modifications and oxidation catalysts, and a particulate filter, of which there are several kinds, will have to be used. Coming (2000-01-0184) derived and experimentally verified a pressure-drop model for cordierite wall-flow filters. Agreement between predicted and measured pressure drop was excellent. The approach is being extended to filters loaded with soot, and preliminary data for lightly loaded filters were presented: lower cell densities are appropriate for longer filters, and higher cell densities for short ones. Extension of this work should permit prediction of optimised filter length, volume, and cell density for particular applications. Ishida and Peugeot (2000-01-0185) studied the characteristics of silicon carbide wall-flow filters along similar lines, and concentrated on the thermal durability and high temperature resistance. Their model for a loaded filter assumed a uniform soot layer, with ash collecting at the end of the channels forming an inert zone.

The Continuously Regenerating Trap

For continued operation it is necessary to remove trapped soot from a diesel particulate filter, and several ways of doing this have been investigated. Johnson Matthey (2000-01-0480) reviewed heavy-duty diesel experiences with a successful approach which uses nitrogen dioxide (NO$_2$) to combust trapped soot at temperatures much lower than it burns in air. The required NO$_2$ is obtained by oxidation of nitric oxide (NO) over a platinum catalyst before the filter, this also oxidises HCs and CO. Under most operating conditions soot is continuously removed, so the system is referred to as a continuously regenerating trap (CRT™). Over six years more than 6000 of these have been utilised in European countries where the necessary low sulfur fuel was promoted – Sweden, Germany, the U.K., and to a lesser extent in several other countries. A selection of CRTs which had been used for up to 600,000 km was tested under laboratory conditions. There was virtually no deterioration of performance, confirming the robustness of this system in actual use. A lighter duty application of the CRT™ was described by AVL (2000-01-0181) who have developed a diesel engine for Sports Utility Vehicles (SUVs) which meets the American Tier 2 emissions levels.

Peugeot (2000-01-0473) used a CRT configuration of a platinum oxidation catalyst in front of a silicon carbide wall-flow filter on a European diesel car which was soon to be in production. Strategies are incorporated to increase exhaust gas temperature through post combustion fuel injection, and the fuel is dosed with a cerium additive to facilitate soot combustion. Faurecia (2000-01-0475) discussed cordierite and silicon carbide wall-flow filters, and proposed an oxidation catalyst in front of the filter in a CRT configuration that included an electrical heater close to the filter to increase gas temperature when appropriate.

Control of Diesel NOx Emissions

Lean-NOx Catalysts

Diesel exhaust contains low levels of reductant (CO, HC) in the presence of a vast excess of oxygen, and most of the reductant is oxidised by the oxygen over platinum oxidation catalysts. Little reductant remains to reduce NOx (and only over a small temperature range), so normally only a relatively small amount of NOx is removed by what are called lean-NOx catalysts under normal conditions, and this can be somewhat increased if additional reductant is added to the exhaust.

Selective Catalytic Reduction

To achieve significant direct NOx reduction additional reductant that selectively reduces NO in the presence of oxygen must be introduced – a process called selective catalytic reduction (SCR). Ammonia is an excellent reductant in SCR systems, and although at present it appears inappropriate to use PGM-based SCR catalysts, platinum catalysts are used in two different roles in these systems. Urea is potentially a convenient source of ammonia, and Degussa (2000-01-0189) described a urea-based SCR system for heavy-duty
HEALTH EFFECTS OF VEHICLE EMISSIONS
A REVIEW FROM THE SECOND INTERNATIONAL CONFERENCE

The Second International Conference on Health Effects of Vehicle Emissions was held in London from 23rd to 24th February, 2000. Some 165 delegates from 16 nations, and a variety of industrial, environmental, government and academic backgrounds, met to discuss issues concerned with reducing the environmental impact and health risks associated with vehicle emissions.

J. Wallace (Ford, U.S.A.) summarised some U.S. steps with respect to vehicle emissions. Since 1966 vehicle emissions have been reduced by a factor of 25. Hydrocarbon emissions have decreased by...
Aftertreatment for Low Emission Vehicles

A SELECTIVE REPORT FROM THE 1999 SAE ANNUAL CONGRESS

The 1999 annual congress of the Society of Automotive Engineers (SAE) took place in Detroit from 1st to 4th March with 46,309 delegates and 1104 companies exhibiting new products. Some 1120 papers were scheduled for presentation covering all the automotive technologies, although fire curtailed some sessions. Papers on exhaust gas aftertreatment focused on tighter emissions requirements from conventional gasoline, lean-burn gasoline and diesel engines. Some new legislation and a selection of papers are reviewed here, with SAE numbers being given.

New Legislation
In 1998 a number of new emissions levels were introduced or proposed. In the U.S.A. National, NLEV, standards were adopted in 49 states, and the Environmental Protection Agency (EPA) concluded that the more stringent Tier II standards were needed. California adopted a LEV II programme, stringent standards for hand-held engines, a three-way catalyst (TWC) based standard for off-road spark ignition (SI) engines less than 25 hp, tight standards for recreational marine engines, and higher requirements for some motorcycles. The EPA announced plans to establish a voluntary heavy-duty diesel engine retrofit programme. The revised LEV and ULEV standards involve major hydrocarbon (HC) and nitrogen oxides (NOx) reductions, and the SULEV standard has exceptionally demanding emission levels.

In Europe gasoline car emissions have been agreed for 2000 (Stage 3) and 2005 (Stage 4). A range of measures will be developed for on-board diagnostics (OBD), cold start and in-service compliance along with tax incentives allowed for early introduction of Stage 4 standards. Gasoline and diesel fuel sulfur levels will also be markedly reduced.

Conventional Gasoline Engines
Low emissions demand that aftertreatment systems operate immediately after starting the engine. High activity catalyst formulations have low temperature light-off, and when combined with effective heat - and mass transfer and low heat capacity, respond quickly. Mounting the catalyst close to the manifold (close-coupled) minimizes the time the catalyst takes to reach working temperature.

In the U.S.A., SWRI and MECA (1999-01-0774) demonstrated that LEV II ULEV levels can be obtained by combining advanced catalysts on high cell-density substrates with insulated exhaust components. In examining systems for Europe – Elasis, Napoli University, Magneti Marelli and Fiat in Italy (1999-01-0775) concluded that a close-coupled starter catalyst and a main underfloor catalyst, or a closed-coupled main catalyst, are cost-effective solutions.

Thin Wall High Cell-Density Catalysts
These catalysts have high geometric surface area with lower heat capacity and backpressure than standard materials. BMW, NGK and Friedrich Boysen (1999-01-0767) developed a system with a relatively thin wall substrate (400 cpsi/4.3 mil, cells per square inch/thousandths of an inch) for a LEV/Stage 3 V8 engine. This had a close-coupled high palladium tri-metal catalyst on each air-gap insulated manifold, and an underfloor palladium/rhodium (Pd/Rh) catalyst. Corning, Johnson Matthey and DaimlerChrysler (1999-01-0273) compared physical durability of standard (400 cpsi/6.5 mil) and thin wall substrates (600 cpsi/4.3 mil and 400 cpsi/4.5 mil) coated with high temperature stable washcoats. Predicted and measured thermal shock parameters agreed, showing that the new catalysts have superior thermal shock resistance and are suitable for close-coupled positions.

Corning (1999-01-0269) confirmed improved thermal shock characteristics are due to a lower coefficient of expansion resulting from improved composition and manufacturing processes. Delphi, Corning, SWRI and ASEC (1999-01-0271) had benefits using 600 cpsi/3.5 mil substrate over standard 400 cpsi/6.5 mil material;
but 600 cps/4.3 mil had more backpressure, restricting acceleration, which was not the case with the 600 cps/3.5 mil substrate.

DaimlerChrysler, Degussa and NGK (1999-01-0272) reported a similar study for V6 and V8 engines for Stages 3 and 4. Their system used close-coupled (600 cps/3.5 mil) and two underfloor catalysts (400 cps/4.3 mil). Contributions from the washcoat thickness to the backpressure of high cell-density catalysts were noted. Mazda (1999-01-0307) varied the amount and ratio of platinum group metals (ppm), catalyst promoters, catalyst layering and cell-density. Both 600 cps/4 mil and 900 cps/2 mil substrates were examined, the latter giving 35 per cent lower tail-pipe HC emissions. Honda and NGK (1999-01-0268) compared 600 cps/4.3 mil and 1200 cps/2 mil catalysts. High conversion was obtained with the high cell-density catalyst, but mechanical strength was a concern.

Honda’s (1999-01-0772) ZLEV system (one-tenth of the ULEV limits) had reduced engine emissions due to high swirl with variable valve timing and lift, and improved spark plugs with durable small-diameter iridium centre electrodes. They maintained high temperature and prevented quenching. Fuel control was optimised during start-up, and precise air: fuel control was maintained by controlling the air: fuel ratio in each cylinder. Retardation of the ignition gave fast heating of a close-coupled high cell-density Pd-only starter catalyst (1200 cps/2 mil), followed by TWCs and a two layered catalyst comprising a HC-trap with a top layer TWC. At low temperature HC is trapped, but is released as the system warms to 100°C, when the TWC layer converts part of the released HC.

Electrically Heated Catalysts

Trapping HC’s when cold then releasing them onto a working catalyst has several variations. Other methods of treating HC’s include Exhaust Gas Ignition (EGI) when air-diluted rich exhaust gas is combusted ahead of a TWC, and the use of a special catalyst which oxidises carbon monoxide (CO) at low temperature. Electrical pre-heating has been widely researched and Emitec (1999-01-0770) reviewed the advantages of Electrically Heated Catalysts in SULEV systems. Increasing the gas temperature by electrical heating can offset thermal mass effects and shorten the catalyst light-off time.

Platinum Group Metals in Catalysts

Originally TWC’s were predominately platinum/rhodium (Pt/Rh) formulations. Legislation, particularly in the U.S.A., emphasised attaining low HC emissions, and Pd-containing catalysts can achieve high HC conversions. Using these catalysts resulted in a wider use of Pd at increasingly higher loadings. Three types of Pd-containing TWC’s are available: Pd-only, Pd/Rh, and tri-metal (Pd/Rh/Pt). The amount of Pd used in autocatalysts now exceeds that of Pt and Rh, and greater flexibility in the metals used might help future supply/demand considerations.

Johnson Matthey examined (1999-01-0309) conditions favouring Pd/Rh compared with Pd-only catalysts for NOx control. At low temperature both perform similarly, but high temperatures accentuated differences which give advantages to Pd/Rh catalysts in NOx conversions. This is because sulfide poisoning becomes more significant at high temperature when the exhaust is rich (reducing), so actual catalyst choice depends on the vehicle. Johnson Matthey (1999-01-0308) showed that increasing the Rh:Pd ratio in a standard lower loaded Pd/Rh catalyst maintained acceptable performance, but new improved formulations have lower Pd content. The activity of a new low-loaded Pd/Rh catalyst is better than the standard with twice the amount of ppm. This will allow Pd load reductions or improved performance at standard loadings. Pd/Rh catalysts with higher activities than standard Pd/Rh formulations have also been developed, thus giving options for managing ppm demand.

Lean-Burn Gasoline Engines

Direct injection (DI) gasoline engines capable of lean operation offer reduced fuel consumption, but their NOx control is a challenge. One method is to store NOx and release it for reduction over a TWC. A NOx-trap combines these. Ricardo (1999-01-1281) had a fast
light-off close-coupled catalyst and underfloor NOx-trap on a car with a stratified charge DI engine. With significant engine management modifications low tail-pipe emissions can be achieved, and effective NOx-traps allow engine calibration for fuel economy.

Control of operating parameters is critical for optimum performance and Ford (1999-01-1283) measured stored NOx from the quantity of fuel used in regeneration. Bosch (1999-01-1284) described a management system for DI gasoline engines, aftertreatment assumed a fast heated catalyst for early HC conversion, a NOx-trap with low oxygen storage (OSC) and a TWC with significant OSC. Temperature and oxygen sensors provided control inputs. Toyota (1999-01-1279) analysed NOx-trap sulfur poisoning, and suggested a hexagonal cell substrate of uniform washcoat thickness containing components which form hydrogen via steam reforming. While progress has been made, NOx-traps need low sulfur fuel, which should become increasingly available.

Diesel Aftertreatment

Diesel engines run lean with excellent fuel economy, but reduction of their NOx and particulate matter (PM) is difficult to achieve. Michael Walsh (1999-01-0107) reviewed diesel legislation and the tremendous progress in diesel combustion engineering, fuelling, and oxidation catalysts. A few modern diesel cars already meet Stage 3 emissions levels and a few small cars may meet Stage 4 requirements before 2005, but most vehicles will require effective NOx aftertreatment.

NOx Reduction and Soot Removal

Methods to remove NOx were discussed by the German FEV (1999-01-0108). Diesel exhaust contains only a small concentration of reducing species, limiting lean-NOx catalysts to about 15 per cent conversion. Injecting fuel, via the engine or directly into the exhaust, increases the available reductant and can increase NOx conversion to about 30 per cent. Degussa and ICT (1999-01-0109) showed how two Pt catalysts could be optimised. Unfortunately, such approaches will be insufficient in many situations, and methods able to provide high NOx conversions are needed, Selective Catalytic Reduction (SCR) being one. Ammonia, or a derivative such as urea, is injected into the exhaust before a SCR catalyst. This can give NOx conversions of 75 per cent, but there is no infrastructure for urea distribution and the weight and volume of an additional tank for refuelling must be considered. Another emerging technology is NOx-trap technology, similar to that for DI gasoline engines and operating at the lower temperatures of diesel exhaust. Sulfur tolerance, low temperature operation and obtaining regenerating conditions are concerns.

Soot (or PM) removal from diesel exhaust is necessary to meet future legislation. Major engine-based improvements have been successful, but more are needed. Hino (1999-01-0471) stated that with low sulfur fuel, high loaded Pt oxidation catalysts can remove some PM, but with high sulfur fuel sulfate forms over the catalyst and thus increases the PM. The Continuously Regenerating Trap (CRT™) uses a Pt catalyst to provide nitrogen dioxide which oxidises filtered PM at low temperature and prevents soot build-up in the filter and possible uncontrolled burning which can destroy filters. FEV described (1999-01-0108) a light truck fitted with a CRT™, cooled and filtered recycled exhaust gas, and fuelled by low sulfur fuel. The exhaust temperature of 200-500°C was suited to a CRT™ and is likely to be used more in future. FORTH/CPERI from Greece and Johnson Matthey (1999-01-0468) described design and selection criteria for sizing CRT™ filters. This employed a filter flow model that was validated by experimental measurement.

Conclusions

The Detroit SAE Congress has again been a focus for reviewing developments in emissions control technology; catalyst systems containing pgms clearly will still play a most crucial role in exhaust aftertreatment of low emission vehicles. SAE papers may be obtained from http://www.sae.org/products/sae99pap.htm or 400 Commonwealth Drive, Warrendale, PA 15096. M. V. TWIGG
Emission Control Technology at Detroit

A SELECTIVE REPORT FROM THE 1998 SAE ANNUAL CONGRESS

The 1998 Detroit “Congress and Exposition” of the Society of Automotive Engineers (SAE) took place in the Cobo Center during the last week in February, with the theme “Engineering the Product Development Revolution”. There were 46,100 registered attendees, with representatives from all countries concerned with the manufacture of motor vehicles and their components. In total, 1,146 papers were presented, covering all the technologies associated with the industry. This review focuses on the roles that platinum group metals (PGM) play in exhaust aftertreatment, the demands of diesel engine technology and the new lean-burn gasoline engine technologies. The numbers of the relevant SAE papers are given in parentheses.

 Legislative Trends

R. Becker and R. Watson (Environex) reviewed (980413) trends in emissions control, emphasizing that 1997 U.S. LEV (Low Emissions Vehicles) standards already typically require more than 98 per cent reduction in hydrocarbons (HC), and 95 per cent reduction of carbon monoxide (CO) and nitrogen oxides (NOx). Future standards require even higher conversions, and the use of on-board diagnostics demands the optimisation of sophisticated engine emissions feedback control, in combination with high performance catalysis incorporating activity monitoring.

Fuel-efficient diesel engines may help towards lowering carbon dioxide (CO₂) emissions. Diesel engines operate under very lean conditions, and their low CO and HC emissions are further reduced by platinum oxidation catalysts. However, removal of particulate matter (PM) and NOx emissions is not straightforward, and Michael Walsh, consultant, reviewed (980186) how regulatory authorities are focusing on these pollutants. Current PM regulations target the mass of the particulates, but the size and numbers of PM may also be important, and future regulations could be concerned with both.

Decreasing the emissions from automobiles continues, irrespective of the type of internal combustion engine, and some of the strategies for accomplishing this are described below.

Three-Way Catalysts

Renault and Johnson Matthey discussed (980936) gas flow variations across catalyst faces. Cone dimensions and inlet pipe sizes were modelled, and their effects on catalyst ageing, light-off and performance on bench engines and cars were measured. Exhaust gas maldistribution significantly affected catalyst performance. In a related paper, Eberspächer and Fachhochschule Darmstadt, considered (980424) cone geometry and the distance between two monoliths in a converter. The space between the monoliths influences flow distribution in the first and second catalysts, and a distance of about 10 mm may be optimal. W. Maus and R. Brück (Emitec) gave a paper (980414) on the catalyst in converter cones. These “conical catalysts” provide additional catalyst, and possibly allow a reduction in volume of the main catalyst. Other benefits resulting from conical catalysts should be a shortened cone length and more efficient catalyst usage by forcing gas impinging on the main catalyst into desirable flow patterns. M. Laurell, I. Gottberg and T. Idoffson (Volvo) reported (980416) converter optimisation with three catalysts; this included modifying the gas flow distribution, the cell density and the PGM loadings.

Mounting the catalyst close to the engine reduces the warm-up time, but this location is “materials demanding” in terms of thermal durability. Corning described (980042) how the high-temperature matt deterioration experienced with oval-shaped ceramic catalysts was overcome by new designs. Emitec indicated (980420) that low thermal mass catalysts can facilitate fast warm-up, while G. Faltermeyer and B. Pfalzgraf (Audi), R. Brück (Emitec) and A. Donnerstag (Volkswagen) reported (980417) some conflicts.
in close-coupled designs. These include mechanical deterioration due to vibration and turbulence, and good gas flow distribution to obtain maximum catalyst efficiency while maintaining engine torque and optimised warm-up times. E. Otto, F. Albrecht and J. Liebl (BMW) discussed (980418) a six cylinder engine programme which came to broadly similar conclusions.

Johnson Matthey reported (980421) progress in developing a new ultra-low emissions concept involving close-coupled three-way catalysts for NOx control, and underfloor trap technology with a novel palladium ambient-temperature CO oxidation catalyst operating under lean conditions. With this catalyst, CO oxidation has positive order kinetics in CO concentration, and a large exotherm occurs during rich start-up. Data were given for a standard 1995 model year vehicle, modified for rich start-up. This achieved emissions 50 per cent lower than the ULEV (Ultra Low Emissions Vehicles) requirement.

Honda described (980415) how ULEV emissions can be achieved with underfloor catalysts, by the optimisation of a variable valve timing and lift mechanism, a new catalyst, precise air/fuel control with a lean air/fuel ratio after starting, and exhaust components having low heat capacity. A high loading palladium catalyst facilitated light-off, and effective oxygen storage enhanced hot HC oxidation. A substrate of high cell density (600 cpsi) and low thermal mass was additionally employed.

Lean-Burn Gasoline Engines

In paper (980933) Johnson Matthey described a high temperature stable aftertreatment system for lean-burn engines. A new close-coupled fast light-off catalyst was formulated not to degrade reduction under rich conditions of stored NOx, in a new high-capacity underfloor trap.

Sulfur compounds in fuel are detrimental because they are oxidised to sulfur dioxide (SO2) in the engine and then block NOx storage sites on the catalyst. Sakai Chemical Industry Company and Tottori University reported (980932) results for a variety of sulfur oxides (SOx) traps. These absorb SOx under lean conditions and desorb it at high temperature under rich conditions. A contribution from Next Generation Catalyst Research Institute in Japan, discussed (980930) a two-catalyst, SOx resistant system. The first catalyst is copper/zeolite which stores SOx as sulfate, so protecting the rear, platinum/gold catalyst supported on titania.

Reliable ageing cycles are important for the development of lean-NOx catalyst systems. J. M. Kisenyi (Ford) presented (980934) work by Ford and Tickford Ltd where the relationships between vehicle emissions and catalyst, aged in a high temperature dynamometer cycle, were established. The cycle had significant lean phases obtained by periodic injection of air into the exhaust of an engine running rich. Good correlation was achieved, with 75 hours of dynamometer ageing being equivalent to a distance of 80,500 km.

Diesel Aftertreatment

Oxidation and NOx Removal Catalysts

Diesel engines are very fuel-efficient under part-load/idle conditions, and the University of Central England confirmed (980192, 980193) that exhaust gas temperature might then be too low for underfloor oxidation catalysts to perform well. At higher load, temperatures are higher, resulting in good oxidation conversions. One improvement that could be made to meet more stringent emissions is to mount catalysts in a hotter location close to the engine, and in the usual underfloor position. N. E. Chemcat Corporation discussed (980931) two-catalyst systems, and the role of zeolites in platinum catalysts to enhance NOx conversions. They highlighted a need to control HC/NOx ratios for optimum performance. A. Peters (Daimler-Benz) presented a paper (980191) with Degussa on the optimisation of a two-catalyst system on an engine with common rail fueling. Here it is possible to control the exhaust HC/NOx ratio for optimum NOx reduction, and with two catalysts it is possible, during low speeds, to have the front one operating in the NOx reduction temperature window characteristic of platinum catalysts, and to have the underfloor one operating in this temperature range at high speeds.
Optimal NOx removal can then be obtained under most operating conditions. Toyota illustrated (980195) that zeolites can absorb HC when the catalyst is cool, and enhance NOx reduction. Zeolite can convert high molecular weight soluble organic fraction (SOF) to smaller molecular fragments, so aiding their oxidative destruction; and sulfate production can be minimised by using washcoat materials having low affinity for SOx.

**Particulate Control**

Sulfur is a catalyst poison, and can affect the amount of particulate present in diesel exhaust after oxidation catalyst treatment. Degussa, ICT and The Technical University Darmstadt confirmed (980196) that the SOF of diesel particulate can be reduced by a platinum oxidation catalyst at the temperatures present in automobiles, whereas at higher temperatures, around 350°C, oxidation of SO2 to sulfur trioxide (SO3) and hence sulfuric acid takes place. This is adsorbed on PM. As a result, at low temperatures, SOF is oxidised and PM mass is reduced, but at higher temperatures the formation of sulfate increases the observed amount of PM. They also described how PM analysis itself can influence the measured values, due to droplet formation. A related paper (980525) from the University of Minnesota and Perkins Technology Ltd came to broadly similar conclusions.

The European VERT project described (980539) a new hypothesis for diesel engine soot formation involving fuel dissociation to produce fast diffusing hydrogen which is then burned, leaving carbon in oxygen-depleted zones. A range of aftertreatment diesel particulate filters (DPFs) were tested, and their characteristics reported in combination with different hydrocarbon soluble fuel additives. These are converted to metal oxides in the engine, and appear to reduce raw emissions and to catalyse the combustion of trapped soot at moderate temperatures. Concerns include the build-up of soot during extended low speed driving and nanosized metal oxide particles possibly passing into the environment, which would not be "toxicology permissible" for many additives.

L. Montanaro and A. Negro found (980540) sodium compounds, derived from fuel additives, were the most reactive species, in potentially detrimental reactions with filter materials; and a contribution from Aristotle University, RhônePoulenc and Renault reported (980543) results for different filter positions on a light truck.

A well-attended paper (980189) from Johnson Matthey, HJS Fahrzeugtechnik, Corning, Fraunhofer-Institute of Toxicology and Aerosol Research, and FEV Motorentechnik described further studies on Continuously Regenerating Traps (CRTs) which can overcome some diesel particulate filter deficiencies when low sulfur fuel is used. In this system a high proportion of CO and HC (including non-regulated emissions like aldehydes) are oxidised over a platinum-based catalyst. Most HC species downstream of the CRT were too low to be measured accurately. Most of the nitric oxide in the exhaust gas is oxidised to nitrogen dioxide (NO2) over the catalyst, and particulate emissions retained in a filter are burnt via reaction with NO2. Because this is a relatively low temperature reaction, particulate removal from the filter takes place at all but very low temperatures. It is well established that this system dramatically reduces particulate mass emissions, so the work described focused on particle number emissions. These were recorded down to a primary diameter of 15 nm, and had been reduced by one to two orders of magnitude, and even the nanosized particles were effectively reduced.

**Conclusions**

Most of these papers are collected in SAE "Single Publications"; the most pertinent being:

"Diesel Exhaust Aftertreatment 1998" (SP1313), "General Emissions (SP1335), "Advanced Converter Concepts for Emission Control" (SP1352) and " Catalysts Emission Control and Lean-NOx Technologies" (SP1353). Once again, the Detroit SAE Congress provided a focus for developments in emissions control technology, and it is clear that PGM-containing catalysts have a major role in achieving the emissions standards soon to be introduced.

M. V. TWIGG
Emission Control Technology at Detroit
A SELECTIVE REPORT FROM THE 1997 SAE ANNUAL CONGRESS

Traditionally, the main annual Congress of the Society of Automotive Engineers (SAE) takes place each year in Detroit during the last week of February. This year it was held from 24th to 27th February, inclusive, and the scale of the event can be judged from the 800 exhibiting companies in the “exposition” areas, and the 45,180 officially registered participants, drawn from all the countries concerned in the manufacture of cars or their components. In total 1008 papers were presented, covering all aspects of automobile technologies; each day there were sessions dealing with exhaust emission control. Within this area a wide range of topics was considered. Most of the papers are available in SAE “single publications” SP1227, SP1238, SP1246, SP1248 and SP1260.

Here, a selection of these papers has been chosen to illustrate the changing roles that platinum group metals have in the important area of exhaust aftertreatment, and the direction that catalyst technology is taking. The SAE reference numbers of the original papers are given in parentheses.

The main emphasis in emissions control this year, as last year, included cold start strategies and three-way catalysts (TWCs) for conventional gasoline engines. Additionally, there was a high level of interest in the treatment of exhaust gases from diesel and other lean burn engines.

Cold Start Strategies
Electrically Heated Catalysts

Last year several reports were presented on the use of electrically heated catalysts (EHC) for dealing with cold start emissions (1). This year Alpina, BMW and Emitec (970263) gave an update on the only European production car fitted with EHCs. Of the 100 vehicles produced, each was started on average four times per 100 km, and more than a third of them were cold starts where the coolant temperature was below 40°C. The EHCs worked well and had good mechanical durability during the first year of service. However, with the present combination of a 110 Ah battery and 150 A alternator, the EHC system is not capable of dealing with low temperature starting, for example, at -7°C, mainly due to the high internal resistance of the battery under these conditions. Clearly, further developments are needed in this area before EHC technology is capable of being introduced more generally. A paper by the Polish company Bosmal (970740) emphasised that low ambient temperatures are common during winter in much of Eastern Europe and many parts of North America, and described the effects this has on the initial emissions.

A rich-start strategy with secondary air injection, and an EHC for rapid increase in the temperature of a low light-off catalyst, was discussed in a paper by Nissan (971022). Nissan noted that the volume of exhaust gas increases as the alternator load rises, which has the disadvantage of reducing the rate of the desired exothermic reactions over the catalyst. It was concluded that it is preferable to supply electric power for the EHC from a battery, but no comments were made on low-temperature starting. Interestingly, a correlation between fuel distillation temperature and exhaust gas temperature was observed, which suggested that fuel composition could influence the performance of the cold start catalyst.

Hydrocarbon Traps

Development of hydrocarbon trap technology to minimise cold start emissions for ULEV (Ultra Low Emission Vehicles) applications continues, and Johnson Matthey (970741) described how in situ mass spectrometry techniques showed that hydrocarbon traps are effective for trapping aromatic species, C<sub>9</sub> and higher alkanes and alkenes, but ineffective for the very volatile methane, ethane and ethylene constituents. The trapping performance for C<sub>9</sub> to C<sub>10</sub> hydrocarbons is improved when competition with water is minimised by using a “water trap”
upstream of the hydrocarbon trap. Hydrocarbon trapping efficiency then increases from about 40 to 60 per cent during the first 10 seconds of a cold start.

Three-Way Catalysts
Promoters
Several papers discussed the roles of promotors, stabilisers and other components in autocatalyst formulations containing platinum group metals; these included an explanation of the chemistry of the NOx trap. A highlight was two entire sessions devoted to the uses of zirconia in emissions control applications, ranging from oxygen sensors to autocatalysts. A contribution from MEL Chemicals (970460) provided a useful general overview. The chemical inertness and refractory properties of zirconia have been exploited in high temperature chemical process catalysts in the past, and over recent years zirconia has been used both as a support for platinum group metals in autocatalysts to impart improved thermal resistance, and in oxygen storage components in combination with other oxides. N. E. Chemcat (970466) reported on the effects of dopants on the thermal stability of the surface area of zirconia — barium, calcium, lanthanum being the most effective dopants. They measured the oxygen storage properties of various ceria/zirconia mixed oxides. This was also a topic covered by other papers, for example, Rhône-Poulenc (970463) focused on the characterisation of cerium-rich ceria/zirconia mixed oxide phases.

A contribution from the University of Pennsylvania and W. R. Grace (970461) pointed out that conventional characterisation studies, such as X-ray diffraction, of these mixed oxides can result in misleading conclusions. This is because it is not the bulk structure of defective oxides that is important in controlling surface reactions, but rather local structure at the atomic level.

Sulfur Poisoning
In meeting emission requirements, high conversions of pollutants take place over modern TWCs, but even small changes in performance can affect tail-pipe emissions. Factors such as catalyst poisoning are therefore important. In fact, two papers from Johnson Matthey were concerned with poisoning due to sulfur. One paper (970739) concluded that the performance of standard palladium-only catalysts is more sensitive to sulfur poisoning than platinum/rhodium, palladium/rhodium, or platinum/palladium/rhodium catalysts. Also, controlling interactions between the palladium and cerium-containing components in the washcoat is critical for the achievement of high catalyst activity at high sulfur levels. However, optimised palladium-only catalyst is more active than standard palladium-only catalysts in the presence of relatively high sulfur levels, and recovers activity more quickly as sulfur levels are lowered.

This paper, and a second one (970737) showed, as expected, that palladium-only catalysts generally have superior hydrocarbon performance under all conditions, and that sulfur affects carbon monoxide and NOx conversions more adversely over palladium-only catalysts, than over formulations containing rhodium. A paper from the University of Dundee and MEL Chemicals (970468) suggested that the addition of zinc to palladium-only TWC formulations can have advantages when operating in the stoichiometric to lean-burn range.

NOx Traps
The main engine exhaust component of "NOx" is nitric oxide (NO) and, although thermodynamically it is unstable compared with nitrogen and oxygen, its dissociation is virtually impossible under normal engine exhaust conditions. Therefore, NO is most conveniently treated by reducing it catalytically to nitrogen, and water or carbon dioxide, depending on the reductant concerned. One of the most demanding challenges for catalytic emission control is thus the removal of NOx under lean conditions. Such conditions exist in diesel engine exhaust, and will become increasingly commonplace as lean-burn gasoline engines are introduced for improved fuel efficiency.

One means of treating NOx under lean conditions is to adsorb it in a "NOx trap" as a surface nitrate species. When the trap is saturated
it is purged with a short, concentrated pulse of reductant to reduce the adsorbed NOx. All of the NOx traps so far described contain platinum and rhodium, and the main objective of this technology is to remove NOx without deterioration of vehicle driveability, or significant fuel penalty. In a paper from N. E. Chemcat (970745), the thermodynamics of the processes involved in NOx traps were discussed. Under lean conditions NO is oxidised to NO2 over platinum, which then reacts with alkaline metal carbonate in the trap to form nitrate species. When conditions are reducing, the nitrate species are unstable, and decompose to the metal oxide and NOx. The latter is reduced to nitrogen over platinum/rhodium, and the metal oxide reacts with carbon dioxide to reform the carbonate.

In a joint paper, Mercedes-Benz, Daimler-Benz and Degussa (970746) concentrated on the modes of deactivation of NOx traps. They stressed the need for low sulfur fuel to prevent sulfate formation, and showed that high temperature treatment can even improve stoichiometric three-way performance, but NOx storage features are irreversibly lost. This was identified as being due to the NOx absorption components reacting with washcoat components to form stable compounds, such as aluminates, zirconates and titanates. A second deactivation mode involves sintering of the platinum and rhodium (as well as the adsorbent species) and leads to loss of surface area, thus significantly reducing the interface between these two materials, with the result that the rate of NOx spillover from the active metal, where it is formed, is markedly lowered.

**Diesel Aftertreatment**

In an update of global trends in diesel emissions control, Michael Walsh (970179) pointed out that the number of diesel engined light duty vehicles is steadily increasing in many parts of the world. This can result in positive environmental benefits: lower fuel consumption (reduced CO2 emissions), reduced hydrocarbons and carbon monoxide emissions (enhanced by using platinum oxidation catalysts), and very low evaporative hydrocarbons, when compared to their gasoline counterparts. However, diesel engines have relatively high NOx and particulate emissions, but new advanced engine design and catalytic aftertreatment strategies are improving the situation. A related paper from Mitsubishi (970753) reviewed the global situation with heavy duty diesel vehicles, and had similar conclusions.

Sun Electric (970748) described a potentially versatile 90° backscatter measurement of particulates using a red laser that could be developed and refined for on-board applications using small solid state devices. Comparisons were made with opacity methods, and the advantages and disadvantages were discussed. Soot is a problem, with heavy duty diesel engines in buses and other vehicles used in inner cities for delivery and collection duties. A joint paper from Engine Control Systems, Environment Canada and the Ontario Ministry of Transportation (970186) reported the results of retrofitting platinum oxidation catalysts on heavy duty diesel vehicles. They concluded that oxidation catalysts can reduce particulate matter — mainly soluble organic fraction — and can significantly lower carbon monoxide and hydrocarbon emissions without increasing fuel consumption.

A joint paper from Johnson Matthey, HJS Fahrzeugtechnik, Elinox, Swebus and PESAG (970182) described extensive successful experiences of Continuously Regenerating Traps (CRTs) in heavy duty applications. The CRT removes a high proportion of carbon monoxide and hydrocarbons, and eliminates soot emissions by using the NO2 formed over a special platinum catalyst to burn soot retained in a filter; this is a combustion process that takes place at relatively very low temperatures (2).

**Conclusions**

The Detroit conference this year has again shown that the platinum group metals have key roles to play in the technologies that enable vehicles to comply with increasingly stringent legislative demands.

**References**

Emission Control Technology

PROGRESS REPORTED AT THE SPRING SAE CONFERENCE

It was unusually warm during the traditional end-of-February Congress of the Society of Automotive Engineers (SAE), held this year from 24th to 27th February – there was no snow on the downtown Detroit streets! This Spring conference is the major, general SAE conference covering all aspects of automotive engineering, with over 47,000 delegates attending this year. Fine weather and a broad range of interesting papers concerned with exhaust after-treatment made this a memorable event for those concerned with emissions control, and the continuing importance of developments in this area was reflected in the high attendance at the sessions.

Space prevents a review of all the relevant papers, so a selection has been made to illustrate the direction catalyst technology is taking in response to increasingly stringent legislation on emissions. Reference numbers of the original papers are given in parentheses.

Autocatalyst formulations have become more complex over recent years and may, for example, involve separated platinum metals each with an optimal promoter package. A paper by Degussa (960802) gave some insight into the design of such formulations, and a comprehensive study by Volvo (960801) of reactions over a double-layer trimetal (platinum-palladium-rhodium) catalyst enabled a dynamic kinetic model to be developed, which included sulphur dioxide effects.

**Solving the Cold Start Problem**

**Starter Catalysts**

Reduction of emissions during the “cold start” period is the key objective for meeting future regulations, and the use of low temperature light-off catalysts mounted close to the exhaust manifold to decrease warm-up time is an attractive approach for achieving this. However, operation in this position demands particularly good thermal durability of the catalyst. Space constraints often preclude location of large volume close-coupled catalysts near the exhaust manifold, and combinations of a small close-coupled starter catalyst with a larger underfloor unit can provide an effective system.

Toyota (960797) explored the effectiveness of such two-catalyst systems, and Johnson Matthey (960799) demonstrated that both the U.S.A. LEV/ULEV and European Stage 3 standards can be met with suitable high-activity catalysts of good thermal durability.

The attainment of low emission levels depends on rapid warm-up of the front catalyst and the presence of a sufficiently large total catalyst volume to maintain performance under normal operating conditions. Audi (960261) stressed the roles of engine management in rapid heating, and secondary air injection to enhance catalyst light-off. Starter catalyst performance depends on several parameters: a small volume heats up quickly, but a larger volume produces a greater exotherm (temperature rise), and this is reflected in the accumulated hydrocarbons emissions during a test cycle. Starter catalyst cell density also affects performance; there is a monotonic improvement as it increases. However, when a starter catalyst is combined with an underbody catalyst the system performance is less dependent on the characteristics of the starter, provided that it quickly gives a sufficient exotherm to light-off the main catalyst.

Metallic monoliths have typically been used in starter applications, and Corning (960262) reported a comparison of ceramic and metal foil-based starter catalysts. From their tests, they concluded that with the same outside diameter and back-pressure characteristics similar emission and durability performance can be obtained. Corning (960349) and NGK (960565) reported additional thermal durability results for ceramic monoliths in close-coupled locations. The latter proposed a design using a dual cone structure for both the converter inlet and outlet to minimise heat conduction, thus decreasing the temperature of the surrounding mat and...
lowering the surface temperature of the converter to below 450°C — when the catalyst itself is at a temperature of 1050°C.

**Electrically Heated Catalysts**

An alternative approach for reducing cold start emissions is to preheat electrically a small platinum group metal containing catalyst in front of the main catalyst. High electrical power requirements have tended to inhibit adoption of this concept, but the first electrically heated catalyst (EHC) application was described by Alpina/BMW and Emitec (960349), and it is interesting to note that, on the car which they describe, the power is switched between two EHCs on either side of the engine in order to minimise power consumption.

Emitec (960339) presented a separate paper on the general applicability of foil-based EHCs, and W. R. Grace (960341) also presented system performance with related EHCs. Honda (960342) compared foil-based and extruded EHCs in vibration, heat impact and distortion durability tests, and discussed the use of battery and alternator power supplies. They opted for a special alternator. In contrast, Hyundai (960350) investigated characteristics of both conventional lead/acid and nickel/metal hydride batteries for supplying EHC current, and concluded that the latter has significant attractions — as lead/acid batteries do not sustain the necessary heavy current/depth of discharge over many cycles.

NGK (960340) gave details of the design concepts and durability data of extruded metal EHCs and Corning (960345) presented vehicle durability results for their latest EHC design. Clearly, EHC-based technology has been developed to a stage where it could be used in series production, but it appears that in practice passive starter catalysts are more favoured, due to their low need for associated equipment.

**Lean-Burn Technology**

Catalysts for lean-burn engines are likely to become increasingly important; a concern here is NOx reduction in the presence of excess oxygen. Orbital (960361) highlighted the fact that extremely lean operation of a direct injection stratified charge two-stroke engine results in inherently low NOx levels, while Degussa (960133) showed how zeolite can be used to store and activate hydrocarbons in diesel engine exhaust during the start-up phase. This improves NOx reduction. Corning (960343) described a by-pass system (two conventional ceramic platinum group metal catalysts and an adsorber) in which zeolite is used to absorb hydrocarbons during the cold start of a conventional gasoline engine. They also described (960348) an in-line adsorption system which uses a flow of air to prevent exhaust gas passing through a central bypass in an adsorber monolith during start-up.

**Developments in Sensors**

Sensors are important for the correct operation of emission control systems. Oxygen sensors are used to maintain accurate air/fuel ratios, and in the future it seems likely that other types of sensors will be needed. Several reports were concerned with other sensors: Matsushita/Panasonic described (960336) a wide range thermistor for exhaust gas temperature measurement. NGK reported a new high performance platinum resistive temperature sensor (960333), and discussed its possible use in on-board diagnostic applications in which the predicted temperature rise on a catalyst is compared with the corresponding measured increase.

Another NGK paper (960334) described a new NOx electrode; this multi-layer zirconia system, operating at 600 to 700°C, involves oxygen pumping with platinum electrodes and, in a separate zone, dissociation of nitric oxide takes place over porous rhodium. The oxygen formed is measured with an oxygen electrode, and the concentration is found to be proportional to the amount of NOx originally present. Gold is used to inhibit nitric oxide dissociation on platinum electrodes, and to improve off-set current characteristics.

Thus, once again the SAE conference has highlighted the key role played by the platinum group metals in emission control technology, and has demonstrated the amount of worldwide effort and expertise committed to improving the performance of emission control systems. M.W.T.
Developments in Emission Control Technology

The main "Congress and Exposition" of the Society of Automotive Engineers (SAE) takes place in Detroit each Spring and smaller meetings are also held. One such meeting was the 1998 "International Fall Fuels and Lubricants Meeting and Exposition" held in San Francisco, October 19th to 22nd, 1998. Some 306 papers were presented to 1163 participants and a selection from sessions on the aftertreatment for petrol and diesel engines are reviewed here.

**Plasma Technology**

Plasma is formed when very high voltage is applied across a zone through which exhaust gas flows. A variety of often novel chemical reactions is induced which might be useful in destroying pollutants. The papers presented probed fundamental questions. Siemens (982428) used dielectric barrier discharge devices in diesel exhaust gas to show that non-thermal plasma oxidation of NO to NO₂ is unfortunately favoured over dissociation to nitrogen and oxygen! Addition of ammonia in the presence of a Selective Catalytic Reduction catalyst brought about NOx reduction at 100°C. A related contribution from Lawrence Livermore National Laboratory, Northwestern University and Engelhard (982508) reported that SO₂ is not oxidised under conditions where NO₂ is formed. This could be useful in situations where sulphate formation is detrimental.

**Three-Way Catalysts (TWCs)**

Ford (982549) reported on hydrocarbon (HC) conversion efficiencies over Pd-only, Pt/Pd/Rh, Pd/Rh and Pt/Rh formulations during stoichiometric and rich operation. Their Pd-only and Pt/Pt/Rh catalysts had higher HC efficiency than Pt/Rh or Pd/Rh catalysts, the conversion efficiency for ethylene was > 98% for Pd-based catalysts, and > 96% for methyl t-butyl ether (MTBE) with all catalysts. MTBE and formaldehyde emissions from a warm engine were concluded not to be environmentally significant. Concentrations were given for the ten most abundant HCs in fuel, exhaust gas and post-catalyst gas and, with the exception of methane, there was significant reduction of already low HC levels over the catalyst. This paper has data for conversions for 154 HCs over aged Pt/Pd/Rh catalyst. Toyota (982706) described work on thermal deterioration of Pt/Rh TWCs and found that oxygen storage capacity depends on Pt metal particle size.

The complexity in providing On-Board Diagnostics compliance and low emissions was evident in papers from Hyundai (982551) and Engelhard (982553). The former included evaporative and catalyst requirements, while the latter focused on development of ULEV catalysts, and included geometric surface area and heat capacity effects on catalyst light-off. The influences of substrate cell structure and catalyst configuration were emphasised by Corning, Johnson Matthey, Daimler Chrysler, and Southwest Research Institute (982634). There is advantage in having high cell density (high geometric surface area) during cold start; low thermal mass is important, and square cross-section cells are better than triangular ones. The viability of thin wall substrate in terms of processing necessary for incorporation into exhaust systems was confirmed by Corning (982635); thermal shock properties can be better than with conventional products. Emittec (982633) reported that conical metal substrates give enhanced gas flow over the main catalyst, and provide improved light-off due to heat cascade.

**Lean-Burn Gasoline Engine Aftertreatment**

Contributions from Daimler-Benz, Johnson Matthey, Chalmers, Leuven and Strasbourg Universities (982592) described the use of an absorber to trap NOx and intermittently recycle it back to the engine. A second paper (982593) focused on trap materials for this application. With appropriate formulations NOx-traps can be regenerated in-situ in lean-burn gasoline or diesel engine applications. A major problem is sulfation of the trap components, which leads to performance deterioration. Renault (982607) found that temperatures of at least 600°C were needed for complete regeneration of a development NOX-trap.

**Two-Stroke Engine Aftertreatment**

Exhaust emissions from 2-stroke engines contribute to urban pollution in developing countries. Because of high HC levels, exotherms during oxidation can increase gas temperature to 900°C. In addition, low oxygen content limits CO/HC oxidation under some conditions, and so HC steam reforming and reaction of CO with steam (water gas shift reaction) are important in the design of 2-stroke catalysts. ICT and Degussa (982710) reviewed these requirements and their achievement by thermal stabilisation of washcoat components, appropriate selection of active metals and maintaining ceria surface area under rich ageing conditions.

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