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Rôles of catalytic oxidation in control of vehicle exhaust emissions

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Abstract

Catalytic oxidation was initially associated with the early development of catalysis and it subsequently became a part of many industrial processes, so it is not surprising it was used to remove hydrocarbons and CO when it became necessary to control these emissions from cars. Later NOx was reduced in a process involving reduction over a Pt/Rh catalyst followed by air injection in front of a Pt-based oxidation catalyst. If over-reduction of NO to NH_3 took place, or if H_2S was produced, it was important these undesirable species were converted to NOx and SOx in the catalytic oxidation stage. When exhaust gas composition could be kept stoichiometric hydrocarbons, CO and NOx were simultaneously converted over a single Pt/Rh three-way catalyst (TWC). With modern TWCs car tailpipe emissions can be exceptionally low. NO is not catalytically dissociated to O_2 and N_2 in the presence of O_2, it can only be reduced to N_2. Its control from lean-burn gasoline engines involves catalytic oxidation to NO_2 and thence nitrate that is stored and periodically reduced to N_2 by exhaust gas enrichment. This method is being modified for diesel engines. These engines produce soot, and filtration is being introduced to remove it. The exhaust temperature of heavy-duty diesels is sufficient (250–400 °C) for NO to be catalytically oxidised to NO_2 over an upstream platinum catalyst that smoothly oxidises soot in the filter. The exhaust gas temperature of passenger car diesels is too low for this to take place all of the time, so trapped soot is periodically burnt in O_2 above 550 °C. Catalytic oxidation of higher than normal amounts of hydrocarbon and CO over an upstream catalyst is used to give sufficient temperature for soot combustion with O_2 to take place.

Keywords: Catalytic oxidation; Vehiculor emissions; NOx-control; Particulate control

1. Introduction

The activity of Pt in catalytic combustion was discovered by Humphry Davy in 1817, who found hot platinum wire became white hot in a coal gas/air mixture. He also observed [1] the catalytic oxidation of ethanol and diethylether to acetaldehyde and acetic acid over Pt, Reactions (1)–(3). Three years later his cousin, Edmund Davy [2] prepared Pt black, and noted its activity in the catalytic oxidation of ethanol.

$$CH_3CH_2OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O \quad (1)$$

$$CH_3CH_2OCH_2CH_3 + O_2 \rightarrow 2CH_3CHO + H_2O \quad (2)$$

$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3CO_2H \quad (3)$$

Döbereiner extended this work, and prepared the first supported heterogeneous catalyst, based on small pipe clay pellets [3]. He studied the Pt catalysed H_2/O_2 reaction that was incorporated into lighters that were widely sold. At this time Peregrine Phillips worked on oxidation of SO_2 to SO_3 for H_2SO_4 production, Reactions (4) and (5), and in 1831 his patent was published [4] describing the catalyst as fine Pt wires or Pt in ‘‘any finely divided state’’. When it was commercialized

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3 \quad (4)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (5)$$

many years later the supported Pt catalyst was too readily poisoned (especially by arsenic derived from the metal sulphides that were burnt to produce SO_2 at that time) and the less poison sensitive vanadium oxide-based process was introduced [5]. In the meantime Michael Faraday at the Royal Institution worked on the Pt catalysed H_2/O_2 reaction during work on electrolysis [6]. He proposed catalysis involves simultaneous adsorption of reactants on the Pt surface, and that a clean surface is essential. Also during electroysis experiments, Schönbein in 1838 noticed when the electricity was switched off there was a reversed potential across the Pt electrodes [7].

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This was taken up by Grove who developed the first fuel cell [8]. Another application of Pt catalysts was selective oxidation of NH_3 to NO for HNO_3 production shown in Reactions (6)–(8). Kuhlmann in 1838 detailed [9] the oxidation of NH_3 in air over Pt sponge at 300 °C. Later Ostwald showed optimum results were obtained with short contact time at high temperature [10], and this led to the industrial use of Pt gauze catalysts for HNO_3 production in 1910 [11]. This increased in importance when the Haber-Bosch process for NH_3 was scaled-up to industrial production just before the First World War [12]. When it became apparent catalytic oxidation could control some exhaust gas emissions from cars Pt-based catalysts were then used widely in laboratories and chemical plants. It was obvious their effectiveness should be tested as autocatalysts. A variety of base metal catalysts were also tested, but only those containing Pt and two of its allied metals, Rh and Pd, were successful in real-world applications. This article briefly reviews the origins of atmospheric pollution caused by engine exhaust emissions before detailing the ways catalytic oxidation has been used to combat this problem.

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

$$2NO + O_2 \rightarrow N_2O_4 \quad (7)$$

$$N_2O_4 + 2H_2O + O_2 \rightarrow 4HNO_3 \quad (8)$$

2. Atmospheric chemistry

By the 1940s and 1950s air quality problems caused by cars were experienced in some urban cities [13–18], especially in locations such as the Los Angeles' basin where temperature inversions trap and recycle polluted air [19]. Gasoline oxidation in the engine to CO_2 and H_2O was far from completely efficient, Reaction (9), and the exhaust contained significant amounts of hydrocarbons and lower levels of partially combusted products like aldehydes, ketones and carboxylic acids, together with large amounts of CO, Reaction (10). Unburned fuel, hydrocarbons formed by pyrolysis, and various oxygenated species are called ''hydrocarbons'' and designated HC. At high temperature during combustion in the cylinder N_2 and O_2 react to establish the endothermic equilibrium with NO, Reaction (11). This equilibrium is frozen as the hot gases are cooled and ejected into the exhaust manifold. The combination of NO and any NO_2, is referred to as NOx, and more than a 1000 ppm can be present in exhaust of a gasoline engine. The three major primary pollutants in the exhaust gas from cars are therefore NOx, HC and CO.

$$HC + O_2 \rightarrow H_2O + CO_2 \quad (9)$$

$$HC + O_2 \rightarrow H_2O + CO \quad (10)$$

$$N_2 + O_2 \rightleftharpoons 2NO \quad (11)$$

In some American cities irritating photochemical smogs became so frequent air quality was a major health concern. The origin of these photochemical smogs was the primary pollutants from cars, that were of concern in their own right, that underwent photochemical reactions to generate a strong oxidising irritant [20]. Fig. 1 shows the increase in atmospheric oxidant levels during a day in Summer in Los Angeles during the early 1970s; peak levels were reached during the early afternoon. This trend followed the sunlight intensity, and it was established ozone was the main ''oxidant'' that was produced via the photochemical dissociation of NO_2, Reaction (12), followed by the reaction of the atomic oxygen with O_2, Reaction (13), in which ''M'' is a ''third body'' that removes energy that would otherwise cause the dissociation of O_3. However, it is mainly NO that is formed in engines, and not NO_2, and the oxidation of NO to NO_2, Reaction (14), is a third order reaction the rate of which depends on the square of the very low NO concentration [21], as in Eq. (15). The formation of NO_2 from NO is therefore extremely slow, so direct oxidation of NO was not the route to NO_2. The actual oxidation of NO to NO_2 in air, the ozone precursor, involves free radical oxidation of HC or CO, and

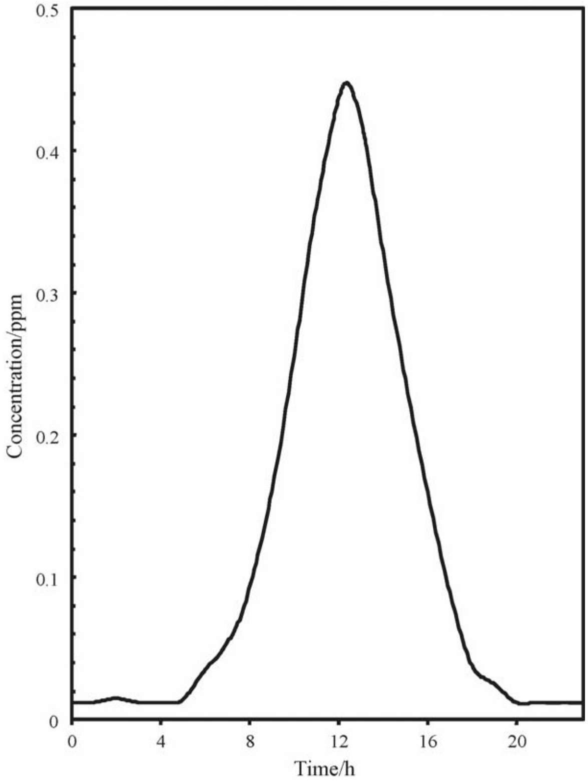


Fig. 1. Variation of ambient atmospheric ''oxidant'' levels in a California City during a Summer day in the 1970s. The ''oxidant'' is mainly ozone, and peaked in early afternoons.

$$NO_2 + h\nu \rightarrow NO + O \quad (12)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (13)$$

$$2NO + O_2 \rightarrow 2NO_2 \quad (14)$$

$$\frac{d\,NO_2}{d\,t} = kP_{O_2}P_{NO}^2 \quad (15)$$

$$OH + RCH_3 \rightarrow H_2O + RCH_2$$

$$RCH_2 + O_2 \rightarrow RCH_2O_2$$

$$RCH_2O_2 + NO \rightarrow RCH_2O + NO_2$$

$$RCH_2O + O_2 \rightarrow RCHO + HO_2$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$RCH_3 + 2NO + 2O_2 \rightarrow RCHO + 2NO_2 + H_2O$$

Scheme 1.

one of the more important series of free radical reactions leading to it is summarised in Scheme 1. Overall the process corresponds to the oxidation of hydrocarbon in the presence of NO to give NO_2, an aldehyde and H_2O. The reactive aldehyde can undergo further reactions with NO_2 to give, for example, peroxyacetylnitrate (PAN) accordingly to Reactions (16)–(18). PAN is a very strong lachrymator [22,23], and even traces of it cause serious eye irritation and painful breathing.

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \tag{16}$$

$$CH_3CO + O_2 \rightarrow CH_3COO_2 \tag{17}$$

$$CH_3COO_2 + NO_2 \rightarrow CH_3COO_2NO_2 \tag{18}$$

Levels of tailpipe pollutants from American cars in the mid-1960s were typically HC 15 g/mile; CO 90 g/mile; and NOx 6 g/mile [24]. Engine modifications could not alone meet the demands of the 1970 Clean Air Act [25], so as a result, catalytic systems were introduced to control exhaust emissions.

3. Choice of catalyst types

Engine exhaust is a demanding environment, and unlike the steady-state operation of chemical plant processes [26]. The catalyst must function at low temperature, resist effects of excursions up to 1000 °C, tolerate the presence of poisons (especially sulphur species), and not be affected by gas flow pulsations and mechanical vibrations. At first it was necessary to oxidise HC and CO, and catalysts containing copper and nickel were tested, but they were sensitive to poisoning (initially by lead, halide and sulphur compounds), and they did not have thermal durability [27,28]. Some important properties of selected metals are summarised in Table 1; the Pt-group catalysts were very active, and much work was done with Ru, but its oxides are volatile, and it was not possible to prepare catalyst that did not lose Ru during use [29]. Even Ir oxides are too volatile at high temperatures, so this metal could not be used [30]. However, especially Pt, as well as Pd and Rh met the requirements of having the nobility to remain metallic under most operating conditions, and not have volatile oxides that led to metal loss; these three metals have been used in autocatalysts since their introduction [31]. Of these Pt is the most noble, but when very hot and exposed to O_2 for long periods it can sinter through a process involving migration of oxide species. Pd forms a more stable oxide than does Pt, and this is catalytically active in oxidation reactions. Rh_2O_3 is readily formed from the metal under hot oxidising conditions, Reaction (19), and this can undergo reactions [32] with catalyst support compounds such as alumina as shown in Reaction (20). The main role of rhodium is in NOx reduction, and since it is reduced rhodium that is active, it is important this can be made available rapidly when any oxidising conditions return to being slightly reducing, as is illustrated in Reaction (21).

$$2Rh + \tfrac{3}{2}O_2 \rightarrow Rh_2O_3 \tag{19}$$

$$Rh_2O_3 + Al_2O_3 \rightarrow Rh_2O_3{\cdot}Al_2O_3 \tag{20}$$

$$Rh_2O_3{\cdot}Al_2O_3 + 3H_2 \rightarrow 2Rh + Al_2O_3 + 3H_2O \tag{21}$$

Frequently two or more metals are used in combination in autocatalysts. Pt/Pd was used in some of the early oxidation catalysts, as was Pt/Rh that was also used under rich conditions for NOx reduction. Today three-way catalysts (see below) commonly contain Pd/Rh although Pt/Rh catalysts are still used on some cars, and other now less common formulations combine all three metals.

4. Early oxidation catalysts

The first cars with oxidation catalysts injected air into the rich (excess fuel and reducing) exhaust gas to provide O_2 for oxidation of HCs and CO. Some traditional pelleted platinum

Table 1
Physical and chemical properties of some selected metals and their oxides relevant to their catalytic behaviour

Metal	Atomic number	Atomic weight	Density	MP/K	Reduction potential $M^{n+} \rightarrow M^0$ (n)	Oxide stability
Platinum	78	195.08	21.45	2045	1.19 (2)	Unstable oxides
Iridium	77	192.22	22.56	2683	1.16 (3)	Moderately stable oxides
Palladium	46	106.42	12.02	1825	0.92 (2)	Stable oxides
Rhodium	45	102.91	12.41	2239	0.76 (3)	Stable oxides
Osmium	76	190.2	22.59	3327	N/A (2)	Very volatile oxides
Ruthenium	44	101.07	12.37	2583	N/A (2)	Very volatile oxides
Copper	29	63.33	8.96	1357	0.34 (2)	Stable oxides
Cobalt	27	58.93	8.90	1768	−0.28 (2)	Stables oxides
Nickel	28	58.69	8.90	1726	−0.30 (2)	Stable oxides
Iron	26	55.85	7.87	1808	−0.44 (2)	Stable oxides

Data from [64]. MP: melting point.

catalyst were used in a flat radial flow-like reactor. This configuration was not ideal because of gas by-pass, but at that time the conversions required were not as high as today and sufficient conversions could be achieved. However, attrition of the pellets caused by their movement against each other under the influence of the pulsating gas flow and vibration of the vehicle was a major concern. An alternative catalyst structure made use of a ceramic monolithic honeycomb that overcame these deficiencies.

For strength reasons monolithic honeycombs had relatively low porosity that made them unsuitable as a catalyst support [33], so a thin layer of high surface area catalytically active material was applied to the channel walls [34]. This layer, typically 20–150 μm thick, is referred to as a washcoat. The process of applying it is called washcoating and the washcoat surface area is typically 100 m^2/g. The monoliths made from cordierite have exceptionally low coefficient of thermal expansion needed to prevent them from cracking when thermally stressed during use. Monoliths are manufactured by extruding a mixture of clay, talc, alumina and water with various organic additions, that is dried and fired at high temperature when cordierite is formed [35]. Fig. 2 shows one way a ceramic monolith can be retained in a stainless steel mantle that is welded into the exhaust system. It is wrapped in an intumescent mat typically containing inorganic fibres (such as rock wool), vermiculite and an organic binder. When the converter experiences temperatures above about 310 °C the organic binder decomposes and the vermiculite exfoliates. The force of this expansion exerts a pressure on the monolith that keeps it firmly in place for the life of the vehicle. Fig. 2 also shows a metal foil-based catalyst whose stainless steel mantle can be welded directly into the exhaust system. The impact of fitting oxidation catalysts in the exhaust systems of cars was very significant; there was a very large reduction in HC and CO emissions, but there was little or no effect on the NOx emissions.

5. Control of Nox emissions

NO is thermodynamically unstable, and it is a free radical (enthalphy of formation $\Delta H = +89.9$ kJ/mol, free energy of formation $\Delta G = +86.3$ kJ/mol) yet under practical conditions in the presence of O_2 catalytic dissociation does not take place [36], and it can only be converted to N_2 via a reductive process. The first approach for controlling NOx from engine exhaust was to reduce it to N_2 over a Pt/Rh catalyst in rich exhaust gas before air was added to permit catalytic oxidation of HC and CO [37]. This arrangement, and the earlier oxidation catalyst only system are illustrated in schematically in Fig. 3. The selectivity of the catalyst used and the conditions employed for NOx reduction had to ensure a high degree of selectivity so as not to reduce NOx to NH_3 or SO_2 to H_2S. It was important any NH_3 or H_2S formed was minimised, and that which was formed was reoxidised over the oxidation catalyst to more acceptable NO and SO_2, as shown in Scheme 2. Because of this any reduction of NO to NH_3 represented an inefficiency in overall NOx conversion. Good overall selectivity was obtained and this system enabled markedly lower emissions of HC, CO and NOx to be achieved in a reliable way.

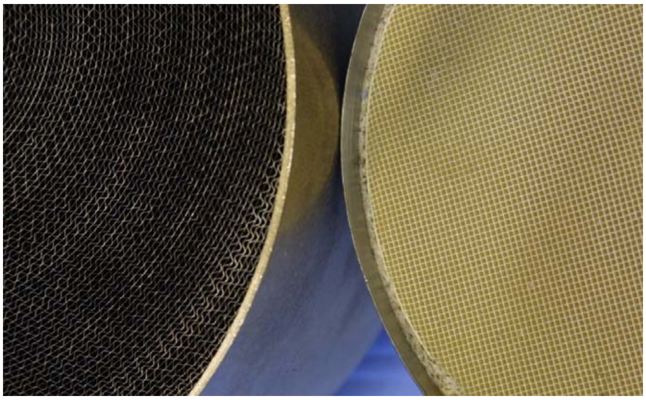


Fig. 2. Examples of a metal-based catalyst (left) and a ceramic-based cordierite catalyst (right). The cordierite monolith is retained in a stainless steel mantle with an intumescent mat. Vermiculite in the mat exfoliates when heated and permanently retains the monolith in place.

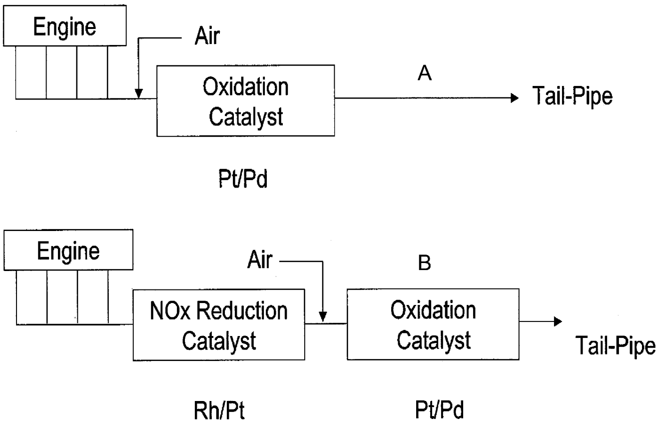


Fig. 3. Schematic arrangement of oxidation catalyst and air injection point used initially to lower HC and CO emissions (A). The later modification (B) used air injection after a platinum/rhodium catalyst operating under rich conditions to reduce NOx, then HC and CO were oxidised in a second stage after air injection. In this way all three pollutants were controlled in a two stage process.

6. Modern three-way catalysts (TWCs)

The gasoline engines with the earliest catalytic emissions control systems were fuelled via carburettors that could not precisely control the amount of fuel that was mixed with the intake air. Often the air/fuel ratio moved randomly either side of

Desired $2NO + 2CO \rightarrow N_2 + 2CO_2$

Undesired $SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$

$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$

Re-oxidation $2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Scheme 2.

the stoichiometric point, and it was observed a Pt/Rh catalyst could, under appropriate conditions, simultaneously convert CO and HC (oxidations) and reduce NOx with high efficiency [38, 39]. This concept became known as a three-way catalyst (TWC), because all three pollutants are removed from the exhaust gas simultaneously. Application of the TWC required three elements:

1. Electronic fuel injection (EFI) so precise amounts of fuel could be metered to provide a stoichiometric air/fuel mixture.
2. An oxygen sensor in the exhaust to provide an electrical signal indicating if the engine is running rich or lean.
3. A microprocessor to control a feedback-loop using oxygen sensor signals to determine the amount of fuel to be injected under specific conditions to maintain the exhaust gas close to the stoichiometric point.

By the early 1980s all of the elements necessary for the operation of TWCs were available, and this became a more efficient means of controlling HC, CO and NOx emissions than earlier two catalyst systems; it was also more cost effective. Soon TWCs were universally adopted.

6.1. Oxygen sensors

Residual oxygen in the exhaust gas of a stoichiometric gasoline engine is determined by an oxygen sensor. Fig. 4 illustrates some of the basic features of the original switching-type sensor that indicated if the exhaust was lean or rich. The stabilised zirconia thimble at operating temperature is conducting, and its surface on the reference air side has a porous Pt coating that acts as an electrode, and a similar electrode is deposited on the exhaust gas side. These coatings are active oxidation catalysts, so HC and CO are oxidised by any excess O_2. A galvanic potential is developed across the electrodes that is related to the excess oxygen concentration in the exhaust gas. A small electric heater inside the zirconia thimble (not shown) heats the sensor to its operating temperature so it can be used soon after the engine is started. The Nernst Eq. (22) describes the emf developed assuming air ($P_{O_2} = 0.21$ atm) is the reference gas. For this to be meaningful in automotive applications it is important the gas phase oxidation reactions are

$$\text{emf} = \frac{2.303RT}{F}\log\frac{0.21}{P_{O_2}} \qquad (22)$$

brought to equilibrium at the electrode surface. Today significantly more complex wide-range sensors are available [40] having a flat and smaller size that are essentially a combination of a conventional sensor and a limit current or ''pump cell'' that are separated by a diffusion zone. A voltage is applied to the ''pump cell'' that removes or adds oxygen to the oxygen sensor location so $\lambda = 1$ condition is maintained at the oxygen sensor via a control loop. The pump cell current then provides an output signal directly related to the excess oxygen concentration over a broad range of oxygen partial pressures, and in practice the λ range 0.7–2.5 can be measured.

6.2. Oxygen storage components

During the development of TWC formulations redox active Ce compounds were incorporated; under lean conditions (oxidising) they absorb oxygen, Reaction (23), and under rich (reducing) conditions oxygen is released from them, Reaction (24). These reactions are a gross simplification of what actually happens because a wide range of non-stoichiometric oxides are involved and formation of Ce_2O_3 only takes place under forcing conditions such as when OBD measurements are being made, see Section 5. A recent excellent review on the structural chemistry of cerium oxides is available [41] and there are good reviews on their rôles in TWCs [42,43]. In this way the composition of the exhaust gas at the catalyst surface is buffered around the stoichiometric point, and this enhances conversion of all three pollutants, especially NOx. Thus reactions involved in oxygen storage make use of the two easily accessible oxidation states Ce(III) and Ce(IV). The total oxygen storage capacity (OSC) is directly related to the amount of cerium oxide present, although kinetically not all of this may be available during short engine transients for kinetic reasons.

$$Ce_2O_3 + \tfrac{1}{2}O_2 \rightarrow 2CeO_2 \qquad (23)$$

$$2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2 \qquad (24)$$

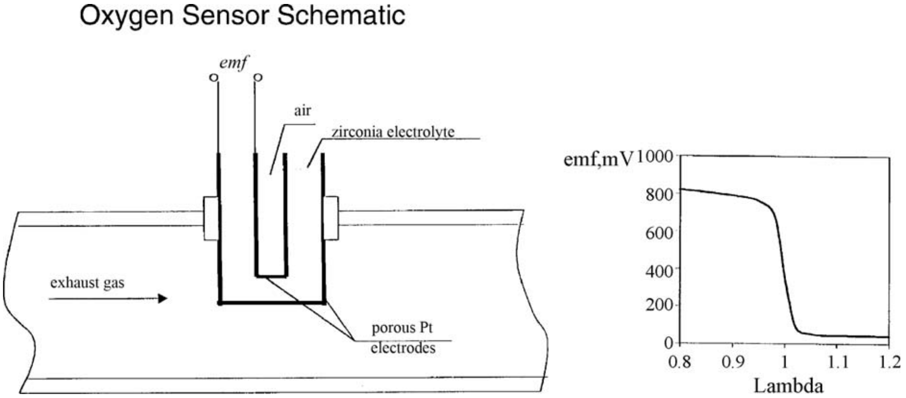


Fig. 4. Basic features of an original switching oxygen sensor involving a stabilised zirconia thimble that is conducting at temperatures above 300 °C. The emf developed across the Pt electrodes is related to P_{O_2} in the exhaust gas.

Since the introduction of oxygen storage components there has been a trend for the use of increasingly thermally stable forms. It is possible to optimise the environment around platinum, and if this is different from that which is optimal for rhodium it is advantageous to physically divide the catalyst into two (or more) layers containing well-separated different active metal dispersions with their specific promoter packages [44]. Usually Pt and Pd function best in oxidation rôles, and they are often located in the bottom part of a two-layer TWC. Rh in the top layer is then exposed to all of the reductant species that reduce NOx before the exhaust gases diffuse to the lower layer where they are oxidised. Physical separation into layers enhances overall catalyst performance and life by preventing alloy formation, separating otherwise incompatible promoters, and encouraging desired reactivity by matching catalytic functionality by imposing appropriate diffusing conditions on reactants.

6.3. *Palladium-only TWCs*

By the correct use of promoters, particularly alkaline earth and lanthanide oxides, it was possible to modify the catalytic properties of Pd so it can function as a TWC and catalyse reduction of NOx as well as oxidation of CO and HC [45]. This entails interplay between catalysis by Pd metal and its oxide, the presence of which can be controlled by close contact with cations that stabilise surface oxygen. Again separating the catalyst coating into two layers can minimise cross-contamination, and help obtain long lasting high activity. There have been numerous studies on the mechanisms of the water gas shift and methanol synthesis reactions over Pd [46] and amongst other surface intermediates formate has been suggested. Perhaps the alkaline promoted NOx reduction reaction with Pd-only TWCs involves the water gas shift reaction that produces hydrogen which efficiently reduces NOx as illustrated in Scheme 3. Here it is postulated surface formate intermediates may be involved in converting CO to H_2 as in some copper catalysed synthesis gas reactions [47], although other mechanisms involving reduced cerium species that abstract oxygen from NO are also possible. Fig. 5 shows how well a modern TWC performs in an engine bench evaluation test, even after it has been harshly aged to simulate performance of the catalyst at the end of the vehicle's life.

6.4. *Substrate types*

Extruded ceramic monoliths are widely used for TWC applications, but in some situations monoliths made by rolling metal foils are used. For example, the use of thin foil can provide, when appropriately coated, a catalyst with low backpressure characteristics that can be advantageous. These metal-based catalysts can be welded directly into the exhaust system [48]. More recently there were advances in extruding thin wall ceramic monoliths, and these have been widely used. They have relatively low thermal mass and high geometric surface area that facilitate fast catalyst light-off after the engine has started. The decision about which type of substrate is used, metallic or ceramic, depends on a balance between these properties and the overall system cost.

$$OH^- + CO \rightarrow HCO_2^-$$

$$HCO_2^- + H_2O \rightarrow H_2 + CO_2 + OH^-$$

$$H_2 + NO \rightarrow \tfrac{1}{2}\ N_2 + H_2O$$

Scheme 3.

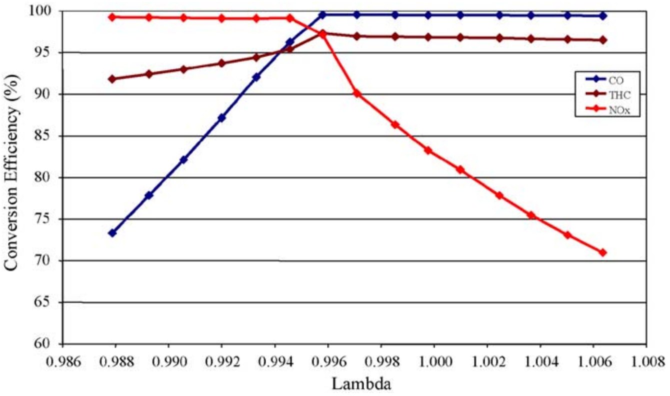


Fig. 5. Engine bench performance of an aged TWC. In the vicinity of the stoichiometric point all three pollutants are converted to CO_2, H_2O and N_2 with high efficiency.

6.5. *TWC on-board diagnostics (OBD)*

Legislation demands the functioning of TWCs is periodically interrogated during actual driving, and if performance is lower than a predetermined level it is reported and stored in the on-board computer [49]. If poor performance persists a malfunction indicator lamp (MIL) is turned on, so the driver can have the fault corrected. The OBD system makes use of two oxygen sensors, one upstream and one downstream of the catalyst. By running slightly lean for a short period the oxygen storage component in the catalyst is converted into its fully oxidised form, at which point the engine is run slightly rich and the time taken for the gas exiting the catalyst to become slightly rich, as detected by the second oxygen sensor, is a direct measure of the oxygen storage capacity. This measurement is related to the catalytic performance, and so it can be used as a criterion for the OBD requirement. In practice this approach, or a modified alternative form, works very well, and Fig. 6 illustrates the fundamentals of monitoring OSC using two oxygen sensors.

6.6. *Gasoline car emissions legislation*

The progress made in reducing exhaust emissions from traditional gasoline cars during the first decade following the introduction of legislation in America can be judged from the decrease in the amount of HC, CO and NOx emitted annually between 1970 and 1990. Initially there was around ten million tons of HC and seventy five million tons of CO, and some five

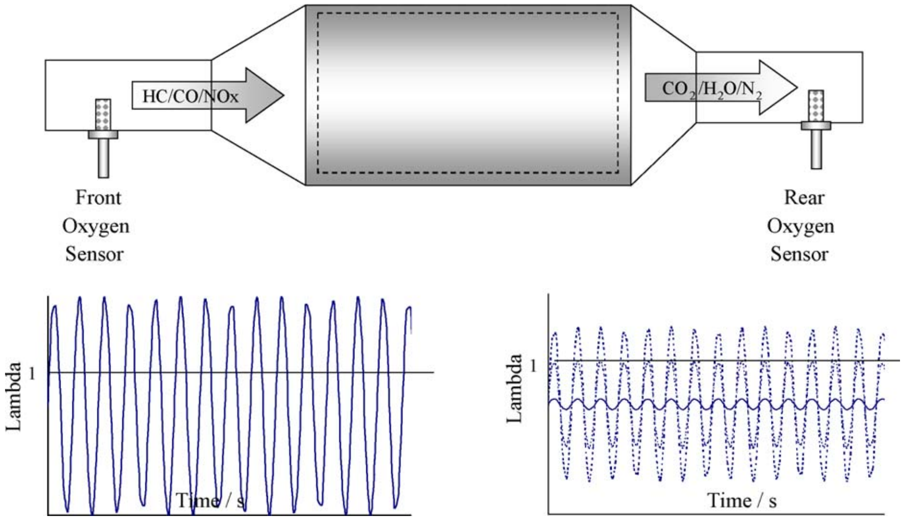


Fig. 6. Arrangement of two oxygen sensors upstream and downstream of a three-way catalyst for monitoring catalyst characteristics during driving. When the catalyst is active the oxygen level oscillations are damped by the oxygen storage components in the catalyst, should deactivation take place the oscillations break through the catalyst as illustrated by the dashed traces.

million tons of NOx emitted each year. The amount of NOx was significant when compared with the nitrogen ‘‘fixed’’ in the Haber-Bosch Process as ammonia mainly for fertilizer use. During the first two decades of catalyst fitment the total HC and CO emissions were reduced by about 70% and some 50% for NOx. The way the legislation was tightened over the years since catalysts were fitted to cars to control emissions is also a measure of progress, and recent California legislation trends are shown in Table 2. The improvements are such, that although the number of cars dramatically increased, the total emissions decreased (Fig. 7), and, for example, the ‘‘alert days’’ in Los Angeles have been effectively eliminated. In fact, the most demanding legislation in the world today, California’s HC SULEV limit (Table 2) is in some cases lower than ambient air. For HC this corresponds to a reduction of about a 2000-fold since the mid-1960s. So, although these emissions are not zero, they are extremely low, and the improved air quality clearly reflects this.

Table 2
California (CARB) Emissions Standards Post-1994

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

NB. PZEV vehicles have same emission limits as $SULEV_2$ with 150,000 miles durability mandated.

[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.

7. Diesel engines emissions control

In traditional stoichiometric gasoline engines the combusting mixture always contains sufficient oxygen to just combine with the fuel. In contrast, in a diesel engine oxygen is always in excess, since only sufficient fuel is injected into compressed hot air in the cylinder to produce the power required at a particular instant [50]. The consequence of this mode of combustion is diesel exhaust always contains excess oxygen, and while this is advantageous for the oxidation of HCs and CO, it makes controlling NOx emissions extremely difficult because under

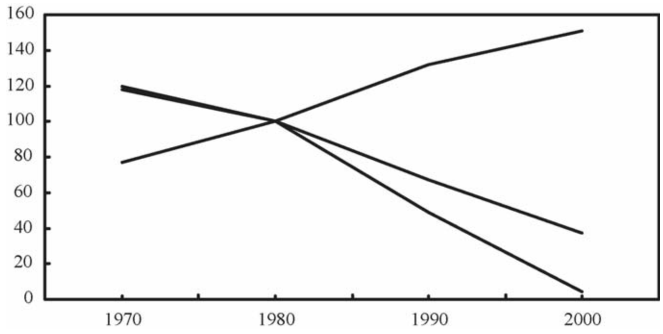


Fig. 7. Decrease in Stage 1 ‘‘Alert Days’’ in Los Angeles (lower decreasing line) compared with the number of cars on the road (upper increasing line). The decreasing peak ozone levels are shown in the upper decreasing line. Total emissions dramatically decreased in spite of the increased number of cars.

practical conditions NOx can only be converted to N_2 by reduction. So far European diesel car legislative NOx emissions requirements have been met by engine control measures alone. But, this may not be possible in the future with lower NOx emissions limits, so some form of lean-NOx control will then be necessary. Because of the nature of the combustion process some carbonaceous particulate material (PM or ‘‘soot’’), is formed by diesel engines. Over recent years engine modifications reduced the amount of PM formed, and reliable means of controlling the remaining PM were devised and successfully introduced. This section is concerned with the control of these three classes of emissions associated with diesel engines, and each of them involve the use of oxidation catalysts.

7.1. Hydrocarbons and carbon monoxide

Catalytic oxidation of HC and CO under the lean conditions in a diesel exhaust should be straightforward. However, the fuel-efficient characteristics of diesel engines results in low exhaust gas temperature, especially during low-speed driving. This, together with SO_2 in the exhaust gas (derived from sulphur compounds in the fuel) that is a catalyst poison, means achieving and maintaining good low temperature catalytic performance is challenging. Pt-based catalysts are used to oxidise CO and HC, and to achieve the performance and durability required catalyst formulations have the Pt in a highly dispersed form, that is well stabilised against thermal sintering. When the engine is started the catalyst is insufficiently warm to oxidise the hydrocarbons initially present in the exhaust, and incorporating zeolites into the catalyst significantly improved the performance during the so called ‘‘cold start’’. The zeolite function by adsorbing HC so preventing them inhibiting the active platinum sites. This improves low temperature CO and apparent HC oxidation performance [51]. At higher temperature the HC is desorbed and oxidised over the platinum catalyst sites. Fig. 8 shows the effect of zeolite addition to a platinum catalyst on HC oxidation performance. The CO oxidation performance is also improved by incorporating zeolite into the catalyst.

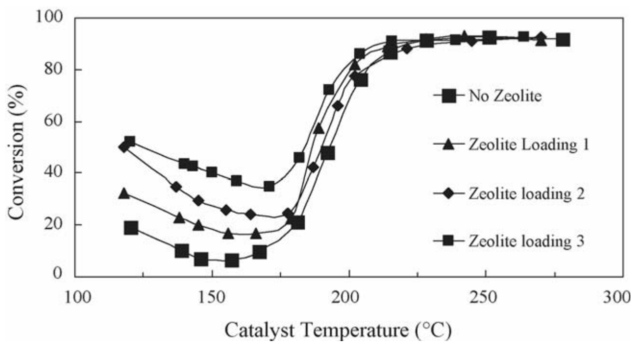


Fig. 8. The effect of incorporating zeolite into a platinum diesel oxidation catalyst. The control of hydrocarbon emissions at low temperature is improved by their retention in the zeolite. At higher temperatures released HC is oxidised over the catalyst.

7.2. NOx control under lean conditions

Although NO is thermodynamically unstable and a free radical, under practical lean conditions it is not possible to achieve its catalytic dissociation to O_2 and N_2. This is because of the high affinity of metallic catalyst surfaces for O_2 compared to that for NO or N_2 that leads to ‘‘oxygen poisoning’’ of the metal surface (especially with Rh that is one of the best metals for NO dissociation). The surface becomes covered with strongly adsorbed oxygen so preventing NO adsorption, and a reducing species is required to remove oxygen from the surface to allow further adsorption and dissociation of NO [52]. This is what takes place smoothly on a three-way catalyst when operating around the stoichiometric point. In contrast under lean conditions the only easy reaction of NO is its oxidation to NO_2, and while this is of value in the context of controlling diesel PM emissions and storing NOx as nitrate (*vide infra*), it is not helpful in the direct conversion of NOx into N_2.

7.2.1. NOx-trapping

NOx-trapping involves storage of NOx as a NO_3^-, phase, Reactions (25) and (26), during lean driving, then periodically, when the NOx-trapping material is becoming saturated, the exhaust gas composition is made slightly reducing for a short period. This destabilises the NO_3^- and releases the stored NOx, as in Reaction (27), which is then reduced over a Rh-containing component in the catalyst to N_2, Reaction (28) [53,54]. In the presence of CO_2 the carbonate is reformed, as in Reaction (29). Evidence for the presence of the NO_3^- phase was been obtained from X-ray diffraction and infrared experiments. In effect, Reaction (29) is like that with a TWC operating around the stoichiometric point. In the NOx storing and the NOx release Reactions (26) and (27), M represents a suitably basic element, typically an alkaline earth, or an alkali metal cation. The oxidation of NO to NO_2 is an equilibrium reaction with a favourable negative heat of enthalpy, so the reaction becomes less favoured at higher temperatures. This is illustrated in Fig. 9 that shows the equilibrium percentage conversion of NO to NO_2 as a function of temperature in the presence of O_2 as in the exhaust gas of a diesel engine (curve A). At temperatures above about 450 °C the formation of NO_2 is severely thermodynamically limited, this and more importantly the stability of the NO_3^- formed limits the degree of nitrate formation at higher temperatures. At temperatures below about 250 °C the catalytic oxidation is kinetically limited, so these two effects combine to form a temperature region, or window, in which NOx-trapping is practically possible. This is also illustrated schematically in Fig. 9. Higher platinum loadings can improve low temperature performance for catalytically oxidising NO while use of extremely stable NO_3^- phases, e.g., those of alkali metals, rather than alkaline earth nitrates, can extend the high temperature region. The data in Fig. 9 were derived from thermodynamics for the metal oxides [55], but in practice carbonates are present under operating conditions. As a result the actual high temperature parts of the curves will be shifted to lower temperatures. A consequence of using a very stable

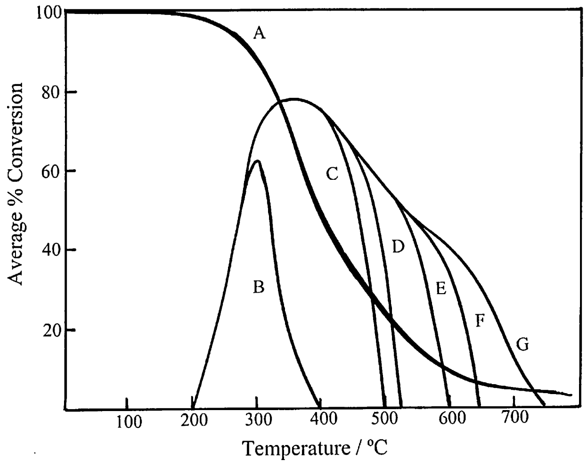


Fig. 9. Theoretical representation of NOx-trap performance while undergoing periodic reductive regeneration for formulations containing increasingly basic absorbants (B = Ca; C = Sr; D = Li; E = Ba; F = Na; G = Cs; H = K). The equilibrium for the oxidation of NO to NO_2 (curve A) is ‘‘pulled’’ to the right by the more basic components that widen the operating high temperature region. These data are based on oxide thermodynamics but carbonates are actually present so in practice the high temperature side of the curves are displaced to the left.

nitrate is it requires high temperature during periodic reductive regeneration. Also, for a particular cation the sulphate is invariably thermodynamically more stable than the corresponding nitrate, and as a result sulphates decompose at higher temperatures than do nitrates. Sulphur compounds in fuel is oxidised to SO_2 during combustion in the engine, and thence catalytically to SO_3 that becomes stored as sulphate in a NOx-trap according to Reactions (30) and (31). This restricts the NOx storing capacity, and the effects of this have to be periodically reversed by decomposing, the sulphate at relatively high temperature; usually in excess of 600 °C.

$$2NO + O_2 \rightarrow 2NO_2 \tag{25}$$

$$NO_2 + MCO_3 \rightarrow MNO_3 + CO_2 \tag{26}$$

$$2MNO_3 \rightarrow 2MO + 2NO + O_2 \tag{27}$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \tag{28}$$

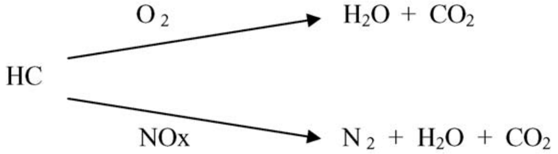
$$MO + CO_2 \rightarrow MCO_3 \tag{29}$$

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{30}$$

$$SO_3 + MCO_3 \rightarrow MSO_4 + CO_2 \tag{31}$$

7.2.2. Selective catalytic reduction

The second lean NOx control method is selective catalytic reduction (SCR) where reduction of NOx successfully competes with the reduction of oxygen, even though the latter is present in a large excess. This is illustrated in Scheme 4 where the reductant is a hydrocarbon.



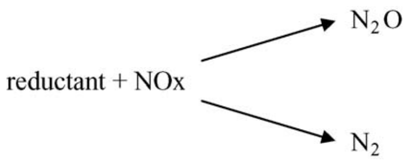
Scheme 4.

Under actual diesel exhaust conditions on a car, with a Pt oxidation catalyst only moderate NOx conversions are obtained unless high ratios of HC to NOx are used. Then the process becomes uneconomical because of the amount of HC consumed. Catalysts explored for HC lean-NOx control include those containing platinum [56], copper [57] and iridium [58], and recently there has been considerable interest in the behaviour of silver catalysts [59]. Here it appears the nature of the support (various modified aluminas) can have a profound effect on the catalytic performance, as can the presence of zeolite that trap hydrocarbons within the catalyst and effectively increase the local HC concentration.

The reactivity of HCs in lean-NOx conversion depends on their nature the catalyst and temperature; different HCs can behave slightly differently. At higher temperatures competitive HC oxidation becomes increasingly important, and then most of the HC reductant is oxidised giving little opportunity for NOx reduction. This is a consequence of the activation enthalpy of HC combustion being significantly higher than that for NOx reduction, and results in a restricted temperature ‘‘window’’ in which NOx reduction can be achieved. The maximum conversion within this temperature ‘‘window’’ can be increased by having more HC present, but this has an economic penalty. Catalyst formulations containing zeolite, can provide enhanced NOx reduction due to their ability of maintaining a high concentration of HC in the catalyst.

A feature of many lean-NOx reduction reactions is there is insufficient reduction capability on the surface to reduce NOx completely to N_2, and a significant amount of N_2O can be formed according to Scheme 5. The relative importance of this depends on the nature of the catalyst surface concerned, the nature and concentration of reductant, and the temperature as well as exhaust gas flow rates, etc. Hydrogen also participates in lean-NOx reduction, and because hydrogen is very reactive it reduces NOx at a relatively low temperature, so its operating window is centred at a low temperature compared to that for most HCs. Fig. 10 shows the behaviour of a range of HCs in lean-NOx reduction in a series of laboratory experiments in which very high NOx conversions were possible.

With an appropriate catalyst ammonia can function as a good selective NOx reductant as shown in Reactions (32) and (33), Pt catalysts can function very well at relatively quite low temperatures, but vanadium-based catalysts are commonly



Scheme 5.

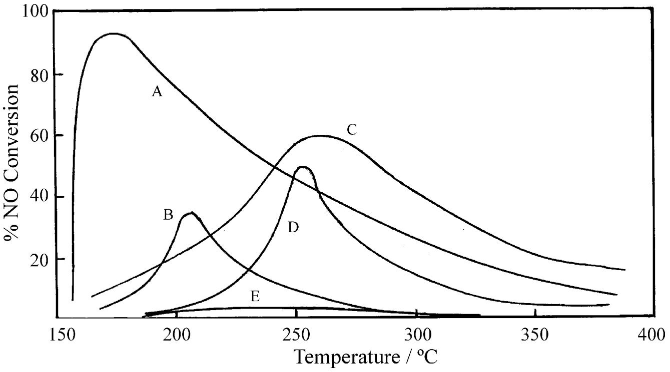


Fig. 10. Effect of different hydrocarbons in the reduction of NOx over a platinum catalyst under lean conditions. A wide range of reactivities are observed, methane (not shown) is unreactive except at high temperatures. In each case the C/NOx ratio was 14; A = *n*-octane; B = methylcyclopentane; C = toluene; D = propene, E = *iso*-octane. Adapted from [63].

used at temperatures typical of heavy duty diesel engine exhaust gas. High NOx conversions are possible, but oxidation of NH_3 affords NO at high temperatures, Reaction (34), so the apparent conversion of NO decreases as increasing amounts of NO are formed from NH_3. The NH_3/SCR process over vanadium catalyst is selective for conversion of NO to N_2 with little formation of N_2O, and it is interesting O_2 participates in the overall reduction process. Ammonia SCR has been used extensively for NOx removal from power generation and chemical plant exhaust gases [60]. It may be expected ammonia SCR will be used for NOx reduction more widely in vehicle applications in the future.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (32)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (33)$$

$$NH_3 + O_2 \rightarrow NO + H_2O \quad (34)$$

$$4NH_3 + SO_2 \rightarrow 4NO + 6H_2O \quad (35)$$

7.3. Diesel particulate control

A characteristic of older diesel engines was "black soot" in their exhausts caused by the combustion process itself in which very small "atomised" droplets of fuel burning in hot compressed air left an unburnt core of fine carbon particles onto which other species in the exhaust gas, including HCs, sulphur compounds, NOx and water adsorbed. Recently tremendous advances were made in the fuelling and combustion processes of modern high-speed diesel engines used in passenger cars. This involved very high pressure pumps, injectors with an increased number of smaller nozzles, and multiple injections. As a result soot or particulate matter (PM), emissions have been reduced to low levels. Nevertheless, there are still concerns about the possible health effects of diesel PM and there is a move to eliminate this by filtration.

A variety of ceramic and sintered metal-based filters have been developed, and the most successful are the so-called wall-flow filter illustrated in Fig. 11. A honeycomb monolithic structure made from porous material with alternate channels that are plugged at both ends so exhaust gas is forced through the channel walls. PM is too large to pass through the walls, so it is retained in the upstream side of the filter. If too much PM accumulates backpressure across the filter will increase and degrade engine performance, and ultimately the engine will cease to function. It is essential the backpressure is not allowed to rise above a predetermined limit. The most satisfactory means of removing trapped PM is to oxidise it to CO_2 and H_2O. On heavy duty diesel vehicles, such as trucks and buses, the engine is often working at high load and the exhaust temperature is in the range 250–400 °C. Under these conditions it is possible to use the already present NO in the exhaust gas in a process that continually oxidises trapped PM. An oxidation catalyst upstream of the filter oxidises HCs and CO to CO_2 and H_2O, and also converts NO to NO_2 that is a very powerful oxidant, and this continually removes PM, as shown in Scheme 6 in which PM is represented chemically as "CH". The advantage of this system is it requires no attention, but the NO oxidation is strongly inhibited by the presence of SO_2, so this technology could not be introduced until low sulphur diesel fuel became available. Now many tens of thousands of these filter units are in service around the world on buses, trucks, and larger delivery vehicles [61].

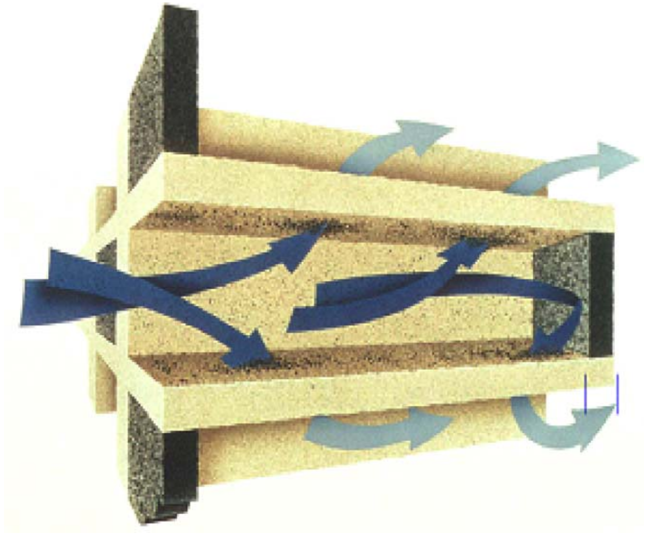


Fig. 11. A schematic representation of a ceramic wall-flow filter. The arrows indicate the gas flow through the walls. Particulate matter is retained in the upstream side of the filter, and this has to be removed to prevent unacceptable pressure-drop across the filter.

The exhaust temperatures of diesel passenger cars rarely exceed 250 °C in town driving, so use of NO_2 to combust PM is inappropriate except when driving at higher speeds when this reaction, in some circumstances, can keep the filter clean. However, the key to employing filters on diesel cars is to use

$$2NO + O_2 \rightarrow 2NO_2$$

$$5NO_2 + 2CH \rightarrow 5NO + 2CO_2 + H_2O$$

Scheme 6.

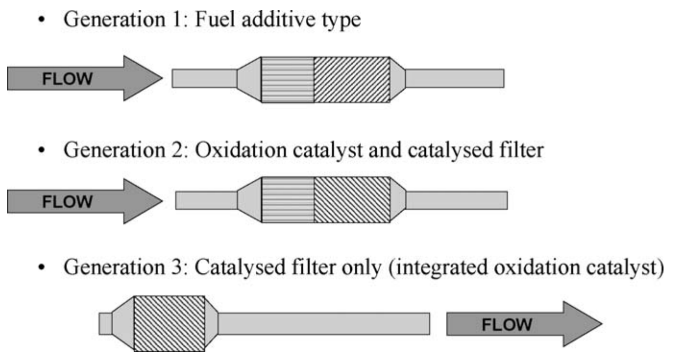


Fig. 12. Three filter systems used on diesel cars. The first has an oxidation catalyst before the filter to burn partially combusted fuel to achieve high temperatures, and a fuel additive is used to lower the PM combustion temperature. No additive is employed in the second generation system, the filter is catalysed to accelerate PM combustion. In the third generation system all of the required catalyst functionality is incorporated in a single filter.

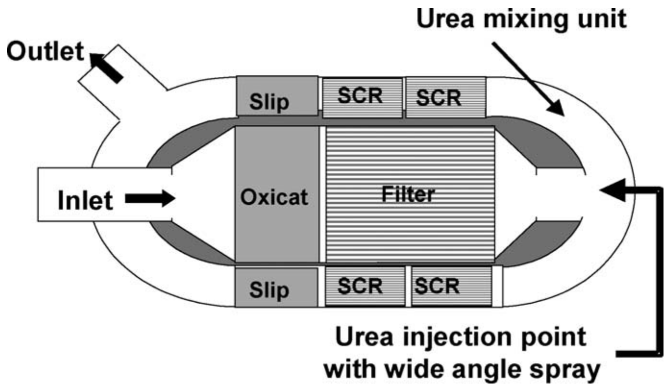


Fig. 13. A compact emissions control design for heavy duty diesel vehicles that includes oxidation catalyst, SCR ammonia NOx control, and PM filter. The first catalyst is a platinum oxidation catalyst to remove CO/HC and oxidise NO to NO_2, the final annular platinum oxidation catalyst is present to remove any adventitious ammonia that may slip from the vanadium-based SCR catalyst.

'active' approaches to cleaning PM from the filter. These increase exhaust gas temperatures at intervals to that at which the soot burns. The three different system architectures for car PM filter systems are shown schematically in Fig. 12. The first utilises a platinum oxidation catalyst in front of a filter to control HC and CO emissions, and also to oxidise NO to NO_2 for low temperature combustion of PM in the downstream filter when driving conditions are appropriate for this to take place. This catalyst is also used to burn partially combusted extra fuel injected into the engine to raise the exhaust gas temperature high enough to promote PM combustion with O_2 (usually above $\sim$550 °C). Variations of this system are already in production in Europe, where a base metal fuel additive is used to help lower the temperature required to combust PM with O_2. The second generation has an oxidation catalyst on the filter that promotes the rate of soot combustion at higher temperatures. The benefit of this over the first generation is that it removes the need for a fuel additive and a means of dispensing it periodically into the fuel tank. The presence of platinum on the filter also removes HC and CO during times when the filter is regenerating. The third generation does not have a separate oxidation catalyst, but comprises only a single catalysed filter. This has all of the necessary oxidation catalyst functionality included in it to oxidise HC and CO during normal driving. In addition, the catalyst oxidises NO to NO_2 to provide some passive PM removal when this is possible, as well as periodically oxidising extra HCs/CO to give sufficient temperature to burn PM with O_2 when it is necessary to clean the filter. This system is the most thermally efficient of the three types because there is only one substrate to heat that is close to the engine so heat losses are minimised, and the reactions on the filter surface create heat in the direct vicinity of the PM.

There are a significant number of first generation filter systems on the road in Europe. Second generation technology have began to appear, and the latest third generation technology has just been introduced into mass production. Future legislation standards are likely to demand PM emissions levels that will force the use of filters on all diesel cars. Given this progress, the diesel car will soon be ''seen'' as a much more environmentally friendly vehicle than it was previously, and oxidation catalysts have key rôles in this.

7.4. Combined diesel emissions control systems

In the future several diesel emissions control systems will be combined into a single unit to minimise space requirements, and for cost and efficiency considerations. Examples of this include oxidation functions in third generation particulate filters already mentioned in the previous section, and in the future NOx control will also be included. Already oxidation catalyst, PM filtration and ammonia SCR for NOx control on heavy duty diesels have been ingenuously combined in a single compact container [62], and this is illustrated schematically in Fig. 13. The exhaust gas first passes through a platinum oxidation catalyst that oxidises CO and HCs, as well as converting NO to NO_2 that continuously oxidises PM in the filter. The exiting NOx is then reduced to N_2 over two SCR catalysts. The ammonia here is obtained from the decomposition of urea that is sprayed into the system as an aqueous solution, and any adventitious ammonia is prevented from passing into the environment by a final oxidation catalyst that would oxidise it to NO.

8. Conclusions

Over the last three decades since the introduction of the first oxidation catalysts on cars there has been a huge reduction in HC, CO and NOx emissions from them, and many millions of tons of pollutants have not been released into the atmosphere. This significantly improved urban air quality with many associated environmental benefits. Now new emissions control systems are being developed for the more fuel efficient (lower CO_2) lean-burn engines, especially for the increasingly popular modern high-speed diesel engine. Here catalytic oxidation is used to control CO and HC emissions. Additionally, filter systems are being introduced to effectively eliminate particulate emissions, that were formerly a characteristic feature of diesel engines. Oxidation catalysts are used to produce NO_2 for low temperature soot combustion, or for oxidising high levels of HC/CO to achieve temperatures needed to burn trapped soot in a filter. Catalytic oxidation of NO to NO_2 is also important in NOx control. It is the key step in storing NOx as NO_3^- in NOx-traps and obtaining an appropriate NO/NO_2 ratio is important in optimising the performance of NH_3 SCR. All of these improvements in controlling automotive exhaust emissions depends on catalysis, and catalytic oxidation has key rôles.

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