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Catalytic control of emissions from cars

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ABSTRACT

Air quality problems in America that were caused by pollutants from car exhaust and their photochemical reactions producing secondary pollutants in the urban environment had become of such a concern by the late 1960s that forcing environmental legislation was introduced in 1970, which became effective in 1975. Only catalysts containing platinum group metals were sufficiently effective, and their fitment in the exhaust line of gasoline cars coupled with other technical advances led to reduced pollutant emissions and significant improvements in air quality. Oxidation catalysts (typically Pt/Pd and Pt/Rh) were introduced first to control hydrocarbons (HCs) and CO emissions. Then these were combined with an upstream Pt/Rh catalyst to control NOx emissions as well. By the early 1980s Pt/Rh three-way catalysts (TWCs) were used in combination with electronic fuel injection, oxygen sensors and a microprocessor to provide closed loop control of the engine around the stoichiometric point. Since their introduction TWC performance has been hugely improved and adopted increasingly around the world. Legislation made catalyst fitment mandatory in Europe in 1993, and as a consequence many millions of tons of pollutants have not been released into the atmosphere with tremendous environmental benefits. More recently in Europe there has been a move towards diesel cars, and they presented technical challenges associated with low temperature exhaust and the presence of excess free oxygen that prevents fitment of TWCs. First Pt oxidation catalysts were used to control HC and CO emissions, and more recently catalysed (Pt/Pd) filters have very effectively controlled particulate matter emissions (soot) that are associated with direct health concerns. Now diesel NOx emissions are beginning to be controlled by Pt/Rh NOx-trapping catalysts that are regenerated by periodic enrichment of the exhaust, and by base metal selective catalytic reduction (SCR) catalysts using ammonia derived from aqueous urea. In the future it may be expected that multi component diesel emissions control systems will be combined into sophisticated four-way single units under computer control in much the same way TWCs are used on gasoline cars.

1. Introduction

Air quality issues in major cities such as Tokyo in Japan and Los Angeles in America had become serious by the late 1960s, and even in the 1940s urban air quality problems were experienced in America, and especially in the Los Angeles' basin that has bright sunlight and frequent ambient temperature inversions that recirculates polluted air. By the late 1960s photochemical reactions of hydrocarbons (HCs) and nitric oxide (NO), had been identified [1–3] as being responsible for the formation of "photochemical smog" containing ozone, Eq. (1), and low levels of other secondary pollutants such as peroxyacetylnitrate (PAN) that are extremely powerful lachrymators. The increasing number of cars was seen as the major source of pollutants causing these problems, and this article focuses on the American experience and the later European developments.

$$\mathrm{HC} + \mathrm{NOx} + h\nu \rightarrow \mathrm{O_3} + \mathrm{other products} \quad (1)$$

2. Tailpipe emissions from gasoline engines

In the 1960s gasoline engines were giving society tremendous mobility, and especially in America where society was increasingly being organized around the car [4], but the combustion of gasoline to CO_2 and H_2O, Eq. (2), was not completely efficient, so small amounts of HCs,

$$4\mathrm{H}_m\mathrm{C}_n + (m+4n)\mathrm{O_2} \rightarrow 2m\mathrm{H_2O} + 4n\mathrm{CO_2} \quad (2)$$

and partially combusted oxygenates, such as aldehydes, together with much larger amounts of CO, Eq. (3), were in the exhaust. Today in the European test procedure total hydrocarbons (THCs) including CH_4 (the most difficult HC to oxidize), are measured – partially oxidised oxygenates are not measured. In contrast in America CH_4 is excluded because it is not significantly involved in ozone forming

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Table 1
California (CARB) emissions standards since 1993.

Year	Category	Emissions (g/mile, FTP test)			
		HC	CO	NOx	PM
1993		0.25[a]	3.40	0.40	
1994	Tier 1	0.25[b]	3.40	0.40	
2003	Tier 1	0.25[c]	3.40	0.40	
2004	$TLEV_1$[d]	0.125	3.40	0.40	0.08
	LEV_2[e,f]	0.075	3.40	0.05	0.01
2005	LEV_1[d]	0.075	3.40	0.40	0.08
	$ULEV_2$[e,f]	0.040	1.70	0.05	0.01
2006	$ULEV_1$[d]	0.040	1.70	0.20	0.04
	$SULEV_2$[e,f,g]	0.010	1.0	0.02	0.01
2007	ZEV_1	0	0	0	0
	ZEV_2	0	0	0	0

Note. LEV: low emission vehicles, SULEV: super low emission vehicles, ZEV: zero emission vehicles.

[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 to 2003.

[d] LEV_1 type emissions categories phasing out 2004–2007.

[e] LEV_2 type emissions limits phasing in 2004 onwards.

[f] LEV_2 standards have same emission limits for passenger cars and trucks <8500 lb gross weight.

[g] $SULEV_2$ onwards 120,000 miles durability mandated.

reactions, but oxygenates are included in "non-methane organic gases" (NMOG) analysis. Moreover, at the high engine combustion temperatures N_2 and O_2 combine via a series of reactions to establish equilibrium with NO, as in Eq. (4). Overall this mechanistically complex reaction is endothermic so the equilibrium concentration of NO increases with temperature. As the combusted gases expand and rapidly cool *en route* to the exhaust system, the high temperature concentration of NO is "frozen", and although thermodynamically unstable at ambient temperature, appreciable amounts (up to 3500 ppm) of NO can be in the exhaust. The three major pollutants from a gasoline engine are therefore HC, CO, and NOx (NO with only traces of NO_2).

$$4H_mC_n + (2n+m)O_2 \rightarrow 2mH_2O + 4nCO \quad (3)$$

$$N_2 + O_2 \Leftrightarrow 2NO \quad (4)$$

Environmental pressures in America brought about the American 1970 Clean Air Amendments Act that required a 90% reduction of CO and HC emissions from 1970 model year levels by 1975, and a 90% reduction of NO emissions from 1971 model year levels by 1976. Initially, engine modifications gave some emissions improvements, but the 1975 US Federal and Californian emissions limits could not be met in this way, and the "catalytic converter" was shown to be the best way forward. The introduction of catalysts necessitated removal of the widely used octane enhancer tetraethyl lead (TEL) from gasoline because it is an extremely powerful catalyst poison. It was substituted by alternative organic additives such as methyl *tert*-butyl ether (MTBE) and other oxygenates and careful blending of appropriate HCs. Even with these measures some engine modifications were needed, including lower compression ratios, for them to operate satisfactorily on lower octane fuels.

3. Legislative requirements

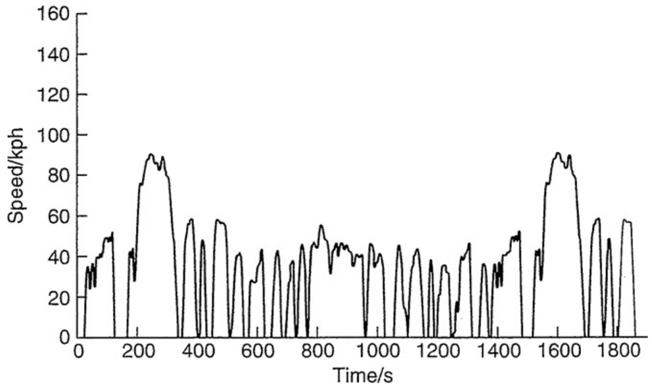

Fig. 1. Speed/time trace for the American Federal Test Procedure (FTP) for passenger cars and light-duty vehicles from 1975.

Legislation has been key in driving down emissions from vehicles, and Table 1 summarizes the development of Californian car legislation since 1993. From 1977 in California, where air quality problems were most pressing they were allowed to legislate lower emissions levels than the rest of the USA, and as a result Californian regulations became the most demanding in the world. They are set by the California Air Resources Board (CARB). Emissions are measured by driving the vehicle on a chassis dynamometer (rolling road) over a test cycle (Fig. 1). This cycle, the Federal Test Procedure (FTP), represented typical driving including on freeways with a maximum speed of 55 mph. Recently an additional high speed driving section was added to make it more realistic of driving patterns today. The tailpipe emissions are collected as soon as the engine is started and analyzed and the reported emissions concentrations calculated with an equation weighting the three different sections of the FTP. Emissions limits decreased steadily, and especially from 1993 onwards. With the introduction of each successive emissions band a small percentage of vehicles were required to meet the next band, and this has culminated in the need for a small number of vehicles with zero emissions, Table 1. The present CARB limits are astonishingly low in the light of what they were in the mid-1960s, then, for example, the HC emissions were typically 15 g/mile!

Emissions legislation in Europe did not demand fitment of catalysts until 1993. In some respects the European test is similar to the FTP, but it represents a more European style of driving. For 1993 and 1996 legislation the vehicle was allowed to idle for 40 s before sampling the tailpipe gases began. Then for 2000 and afterwards sampling started as soon as the engine was started, as in the FTP.

4. Early gasoline oxidation catalysts

Much research was done on base metal catalysts containing nickel, copper, cobalt and iron etc. Some seemed attractive, but they were easily poisoned by sulphur and traces of lead in the fuel, and importantly, they lacked the necessary thermal durability [5]. The catalysts eventually chosen were based on platinum group metals (PGMs) [6], and initially the emissions limits could be met by catalytic oxidation of CO and HCs, Eqs. (2) and (5). Initially the most common oxidation catalysts contained Pt and Pd or Pt and Rh supported on high area alumina – the second metal conferred improved thermal durability under lean conditions. Legislation was then tightened and NOx also had to be controlled, and Pt/Rh catalyst formulations were used for the selective reduction of NO to N_2, under rich conditions Eqs. (6) and (7).

$$2CO + O_2 \rightarrow 2CO_2 \quad (5)$$

$$(8n+2m)NO + 4H_mC_n \rightarrow (4n+m)N_2 + 2mH_2O + 4nCO_2 \quad (6)$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad (7)$$

Early concepts used two catalysts. The engine ran slightly rich to enable reduction of NOx over a Pt/Rh catalyst, then air was introduced for a second catalyst to oxidise the excess CO and HCs. It was important the first catalyst reduced NO to N_2 with high selectivity – if ammonia was formed by over reduction of NO it would be reoxidised over the downstream oxidation catalyst back to NO, Eq. (8), so lowering the overall conversion of NO to N_2.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (8)$$

Some European car manufacturers, notably Volkswagen and Volvo, used Pt/Rh oxidation catalysts, and when operated around the air/fuel stoichiometric point, it was found they could provide good NOx control and oxidize HC and CO at the same time. By 1979, switching catalytic oxygen sensors had been developed and placed in the exhaust close to the manifold to provide closed loop feedback control of the fuelling via a microprocessor, so conditions could be maintained at, or around the stoichiometric point. This enabled relatively good consistent catalytic performance, and the use of Pt/Rh catalysts to control HC, CO and NO_x simultaneously became the preferred system. Because all three major pollutants were controlled by one catalyst, the concept was christened the "three way catalyst" (TWC). Although early TWCs had a narrow operating range over which all three pollutants were converted, they were almost universally fitted to cars in America from about 1980 [7,8]. Considerable technical effort went into improving the performance and widening their operating air fuel ratio window by, for example, the introduction of cerium containing components into the catalysts (see below). This was necessary to provide emissions control of carburetted engines, where the fuelling management was crude and responded slowly. Thus key technologies enabling the introduction of cost effective TWCs were the introduction of oxygen sensors, electronic fuel injection, a microprocessor control system and catalyst developments.

5. Early developments in Johnson Matthey

Early developments in the autocatalyst area took place in companies on both sides of the Atlantic, and those that took place in Johnson Matthey provide an insight into the directions catalyst developments took that were probably mirrored elsewhere. In the 1960s Johnson Matthey was involved with catalytic control of gaseous pollutants such as NOx from nitric acid plants and odours from food processing. So when in 1970 Senator Muskie announced a plan to reduce emissions from US cars by 90% (the "Muskie Standards"), the company was ready to develop catalyst technology for automotive emissions control. Two catalyst substrate structures were tested – pellets and "monoliths" with open parallel channels through which gases flowed. Two types of pellet catalysts were introduced and used for a number of years but Johnson Matthey concentrated on the "monolithic" type that is used in all autocatalyst systems today. They came from two US companies using different technologies: extrusion of a paste that was dried and fired, and the first available that used a paper layering method in which alternate layers of flat and corrugated sheets were rolled together and impregnated with a ceramic dispersion, then dried and fired to gives a rigid monolith. Their properties were different, and a process capable of dealing with both types was devised. The monoliths had no catalytic activity, and just depositing PGMs onto the channel walls gave poor catalytic performance and durability. This was overcomed by treating monoliths with a high surface area material such as γ-alumina, and a process was developed for coating the monoliths with both high surface area alumina and PGMs. It was necessary to ensure an even coating with no channel blocking, since they were wasted channels and increased backpressure. The coating processes was critical, when fired it had to adhere firmly to the channel walls under the pulsating high gas flow when the engine was running. Time was short – a manufacturing process had to be developed and a production plant completed within eighteen months!

Several coating methods were considered and a laboratory continuous process was used to investigate parameters for the design of a plant. Process design ran in parallel with developing improved formulations. Before the end of 1973 the first commercial production line was ready, and contracts were signed with VW and Corning (who manufactured, and became the major producer of extruded cordierite monoliths) to produce catalysts for VW's vehicles exported to America. Negotiations were well advanced with Rolls Royce and British Leyland in the UK, and also with the Ford Motor Company in America that would require construction of a bigger production facility in America. However, before this was done a proving run on the Royston plant was needed to demonstrate process viability. Unfortunately this coincided with the UK three-day working week caused by the coal miners strike in December 1973. As a result electricity was limited, and this was a major problem since the catalyst firing cycles were done in electric furnaces. Catalyst operations were given most of the site power for the "Ford run". All "nonessential" activities ceased, including heating and lighting! The demonstration run was successful, and soon a large production plant was constructed in North America to supply Ford, and later the other American and Japanese car companies as well [9,10].

The Royston plant was officially opened in February 1974, and in April the world's first production autocatalysts were being made for Volkswagen. Soon Rolls Royce, British Leyland and Jaguar also relied on Johnson Matthey for their catalysts, and as production increased, a second line was installed, and catalysts were supplied to other car companies. Catalyst formulation improvements were continually implemented, and an enlarged advanced test facility was built that was better than some customer facilities. All of the outstandingly successful pioneering work was recognised by several prestigious awards, and Johnson Matthey has continued to be at the forefront of autocatalyst research and development supplying catalysts to most of the world's car makers from plants around the world.

6. Catalyst substrate types

The use of metal foil for making monolithic substrates instead of ceramic material was developed from the late 1970s. They have several advantages: they are readily welded into the exhaust line, they have high geometric surface area and low backpressure, and eliminate thermal cracking that ceramic material could be prone to. However, early work in Johnson Matthey identified a key problem was the durability of most iron based alloys in thin strip form when exposed to the extremely corrosive environment of exhaust gas at high temperatures. It was shown iron–chromium–aluminium ferritic steels had the desired resistance through forming an alumina surface film, and the first autocatalysts for production vehicles based on metallic monoliths were made (both monolith fabrication and catalyst coating) by Johnson Matthey at Royston. In the 1980s the manufacture of metal monoliths was stopped at Royston, and effort focused on producing superior catalyst coatings. Metallic substrates have since been sourced from commercial companies, and for some applications they are preferred because very thin foil gives low back pressure and high geometric surface area, combined with good mechanical strength when fabricated correctly [11]. Although the special alloys needed increase cost, in some circumstances the benefits outweigh the cost.

By far the most successful substrate materials are based on compositions which when extruded and fired at high temperature form aligned cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, and some 85% of substrates on cars today are made in this way [12,13]. Fig. 2 shows a typical cordierite and a metal foil substrate and some of their typical properties are summarized in Table 2. A wide variety of substrate

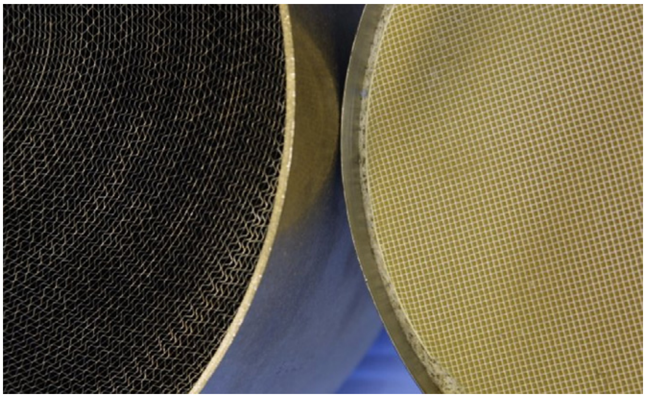

Fig. 2. Typical examples of a metal foil catalyst substrate (left) and an extruded cordierite substrate (right). The ceramic monolith is retained in a stainless steel mantle by an intumescent mat that expands when heated and ensures it is firmly retained in place.

Table 2
Physical properties of typical ceramic and metal monolithic substrates.

Property	Ceramic	Metal
Wall thickness (mm)	0.15	0.04
Cell density (in.$^{-2}$)	400	400
Open facial area (%)	76	92
Specific surface (m^2 1^{-1})	2.8	3.2
Specific weight (g l^{-1})	410	620
Weight without shell (g l^{-1})	550	620
Thermal conductivity (cal s^{-1} cm^{-1} K^{-1})	3×10^{-3}	4×10^{-2}
Thermal capacity (kJ kg^{-1} K^{-1})	0.5	1.05
Density (kg l^{-1})	2.2–2.7	7.4
Thermal expansion (K^{-1})	0.7×10^{-6}	0–15
Maximum working temperature (°C)	1200–1300	1500

sizes with different cell densities and wall thicknesses are available commercially.

7. Gasoline TWC formulation types

Today TWCs are based on combinations of Pt and/or Pd and Rh, alumina and ceria, together with a variety of support stabilizers, activity promoters, and selectivity improvers. Elements used include iron, nickel, manganese, calcium, strontium, barium, lanthanum, neodymium, praseodymium and zirconium. While most commercial catalysts contain one, and usually more, of these minor elements, all contain PGM, alumina and ceria with different proportions in different catalysts.

7.1. PGM components

There are more than adequate reserves of PGMs for foreseeable future autocatalyst use, and now freshly mined material is being supplemented by that recycled from scrapped cars as they become available [14]. The primary driving force in autocatalyst research and development has always been improved performance, while cost is also a consideration. Early oxidation catalysts used Pt with smaller amounts of either Pd or Rh to provide durability under lean conditions. With the need for NOx conversion Pt and Rh were used to give better conversion of all three pollutants than was possible with the individual components alone. As catalysts improved, enhanced performance and lower cost Pd/Rh TWCs were developed. Subsequently, “Pd only” TWCs were developed to achieve better HC removal [15], and while Pd containing catalysts generally have good HC performance, at that time this was offset by a little lower NOx and CO performance and “Pd only” formulations were only commercially viable for limited period, although their introduction represented a major technical achievement. Initially the choice of Pt/Rh or Pd/Rh depended on the balance of HC/CO/NOx from a particular engine and application. Pd is relatively sensitive to poisoning by sulphur or lead, but now lead levels are close to zero and fuel sulphur levels have been markedly reduced so these considerations are now less important than previously, so most modern TWCs are based on Pd/Rh formulations.

7.2. Alumina and ceria

Alumina and thermally stabilized versions have always been important in autocatalysts providing high surface area for dispersion of active components as very small (initially less than 10 nm) crystallites. With a high area support the surface concentration of PGM crystallites is low and their high temperature sintering is inhibited. Alumina also absorbs poisons and this helps retain performance, and it also helps binding the catalyst layer to the substrate. Ceria in various forms also has several roles. It has a stabilising effect on alumina surface area at high temperatures, and it is also capable of stabilising PGM dispersion, and especially that of Pt. In addition, ceria allows two other more performance enhancing phenomena to take place: oxygen storage and the water gas shift reaction, Eq. (9). Storing oxygen as Ce(IV) when the exhaust gas is lean and releasing it when the gas goes rich

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{9}$$

to reform Ce(III), enables CO and HC adsorbed on the catalyst during rich excursions to be oxidised when there is insufficient oxygen in the gas [16]. This improves oxidation performance of the catalyst under rich operation, and ceria also assists the “water gas shift” reaction, which affords hydrogen, which also improves NOx performance under rich operation. Originally ceria was incorporated as such and today various more stable mixed ceria oxides are used. Exact catalyst formulations are proprietary, but it is clear from published information that the forms, and the way in which components are incorporated into the catalyst is very important.

7.3. Gasoline TWCs today

The performance of TWCs today is astonishing compared with that of catalysts introduced three and a half decades ago. Activity is high and thermal stability is so good catalyst is now placed on the exhaust manifold where it heats up rapidly when the engine is started, and in this hot location less PGM is needed than in a cooler downstream location [17]. Thus performance is very high with use of less costly materials than previously was the case. Performance is routinely monitored by on-board diagnostics (OBD) via two oxygen sensors (one upstream and one downstream of the TWC) via computer algorithms that periodically change the exhaust oxygen content and thereby determine the level of active oxygen storage capacity of the catalyst [18]. Moreover, the Californian legislation may require FTP conversions close to 100% over 120,000 or 150,000 miles depending on the level at which a particular car is certified, so TWCs are clearly technologically highly refined, but history suggests further developments will take place in the future as even tighter “LEV3” legislation is introduced!

8. Controlling emissions from diesel cars

The diesel car is a European feature where a tremendous amount of engineering developments together with good fuel economy and a favourable fuel tax situation in several countries led to an increase in the production of diesel passenger cars. Today more than 50% of all new European cars have a diesel engine [19]. The technical developments led to the introduction of powerful turbocharged direct injection high-speed diesel engines that provide

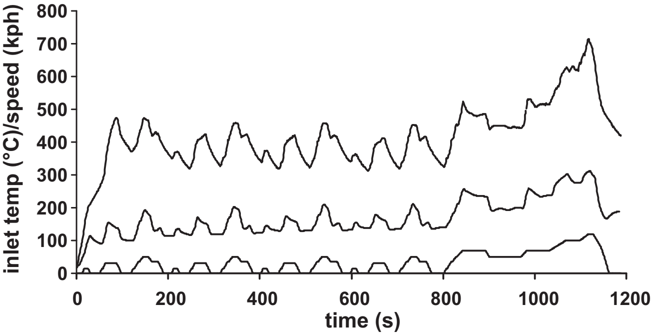

Fig. 3. Exhaust gas temperatures in the European test cycle for the same car with comparable gasoline (1.6 l, upper trace) and diesel (1.8 l, middle trace) engines. The bottom trace is the vehicle speed during the test.

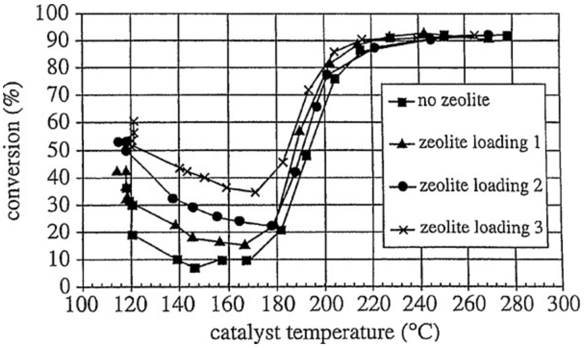

Fig. 4. The effect of incorporating a thermally stable zeolite such as an appropriate beta-zeolite into a diesel oxidation catalyst. The apparent oxidation of hydrocarbons at low temperatures is improved by their retention in the zeolite. At higher temperatures released HC is oxidised by the catalyst.

excellent driving characteristics with high torque at low speed, and very good fuel economy – more recently developments continued with the widespread introduction of high pressure common rail fuel systems. Catalytic control of emissions from these vehicles began with the fitment of Pt monolithic oxidation catalysts to Volkswagen diesel cars in 1989 [20] before demanding European legislation was in place. The catalyst removed the characteristic odour of diesel exhaust and controlled HC and CO emissions. With the introduction of legislation in 1993 fitment of oxidation catalysts to all new European diesel cars became necessary. However, the temperature of diesel car exhaust is low compared to that of a gasoline counterpart, as shown in Fig. 3, and this was a major catalyst design challenge.

8.1. Controlling diesel HC and CO emissions

The oxidation of HCs and CO in diesel exhaust is not straightforward as temperatures are low, due to the fuel efficient nature of the diesel engine, typically around 120–150 °C in urban driving conditions, so higher HCs can absorb on active sites and block them, and poisons, such as sulphur oxides, are strongly adsorbed. Traditionally Pt-based oxidation catalysts are used, and to achieve the performance and durability required catalyst formulations have highly dispersed Pt that is well stabilised against thermal sintering. When the engine is started the catalyst is insufficiently warm to oxidise HCs initially present, and incorporating zeolites into the catalyst significantly improved the performance during the “cold start” [21]. The zeolite adsorbs HC so preventing inhibition of the active Pt sites. This improves low temperature CO and apparent HC oxidation performance. At higher temperature the HC is desorbed and oxidised on the Pt sites. Fig. 4 shows the effect of zeolite addition to a Pt catalyst on HC oxidation performance. The CO oxidation performance is also improved by incorporating zeolite into the catalyst.

Formulation developments also helped to improve the low temperature tolerance to sulphur poisoning. As sulphur levels were reduced over recent years it became possible to substitute some Pt in diesel oxidation catalysts by less costly Pd, and this is commonly done in modern filer systems that periodically experience high temperatures during regenerations (see below) that not only removes soot in the filter, but also desorbs sulphur from Pd containing oxidation catalyst so maintaining their activity. The formation Pt/Pd alloy in these systems is an important contributor to overall performance since the alloyed system shows significant stabilisation against sintering and a much higher activity after the thermal ageing. Stabilisation of the PGM dispersion and the presence of Pt atoms on the surface of the Pt/Pd particles is responsible for the higher catalytic activity of metallic particles in oxidation reactions after ageing. [22].

8.2. Controlling diesel particulate emissions

In a diesel engine a jet of finely ‘atomised’ fuel under very high pressure (up to 2000 bar) is directly injected into compressed hot air causing it to explosively combust. The fuel evaporates and burns 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 may be burnt, and if this is not completed when the mixture is discharged through the exhaust ports, a residue of fine carbon cores remain. As the gas cools during passage into the exhaust manifold, turbocharger and pipes, the carbon particles agglomerate forming high surface area material onto which uncombusted and partially combusted products adsorb, as well as sulphur oxides (SOx) and nitrogen oxides (NOx) formed during the high-temperature combustion. When inhaled the size of some of the smallest nanoparticles enables them to pass almost unheeded deep into the lungs and then even into the bloodstream. It is this mobility, coupled with the cocktail of absorbed species, which gives rise to environmental health concerns [23]. Fig. 5 illustrates the range of particulate matter (PM) that can be present in typical diesel exhaust.

As illustrated graphically in Fig. 6, the European PM emissions limits 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 (0.005 g/km), phased in during 2009, could only be achieved through the fitment of filters [24].

8.2.1. Diesel particulate filter types

Several types of ceramic and sintered metal diesel particulate filters (DPFs) have been developed, and the most successful and most commonly used are porous ceramic wall-flow filters, as illustrated schematically in Fig. 7. Porous refractory materials used to make them include cordierite, silicon carbide and aluminium titanate [25]. 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, as illustrated in Fig. 8, and if this continues it will become excessive, and significantly degrade engine performance – ultimately the engine will stop! It is essential the backpressure is not allowed to rise above a predetermined limit, so periodically PM must be removed from the filter and the best way of doing this is to oxidise it to small amounts of CO_2 and H_2O.

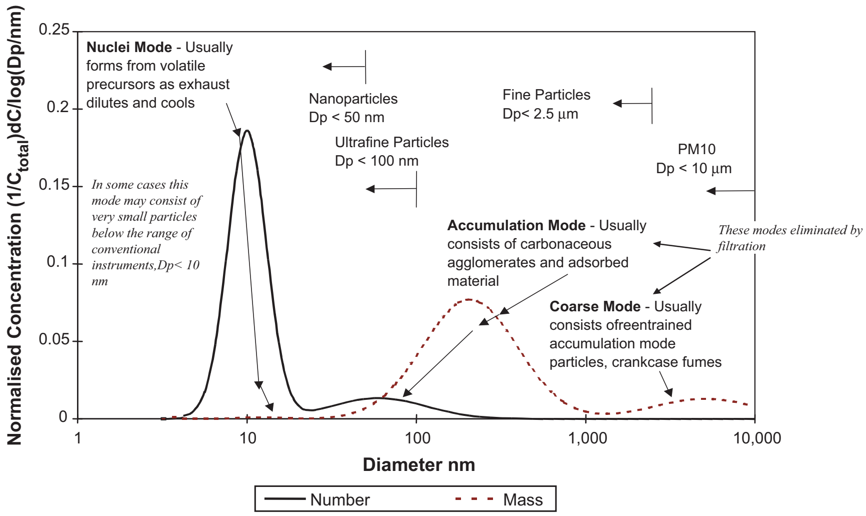

Fig. 5. Classification of diesel engine PM according to size. Most of the PM mass (dashed line) is associated with the accumulation-mode (~100 nm) and coarse-mode particles, but there are very many more nanoparticles (solid line) in the nucleation mode (~10 nm) that are so small they can penetrate the human bronchial system.

8.2.2. Filter regeneration

Burning (oxidising) retained PM in a diesel filter is called regeneration. The temperature of diesel car exhaust rarely exceeds about 250 °C and it is less in urban driving, so the use of NO_2, produced by catalytic oxidation of NO over a Pt catalyst, Eq. (10), for combustion of trapped PM (written as "CH" in Eq. (11)) that takes place at temperatures in the range 250–400 °C can only remove a portion of the PM if sufficient NO is present and when sufficiently high temperatures are achieved.

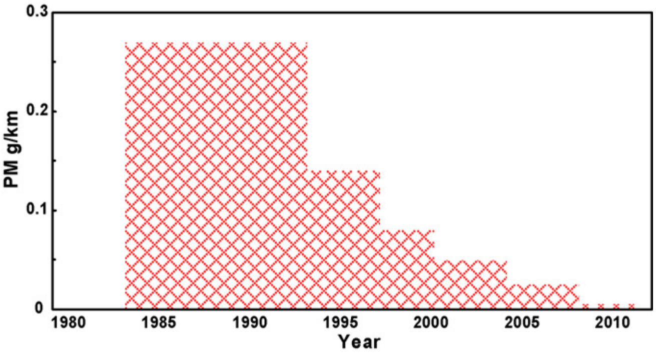

Fig. 6. The decrease in European PM passenger car emission limits. Since the early 1980s permitted emissions have reduced by an order of magnitude, and stringent legislation now in place demands fitment of filters on new diesel vehicles.

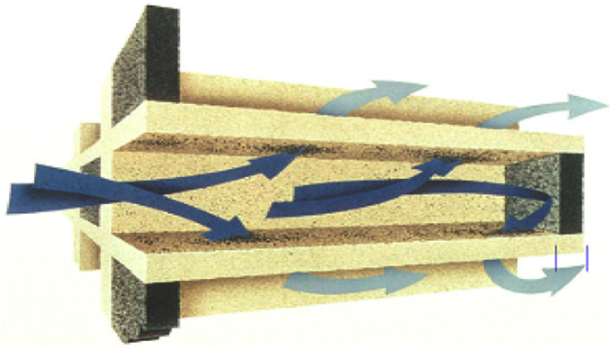

Fig. 7. A schematic representation of a ceramic diesel wall-flow filter. The arrows indicate the gas flow through the walls. PM is trapped in the upstream side of the filter, and periodically this has to be removed to prevent unacceptable backpressure across the filter.

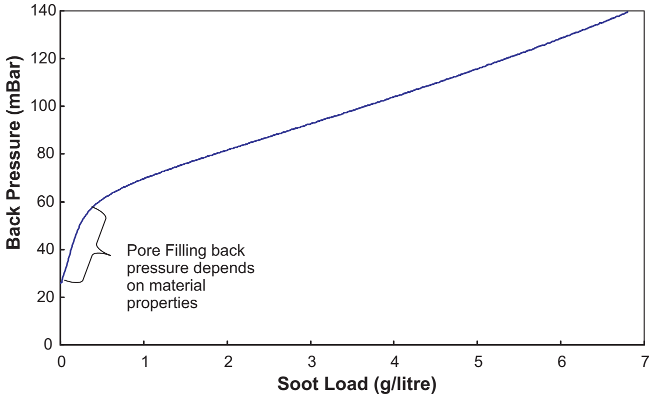

Fig. 8. Typical backpressure across a diesel filter as a function of the amount of PM trapped. The initial rapid backpressure increase is caused by PM trapped in the walls, once a coherent layer is established on the walls, the backpressure increases linearly with the amount of trapped PM until (not shown) the filter becomes choked. Periodic regeneration to remove excessive PM accumulation is essential.

$$2NO + O_2 \rightarrow 2NO_2 \tag{10}$$

$$5NO_2 + 2\text{"CH"} \rightarrow 5NO + 2CO_2 + H_2O \tag{11}$$

While the exhaust temperature of diesel cars during urban driving is too low for this form of regeneration to take place, at higher speeds around 100 km h^{-1} the temperature can be sufficiently high for NO to be oxidised over an upstream Pt oxidation catalyst, producing NO_2, which can in turn oxidise some PM in the filter, as in Eq. (11). This is called "passive regeneration" and it has worked very well on some heavy-duty diesel vehicles where operating temperatures are high. The concept is called the continuously regenerating trap (CRT®) [26,27], but it cannot provide regeneration under all car driving conditions. An "active" form of regeneration must be employed on cars that periodically increases the exhaust gas temperature to burn PM in the filter with oxygen (typically starting at 550–600 °C) every 400–2000 km, depending on actual driving conditions. Here additional fuel from the engine is oxidised over an upstream Pt or Pt/Pd oxidation catalyst to provide the high temperature to initiate PM burning that is then carefully controlled by restricting the O_2 available by throttling the engine.

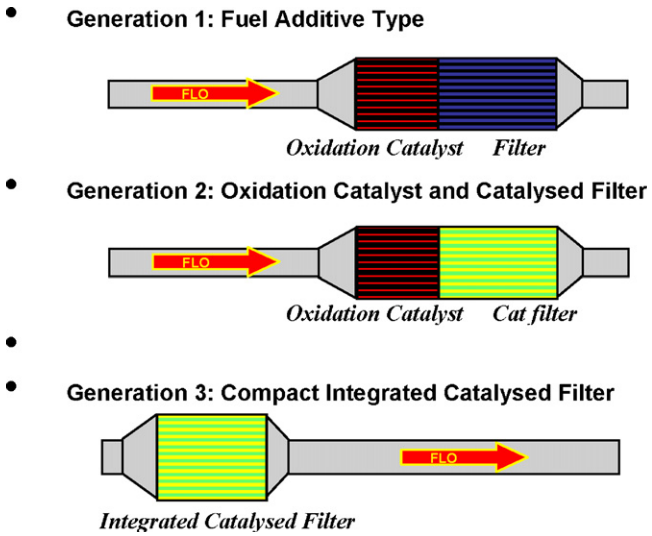

Fig. 9. Three filter systems used on European diesel cars. Generation 1 has Pt oxidation catalyst(s) before the filter to control HC and CO emissions during normal driving and to periodically burn additional partially combusted fuel to achieve high temperatures for regeneration. A fuel additive is used to lower the PM combustion temperature; generation 2 has no fuel additive, the filter contains Pt catalyst to accelerate PM combustion; generation 3 has all of the required catalyst needed incorporated into a single small filter – in some instances Pd replaces some of the Pt in the catalysts.

8.2.3. *Systems incorporating filters*

Three filter systems have been developed and used commercially for cars that use periodic active regeneration in which catalysis has key roles, and these are illustrated in Fig. 9.

Generation 1. This system employs one or two Pt-based oxidation catalysts upstream of a filter to control HC and CO emissions, and to convert NO to NO_2 for passive PM combustion when conditions permit this to take place. The catalyst(s) also oxidise extra partially burnt fuel when it is injected into the engine to periodically raise the exhaust temperature for active PM combustion with oxygen. The system was introduced in 1999 [28] and it requires a base-metal fuel additive that is converted to oxide in the engine which is retained in the filter and can lower the temperature for PM combustion. The first fuel additive used was based on ceria, and others now in use contain Fe, Sr and one based on Pt has been described. These multi-component systems are costly and fuel additive residues retained in the filter as inorganic ash (see below) reduces volume available for PM in the filter and contributes to a higher backpressure, so large filters are used to compensate for this effect.

Generation 2. This system has the advantage of not using a fuel additive, so it does not require a fuel additive tank and the associated pump etc. However, like the Generation 1 system it has one or two separate oxidation catalysts upstream of a filter. The filter has Pt or Pt/Pd catalyst in its channel walls to promote PM combustion, and today many cars use this configuration.

Generation 3. This very compact design was introduced by Johnson Matthey in 2005 following the development and implementation of special catalysts and a new manufacturing process [29]. It requires neither a fuel additive nor upstream catalyst, and it combines in a single small filter (typically silicon carbide, aluminium titanate, or cordierite) all the oxidation catalyst to oxidise HC and CO during normal driving, and to periodically oxidise extra partially burnt fuel to raise the temperature to combust PM with O_2 during active regenerations. The catalyst also oxidises NO to NO_2 to provide some passive PM removal during high-speed driving. This system is thermally the most efficient, and during active regenerations there is only the filter to heat, which is mounted on the engine turbocharger to minimise heat losses. The oxidation reactions used to boost the temperature take place actually in the filter in the same location as the retained PM. In contrast, earlier systems with a separate upstream catalyst lose considerable heat during regenerations to the environment via the pipe between the turbocharger and the filter.

8.2.4. *Inorganic ash*

Inorganic compounds are added to lubrication oils as viscosity modifiers, to provide antiwear and antioxidant properties, and to keep solid matter, especially diesel soot, in suspension. Commonly used compounds contain P, Ca, Zn, Mg and S [30]. These elements can be transported into the exhaust gas, having originated from oil burnt in the cylinder, and they are retained as stable compounds in the filter. Similarly, inorganic species derived from fuel combustion aids are also trapped in first generation of filters, and these can include elements such as Ce, Fe or Sr. Because of the very high temperatures during combustion in the engine, the nature of the species in the exhaust gas is determined by their thermodynamics [31], as normally is the composition of the ultimate deposits in the filter. Typically, compounds such as $Zn_3(PO_4)_2$ and $CaSO_4$, 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 could interfere with catalytic functions, and its presence causes 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 by using a large filter, using lubrication oils with little or no inorganic additives (‘ashless oil’), or using filters with asymmetric channel structures that provide a larger inlet volume compared to that in the outlet side. The last approach causes a slightly higher backpressure when fresh, but this relative difference decreases as ash accumulates in the filter and the asymmetric structure then has a lower backpressure [32]. The advantage of asymmetric channels over the long term is significant, and filters of this type are being used increasingly on diesel cars.

8.3. *Controlling diesel NOx emissions*

Until relatively recently control of NOx emissions from diesel cars was done by engine measures alone, but now NOx emissions limits is beginning to demand some additional catalytic control, and this is done by one of two processes: NOx-trapping (sometimes known as NOx absorbing catalysts – NACs) and selective catalytic reduction (SCR).

8.3.1. *NOx-trapping catalysts*

In these catalysts NO is converted to NO_2 over a Pt-based component that in the presence of excess O_2 forms a stable nitrate of an alkaline catalyst component [33]. Periodic enrichment of the exhaust lowers the O_2 partial pressure to a point where the nitrate phase is not stable at the normal operating temperature and it decomposes, as for example, in Eq. [12], that effectively is the reverse of the storage process. The NO formed is then reduced to N_2 over a Rh component in the same way it is in a gasoline TWC. Depending on the system concerned enriched pulses, obtained by late injection of fuel into the engine, might take place every few minutes and each last less than a minute. The NOx storage components usually include basic alkaline earths such as Sr or Ba, that also form very stable sulphates from traces of SOx derived from fuel sulphur compounds. Their increasing presence decreases NOx capacity, so from time to time it is necessary to have a high temperature reductive regeneration to release sulphate and restore the full NOx capacity of the NOx-trapping catalyst. The NOx-trapping approach has the advantage that the reductant for converting NOx to N_2 (diesel fuel) is already available on the vehicle, but it does require running the engine under extraordinary conditions for a diesel engine, and this illustrates how closely engine operation and catalyst design needs to be done in unison.

$$2M(NO_3)_2 \rightarrow 2MO + 4NO + 3O_2 \quad (12)$$

8.3.2. Ammonia selective catalytic reduction (SCR)

There are several possible ways to directly reduce NOx under lean condition, for example with HCs, and interesting results have been obtained with silver catalysts [34], but the most selective and that being actually used on diesel cars is NH_3 selective catalytic reduction (SCR). An important consideration with all catalytic diesel NOx control systems is selectivity to N_2, emissions of species such as NH_3 and N_2O must be minimal. Some ammonia in diesel exhaust can be produced from the over reduction of NOx during regeneration of NOx-trapping catalyst [35], but it is more usual to derive NH_3 from an aqueous urea solution that is injected into the hot exhaust upstream of the SCR catalyst. The urea hydrolyses to NH_3 and CO_2, Eq. (13).

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \quad (13)$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (14)$$

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \quad (15)$$

The reaction of NH_3 with NO is shown in Eq. (14), and it is interesting to see O_2 is required to form H_2O so as to consume the excess hydrogen from NH_3. The reaction of NH_3 with NO_2 is a much slower reaction. However, equal amounts of NO and NO_2 undergo selective reduction with NH_3 in a reaction that is an order of magnitude faster than with either NO or NO_2 alone, Eq. (15). This has been called "fast SCR", reaction [36], and O_2 does not take part in the reaction as it can be seen NO_2 has the role of consuming the hydrogen that the O_2 did in reaction of NO with NH_3. Since this mixed reaction is indeed "fast" it is important to adjust the NO/NO_2 ratio by appropriate oxidation of NO to NO_2 before the SCR catalyst on a vehicle, and this is done by carefully selecting the catalyst. The original SCR catalysts were used to control NOx emissions from power plants, and they were V-based formulations that operated at temperatures above what is usually obtainable in diesel car exhaust, and for car applications they have been superseded by high activity low temperature zeolite/base metal formulations.

8.3.3. Future combined diesel control systems

To be cost-effective, weight effective and space-effective, some of the catalytic functions needed for the control of emissions from diesel cars will be combined into single components. So SCR or NOx-trapping components are likely to be incorporated into future designs of catalysed filters fitted to diesel cars. When CO, HCs, PM and NOx emissions are controlled by a single unit, the systems are likely to be known as "four-way catalysts" (FWCs).

9. Conclusions

A notable feature in the control of emissions from vehicles is the central roles of PGM catalysts (Pt, Pd and Rh) that have been responsible for preventing huge amounts of pollutants from entering the environment that could have gone on to form noxious secondary pollutants. When the increasing mass production of gasoline cars gave society tremendous mobility it was accompanied by pollution problems that were particularly evident in some American cities in the late 1960s. Engineering modifications and especially the fitment of catalysts brought these problems under control. First Pt-based oxidation catalysts were used to control HC and CO emissions, then NOx emissions were also controlled by an additional upstream Rh containing catalyst. This two catalyst system was followed by the introduction of TWCs in the early 1980s. Refinement of TWCs and their integration into emissions control systems continued, so today extremely low emissions can be realised. Now, and especially in Europe, sophisticated fuel efficient diesel cars have become very popular, and controlling their emissions presents many challenges due to low temperatures and the difficulty of reducing NOx under lean conditions. Special high activity oxidation catalysts were successfully introduced to control HC and CO, and more recently the spotlight has been on preventing diesel PM from entering the environment by wall-flow filters, that periodically undergo high temperature excursions to combust retained PM and prevent the build-up high backpressure. This is done by catalytically oxidising extra fuel that is partially burnt in the engine over a catalyst to achieve the high temperatures needed to burn PM. The latest and most efficient of these systems 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 controlled regenerations. Two types of diesel NOx control systems are being introduced, NOx-trapping and SCR using ammonia derived from an aqueous solution of urea. Once these approaches have been fully developed, it is likely that compact multifunction four-way catalysts (FWCs) will be developed, just like the use of first two catalysts with different functions gave way to TWCs on gasoline cars.

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