Automobile exhaust catalysts
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Abstract
It has now been over 25 years since the introduction of the catalytic converter to reduce emissions from the internal combustion engine. It is considered one of the greatest environmental successes of the 20th century, however, new emission control technologies are still being developed to meet ever more stringent mobile source (gasoline and diesel) emissions. This short review will discuss the basis for improvements and highlight technology area, which will require further improvements in emissions and fuel economy. Some of the issues related to fuel cells which some believe may replace the internal combustion engines for automobile applications is also briefly discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic converters; Gasoline; Diesel; Lean-burn engines; Lean-NOx; Fuel cells

1. Introduction
Since the original clean air act of the 1970s, substantial improvements have been made in reducing the engine out and the tailpipe emissions through the application of catalyst technologies. The main driver for the future emission regulations will be the more stringent regulations imposed by the California Air Resources Board (CARB) moving towards a zero emission vehicle (ZEV). As of 2000, the regulations are as follows:

<table>
<thead>
<tr>
<th>Category</th>
<th>Durability basis (miles)</th>
<th>NMOG (g/mile)</th>
<th>NOx (g/mile)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLEV</td>
<td>50000</td>
<td>0.125</td>
<td>3.4 0.4</td>
</tr>
<tr>
<td></td>
<td>120000</td>
<td>0.156</td>
<td>4.2 0.6</td>
</tr>
<tr>
<td>LEV</td>
<td>50000</td>
<td>0.075</td>
<td>3.4 0.05</td>
</tr>
<tr>
<td></td>
<td>120000</td>
<td>0.09</td>
<td>4.2 0.07</td>
</tr>
<tr>
<td>ULEV</td>
<td>50000</td>
<td>0.04</td>
<td>1.7 0.05</td>
</tr>
<tr>
<td></td>
<td>120000</td>
<td>0.055</td>
<td>2.1 0.07</td>
</tr>
<tr>
<td>SULEV</td>
<td>120000</td>
<td>0.010</td>
<td>1.0 0.02</td>
</tr>
</tbody>
</table>

LEV is the abbreviation for low emission vehicle, while the T is transitional, U is ultra and S is super. The NMOG is non-methane organics.

The year 2000 will see over 500 million passenger cars in use worldwide with an annual worldwide production of new cars approaching 60 million. In addition, there are about 40% more passenger vehicles represented by trucks. The majority of these vehicles (automobiles and trucks) use a spark ignited gasoline engine to provide power and this has become the most frequent form of transportation. Gasoline blend still remains a mixture of paraffins and aromatic hydrocarbons which combust in air at a very high efficiency. The simplified reaction (1) is

\[
gasoline + O_2 (in \text{air}) \rightarrow CO_2 + H_2O + \text{heat} \quad (1)
\]

Due to incomplete combustion in the engine, there are a number of incomplete combustion products. Typical exhaust gas composition at the normal engine operating conditions is

- carbon monoxide (CO, 0.5 vol.%);
- unburned hydrocarbons (HC, 350 vppm);
- nitrogen oxides (NOx, 900 vppm).
HC, CO and NO\textsubscript{x} are the major exhaust pollutants. HC and CO occur because the combustion efficiency is \(<100\%\) due to incomplete mixing of the gases and the wall quenching effects of the colder cylinder walls. The NO\textsubscript{x} is formed during the very high temperatures (>1500 °C) of the combustion process resulting in thermal fixation of the nitrogen in the air which forms NO\textsubscript{x} [1].

Because of the large vehicle population, significant amounts of HC, CO and NO\textsubscript{x} are emitted to the atmosphere. The formation of ground level ozone occurs as a result of a chemical reaction between HC and NO\textsubscript{x} and sunlight. When stagnant air masses linger over urban areas, the pollutants are held in place for long periods of time. Sunlight interacts with these pollutants, transforming them into ground level ozone. Ozone is a major component of smog. Of course, CO is a direct poison to humans. The benefits of catalytic controls have been documented and it is now estimated that by the year 2000, over 800 million tons of combined pollutants of HC, CO and NO\textsubscript{x} will have been abated using auto exhaust catalyst and prevented from entering the atmosphere [2].

2. Historical development of three way catalysts

The basic reactions for CO and HC in the exhaust are oxidation with the desired product being CO\textsubscript{2}, while the NO\textsubscript{x} reaction is a reduction with the desired product being N\textsubscript{2} and H\textsubscript{2}O. A catalyst promotes these reactions at lower temperatures than a thermal process giving the following desired reactions for HC (2), CO (3, 4) and NO\textsubscript{x} (5–7):

\[
\text{oxidation:} \quad C_y H_n + \left(1 + \frac{n}{4}\right)O_2 \rightarrow yCO_2 + \frac{n}{2}H_2O \quad (2)
\]

\[
\text{CO} + \frac{1}{2}O_2 \rightarrow CO_2 \quad (3)
\]

\[
\text{CO} + H_2O \rightarrow CO_2 + H_2 \quad (4)
\]

\[
\text{reduction:} \quad \text{NO (or NO}_2\text{)} + CO \rightarrow \frac{1}{2}N_2 + CO_2 \quad (5)
\]

\[
\begin{align*}
\text{NO (or NO}_2\text{)} + H_2 & \rightarrow \frac{1}{2}N_2 + H_2O \\
\left(2 + \frac{n}{4}\right)\text{NO (or NO}_2\text{)} + C_y H_n & \rightarrow \left(1 + \frac{n}{2}\right)N_2 + yCO_2 + \frac{n}{2}H_2O \quad (6)
\end{align*}
\]

All the above reactions required some heat or temperature on the catalyst surface for the reaction to occur. When the automobile first starts, both the engine and catalyst are cold. After startup, the heat of combustion is transferred from the engine and the exhaust piping begins to heat up. Finally, a temperature is reached within the catalyst that initiates the catalytic reactions. This lightoff temperature and the concurrent reaction rate is kinetically controlled; i.e. depends on the chemistry of the catalyst since the transport reactions are fast. Typically, the CO reaction begins first followed by the HC and NO\textsubscript{x} reaction. When all three reactions are occurring, the term three-way catalyst or TWC is used. Upon further heating, the chemical reaction rates become fast and the overall conversions are controlled by pore diffusion and/or bulk mass transfer. Fig. 1 shows a typical response of a TWC catalyst as a function of the engine air to fuel ratio.

The dominant catalyst support for the auto exhaust catalyst is a monolith or honeycomb structure. For some early history on the use of bead catalyst see [3]. The monolith can be thought of as a series of parallel tubes with a cell density ranging from 300 to 1200 cpsi. Advances in monolith technology, catalyst-mounting methods, flexibility in reactor design, low pressure drop and high heat and mass transfer rates, are the main reasons the monolithic support dominates the entire market as the preferred catalyst support. Ceramic materials were chosen for the initial monolith and they still dominate the market. The preferred material is called cordierite (synthetic cordierite has a composition approximating 2MgO, 5SiO\textsubscript{2} and 2Al\textsubscript{2}O\textsubscript{3} and a softening point >1300 °C) [4]. In preparing the catalyst, this desirable property has to be matched by the thermal expansion properties of the catalyst carrier or washcoat to prevent a mismatch in thermal properties. Fig. 2 shows the surface coating on a modern TWC.

Today, cordierite monoliths of 400 cpsi and 0.004 in. wall thickness and 600 cpsi and 0.004 in. wall thickness are available [4]. Monoliths of 900 and 1200 cpsi
have been made and tested in road-simulated aging and offer benefits for the super ultra low level vehicle (SULEV) type vehicles.

Recently, metallic monolith structures are being used in certain niche markets for exhaust control because they can be made with thinner walls and have open frontal areas close to 90%, allowing lower pressure drop. Cell densities >400 cpsi can be used which permits smaller catalyst volumes and smaller converters. The base material of construction is a ferritic stainless steel alloy having iron/chrome/aluminum/rare earths. Typical monoliths have 400 and 600 cpsi with 0.002 in. wall thickness.

By the year 2000, approximately 30 years of catalyst technology development have been devoted to the automotive exhaust catalyst. Fig. 3 shows a
typical auto catalyst design. These technology advances have been driven by the quest for a ZEV using the spark-ignited engine as the powertrain. Along with the advances in catalyst technology, the automotive engineers were developing new engine platforms and new sensor and control technology. This has resulted in the full integration of the catalyst into the emission control system. The catalyst has become integral in the design strategy for vehicle operation. During this time period the auto catalyst has progressed through the following development phases.

These approaches coupled with the new engine control technologies will meet the majority of emission regulations in the new millennium. This article will address the technology for the ULEV and SULEV applications. Additional background information on the other technology developments from 1970 to 1995 can be found in [3].

3. Low emission control technologies

In order to accomplish the low emissions formulated by CARB for ULEV and SULEV vehicles, a number of approaches have been investigated in the 1990s. The emphasis of the new regulations was the reduction of HCs in the exhaust. A majority of hydrocarbon emissions (60–80% of the total emitted) are produced in the cold start portion of the automobile, i.e. in the first 2 min of operation. Typical composition [5] of the hydrocarbons during cold start is as follows:

<table>
<thead>
<tr>
<th>Hydrocarbon type: approximate hydrocarbon composition (%)</th>
<th>Sampling time (seconds after cold start)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample time (seconds after cold start)</td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
<td>20</td>
</tr>
<tr>
<td>Olefins</td>
<td>45</td>
</tr>
<tr>
<td>Aromatics, C_4, C_7</td>
<td>20</td>
</tr>
<tr>
<td>Aromatics, C_3</td>
<td>15</td>
</tr>
</tbody>
</table>
| The technology race to develop suitable methods to control cold start HC's included both catalytic and some unique system approaches:

1. close-coupled catalyst;
2. electrically heated catalyzed metal monolith;
3. hydrocarbon trap;
4. chemically heated catalyst;
5. exhaust gas ignition;
6. pre-heat burners;
7. cold start spark retard or post manifold combustion;
8. variable valve combustion chamber;
9. double walled exhaust pipe;

All of these approaches contain underfloor catalysts of various compositions. It has become clear that with the development of high temperature close-coupled that this is the leading technology for most LEV, ULEV and SULEV applications. A brief description of each of the various candidate technologies follow along with details of the close-coupled catalyst development.
3.1. Close-coupled catalyst

The concept of using a catalyst near the engine manifold or in the vicinity of the vehicle firewall to reduce the heat-up time has been practiced [6–8]. However, these were relatively low temperatures and in any case, the maximum temperature was severely limited by the use of “overfueling” or “acceleration enrichment” to control the temperature [9]. The practice of “overfueling” or “acceleration enrichment” results in high HC and CO emissions and has come under pressure to be reduced or eliminated. Reducing this protection combined with an increase in the higher speed driving habits of the US and the existing autobahn driving habits increases the engine manifold discharge temperatures to around 1050 °C especially for the four and six cylinder engines, thus, changing the operating envelope of the close-coupled catalyst. In fact a technology assessment published by CARB in 1994 showed the projected technologies for achieving the low emissions and close-coupled catalyst was not a viable option [10]. The dominant technology was the electrically heated catalyst.

Catalyst manufacturers were once again exploring new carriers capable of retaining high surface areas and metal combinations that resist deactivation due to sintering after high temperature exposure. A shift in the technology for close-coupled catalyst occurred when a close-coupled catalyst capable of sustained performance after 1050 °C aging was developed and shown to give LEV and ULEV performance in combination with an underfloor catalyst [11]. The close-coupled catalyst was designed mainly for HC removal while the underfloor catalyst removed the remaining CO and NOx. The concept inherent in this technology was to have lower CO oxidation activity for the close-coupled catalyst, thus, eliminating severe overtemperatures where high CO concentrations occur in the rich transient driving cycle. Subsequent studies on a 1.9l, four cylinder showed that a cascade designed close-coupled catalyst could meet ULEV regulations as shown in Fig. 4 [12]. This shift in technology was significant enough such that when CARB conducted another survey for projected technologies in 1996 for achieving the low emissions, the close-coupled catalyst dominated the technologies,
basically eliminating the electrically heated catalyst [13].

With this benchmark set, other catalyst manufacturers worked on catalyst technologies capable of sustained operation and good HC lightoff after exposure to 1050 °C [14–17]. The characteristic of these close-coupled technologies is that Ce is removed. The Ce is an excellent CO oxidation catalyst and also stores oxygen, which then can react with CO during the rich transient driving excursions. If the oxygen is stored on the catalyst during severe rich excursions (such as fuel enrichment or heavy accelerations), then the CO can react at the catalyst causing a localized exotherm. As a rule, every percent of CO oxidized gives 90 °C rise in temperature. This can cause severe sintering of the catalyst surface reducing the activity.

3.2. Hydrocarbon trap

Another approach investigated was the hydrocarbon adsorption trap in which the cold HC’s are adsorbed and retained, on an adsorbent, until the catalyst reaches the lightoff temperature. Hydrocarbon trap materials considered to date have been mainly various type zeolites (silicalite, mordenite, Y-type, ZSM-5 and beta zeolite) with some studies on carbon-based material. Studies have been conducted to quantify the hydrocarbon species during the vehicle driving cycle [18,19].

For an in line hydrocarbon trap system to work, the hydrocarbons must be eluted from the trap at the exact time the underfloor catalyst reaches a reaction temperature >250 °C as shown in Fig. 5. These HC’s are then desorbed and oxidized in the normal TWC.
catalyst. No hydrocarbon trap materials have been found capable of retaining HC’s at this temperature. Consequently, hydrocarbons pass through the underfloor catalyst unreacted and out the tailpipe.

However, some unique system designs have been proposed. A crossflow heat exchanger designed trap system demonstrated a 70% reduction in the non-methane cold start hydrocarbons during FTP cycle #1 [20,21]. Another trap design utilizes a cylinder with a central hole to allow passage of exhaust gas [22]. This design contains a lightoff catalyst, the trap and a downstream catalyst. Air is injected in the hole during cold start to divert the majority of flow to the trap in the cylinder annulus. The small amount bypassed through the hole pre-heats the downstream catalyst. When the lightoff catalyst is functional and the downstream catalyst heats up to temperature, the air is turned off and the trap desorbs the HC’s. These trap designs are still under evaluation [23–26]. There will be commercial niche markets for trap systems used in combination with close-coupled catalyst or electrically heated catalysts.

3.3. Electrically heated catalyst (EHC)

Another approach to overcoming the cold temperatures during startup is to provide heat to the exhaust gas or the catalytic surface using resistive materials and a current/voltage source. Studies began prior to 1990 to develop an electrically heated monolith capable of providing in situ heat to the cold exhaust gas. If the electrically heated monolith is also catalyzed (an electrically heated catalyst, EHC), then the pre-heat is directly applied to the catalyst surface. The EHC is placed in front of a small lightoff catalyst, which receives the pre-heated gas and, thus, provides a very efficient reaction during the cold start period. Fig. 6 shows the cold start performance of an EHC. An underfloor catalyst being much larger in volume supplies the reaction efficiency during the rest of the driving cycle after the cold start. Electrically heated monolithic catalysts are made two ways [27–31]. One approach is to make a metal foil with the foils arranged to form an electrically resistive element. The catalytic washcoat is deposited on the metal. The element is attached to electrical connection points and can be heated quickly to the lightoff temperature of the catalyst. Another approach is to make a monolith from extruded sintered metal and then deposit the catalytic washcoat. The base material in both cases is ferritic steel with varying amounts of Cr/Al/Fe with additives of rare earths. Substantial advances have been made in reducing the power requirements for EHC’s and recent studies have shown the extra battery can be eliminated and the EHC can be powered off the vehicle alternator [32]. Electrically heated catalysis having low mileage have been shown to achieve ULEV, however, the durability to 100,000 miles is still an open issue [30]. Actual in use experience is being gained on larger vehicles and these studies will give the needed “on the road” experience with EHC’s [33].
3.4. Non-catalytic approaches

Three system design approaches have been proposed and studied in combination with catalysts to reduce the cold start emissions. The pre-heat burner uses the gasoline fuel in a small burner placed in front of the catalyst. The burner is turned on during cold start and the heat generated warms up the catalyst so the catalyst is hot when the cold exhaust from the manifold reaches the catalyst [34].

The exhaust gas igniter involves placing an ignition source (e.g., glow plug) in between two catalysts. During cold start, the engine is run rich and a small amount of air is injected to make the mixture flammable. This is then ignited and heats the catalyst [35].

The chemically heated catalyst uses highly reactive species, usually H₂, which is generated in a device onboard the vehicle. Since this reacts at room temperature over the catalyst, the heat of reaction warms up the catalyst to react during cold start [36].

Engine modifications | Exhaust modifications
---|---
VTEC L-4 with VVT | Low heat capacity manifold
ECU 32 bit microprocessor | UEGO sensor
Air assist fuel injectors lean air/fuel cold start | Low heat capacity exhaust pipe
Precise A/F control STR individual cylinder A/F control | Underfloor catalyst with Pd only front on 600 cpsi
Electric controlled EGR valve | Secondary HEGO sensor

These system approaches rapidly heat the catalyst during cold starts resulting in low emission operation, however, little is known of the system durability and they are complex and expensive [37].

4. Zero emission spark ignited vehicle

This section could be entitled “putting it all together” or the “complete engineered system”. For the past 5 years the working cooperation between the automobile manufacturers, the monolith suppliers, the exhaust system fabricators, the sensor manufacturers and the catalyst manufacturers has intensified so that a complete engineered system approach has been taken to achieve the goal of a “zero emission SI vehicle”. With the advent of a durable close-coupled catalyst, many of the engine modifications to provide rapid heat-up (e.g., spark retard on cold start) of the catalyst were now possible. The ULEV performance requirement for a four-cylinder vehicle, which may range from a hydrocarbon engine out emissions of 1.5–2.0 g/mile, is around 98% hydrocarbon conversion. Of course a ULEV vehicle is >99% hydrocarbon conversion. Because of these high emission reduction efficiencies, monolith suppliers began to make higher cell density substrates approaching 1200 cpsi [38,39].

In addition, the exhaust piping was redesigned to minimize heat loss during the critical cold start with fabrication of low heat capacity piping [40]. Finally, demonstration of these ultra low emission systems became a reality [41–44]. LEV vehicles became common and ULEV vehicles were supplied to the California market in 1998. In 1999, a zero level emission vehicle (ZLEV) vehicle was demonstrated after 100,000 mile aging [43]. The following table represent the main characteristics for the Honda ULEV vehicle.

The key features in regard to catalyst performance are the use of an engine designed lean cold start and fuel management to supply oxygen for the catalytic oxidations and the reduction of heat loss during cold start. The new sensor for control is a UEGO sensor, which is a universal exhaust gas sensor that has a different response than the heated oxygen sensor or HEGO. So with the UEGO sensor the actual air/fuel ratio in the exhaust is known directly. The first underfloor catalyst is a 600 cpsi Pd catalyst for high temperature operation and the remaining underfloor catalyst takes care of emissions during normal operation. After 100,000 mile on a vehicle, the emissions measured were: NMOG (0.03 g/mile); CO (0.35 g/mile); NOₓ (0.12 g/mile).

The Honda ZLEV vehicle is based on the same VTEC platform with additional controls for cold start for hydrocarbons and air/fuel control for NOₓ.
characteristics are summarized below:

**Engine modifications**
- VTEC L-4 with VVT
- ECU 32 bit microprocessor
- Improved atomization fuel injectors
- Precise A/F control STR
- Individual cylinder A/F control
- Ir and Pt spark plugs
- Lean air/fuel cold start with spark retard
- Electric controlled EGR valve
- Catalyst condition predicted control

**Exhaust modifications**
- Low heat capacity manifold
- UEGO sensor
- Low heat capacity exhaust pipe
- Pd close-coupled catalyst on 1200 cpsi
- Underfloor catalysts TWC and HC trap hybrid catalyst
- Two secondary HEGO sensor

The engine utilizes spark retard during cold start to aid in catalyst heat-up and light-off. Also, the Pd close-coupled catalyst is 1200 cpsi followed by an underfloor catalyst system having a separate TWC and an underfloor catalyst hybrid to manage the hydrocarbons during the first 10 s during cold start. After 100,000 mile on a vehicle, the emissions measured were: NMOG (<0.004 g/mile); CO (<0.17 g/mile); NOx (<0.02 g/mile).

The vehicle demonstrated <0.0055 g/mile emissions after 100,000 mile simulation aging [43]. Nissan has also demonstrated and now offers for sale the world’s first certified partial ZEV [44]. This vehicle not only meets the SULEV tailpipe emissions, but also has a zero evaporative emissions system. The engine emission control technology consists of a close-coupled catalysts followed by a series of trap catalyst combinations to further reduce cold start emissions. The Nissan Sentra, CA vehicle has shown 150,000 mile durability and meets requirements for OBD of the catalysts system. This vehicle is also equipped with a PremAir® catalyst coated radiator, which removes ambient ozone [45] (see Section 9). This catalytic device can be used to offset hydrocarbon tailpipe emissions.

5. NOx traps for direct injected gasoline engines

The TWC/TRAP appears to be the most promising solution for NOx reduction for gasoline direct injected lean-burn engines. The TWC catalyst is not effective in reducing NOx when the engine is operated lean of the stoichiometric air to fuel ratio (λ > 1). An alkaline metal oxide trap adsorbs the NOx in the lean mode during the lean-burn operation [45,46]. During steady-state driving the engine operates lean for improved fuel economy up to 15–20% relative to continuous stoichiometric operation. The NO must first be converted to NO2 over the Pt (8) in the lean operation of the catalyst.

\[
\text{NO} + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Pt}} \text{NO}_2 \quad (8)
\]

At temperatures above about 500°C NO2 is not thermodynamically favored, however, because the trap continuously removes the NO2 from the gas stream the equilibrium is shifted towards more NO2.

The NO2 is trapped and stored on an alkaline metal oxide (9) such as BaO or K2CO3, which is incorporated within the precious metal containing washcoat of the three-way catalyst.

\[
\text{NO}_2 + \text{BaO} \rightarrow \text{BaO} - \text{NO}_2 \quad (9)
\]

Sulfur oxides derived from the fuel form alkali compounds (11) more stable than the nitrates and are not removed during the rich excursion. Therefore, the trap
progressively becomes less effective for NO$_2$ adsorption due to poisoning by the SO$x$ [47,48]

$$\text{BaO + SO}_x \rightarrow \text{BaO–SO}_x$$  \hspace{1cm} (11)

$$\text{BaO–SO}_x + \text{H}_2 \rightarrow \text{no reaction.}$$  \hspace{1cm} (12)

Complicated engine control strategies are being developed to desulfate (12), the poisoned trap by operating the engine at a high temperature (>650 °C) and rich of the stoichiometric air to fuel ratio for a short time to remove the adsorbed sulfur oxides [49,50]. The air to fuel ratio must be controlled to prevent H$_2$S from forming at excessive rich conditions. Conditions slightly rich of stoichiometric result in formation of more acceptable SO$_2$ emissions. Reductions in NO$_x$ up to 90% are possible provided the gasoline has <10 ppm sulfur. Therefore, reduction in sulfur content of the fuel is essential to make such a system practical.

Another problem to be solved is the thermal deactivation of the catalyst due to negative washcoat, precious metal and ceramic monolith interactions with the alkaline metal oxide trap component after high temperature excursions.

6. Catalysts for diesel emissions

The sale of diesel vehicles is expected to increase dramatically due to economy of operation and decrease in emission of greenhouse gases, most notably CO$_2$. Diesel fuel is injected into a highly compressed charge of air where the temperature is sufficiently high that combustion occurs. Thus, unlike the spark-ignited engine the diesel is a compression-ignited process. Its lean nature results in a cooler combustion with less NO$_x$ formation [51]. The liberal design of the combustion process does, however, result in larger quantities of unburned fuel, lubricating oil emissions and dry soot. Diesel emissions represent all three phases of matter:

1. **solid**: dry carbon or soot;
2. **liquid**: unburned fuel, lubricating oil (collectively SOF) and liquid sulfates primarily, sulfuric acid (H$_2$O associated with the SO$_3$ is included as a component of the liquid particulate);
3. **gas**: carbon monoxide (CO), hydrocarbons (HC) derived primarily from partially burned fuel, oxides of nitrogen and sulfur.

The role of the catalyst was to reduce the SOF, and gaseous CO and HC emissions, but specifically selective to minimize the oxidation of SO$_2$ to SO$_3$ (H$_2$SO$_4$).

The incorporation of a diesel oxidation catalyst into the exhaust of heavy-duty trucks required sophisticated combustion engineering and catalysis [52]. Engine manufacturers have made great progress in redesigning the combustion process to minimize dry carbon emissions. Through the use of sophisticated flow models [53], the use of a ceramic flow through
monolith without clogging the channels a monolith with parallel channels can be used. The catalytic reactions are

\[ \text{SOF} + O_2 \rightarrow CO_2 + H_2O \quad (13) \]
\[ \text{HC} + O_2 \rightarrow CO_2 + H_2O \quad (14) \]
\[ \text{CO} + O_2 \rightarrow CO_2 \quad (15) \]

Reaction (13) is the oxidation of the soluble organic fraction (SOF: unburned fuel and lubricating oil) portion of the particulate. This coupled with reductions in dry carbon or soot result in compliance with particulate emission standards.

Reactions (14) and (15) are typical of the gasoline vehicle in that the HC and CO are oxidized. The reduction of the gas phase HC positively impacts smog generating photochemical reactions and also decreases odor bearing compound concentrations.

Reaction (16) gives rise to an increase in liquid particulate in the form of sulfuric acid and counters the benefit obtained from the reduction in SOF. This becomes a critical problem in catalyst selectivity: the catalyst must perform only the desirable reactions (14 and 15).

\[ \text{SO}_2 + O_2 \rightarrow \text{SO}_3 \quad (16) \]

6.1. Commercial diesel oxidation catalysts

Diesel engines operate lean and therefore are much cooler than modern stoichiometric operated gasoline engines and, thus, even if the SOF emanating from the diesel engine are gaseous or aerosols, such as in conditions of idle or low power output, they are quickly cooled and condense. The catalyst would, therefore, have to function at much lower temperatures than in the gasoline counterpart and would be required to treat liquids as well as gases. For those low temperature conditions the high surface area washcoat would have to act as a sponge for the liquids and effectively store them until the exhaust temperature increased sufficiently to initiate catalytic combustion. Fortunately, the larger hydrocarbon molecules that make up the SOF, i.e. >C16, are more easily oxidized, with the proper catalyst, at lower temperatures than the lower molecular weight hydrocarbons present as gases. Thus, storage at low temperatures would be followed by catalytic oxidation when the temperatures exceeded about 200–250 °C (see 13). The design of the catalyst had to include hydrocarbon adsorption and storage with an organo-phlic surface and the proper pore size to promote condensation.

The catalyst also must have high selectivity towards the oxidation of gaseous HC and CO (14, 15) while not oxidizing the SO2 as in (16). This was quite challenging because catalysts with high activity for oxidizing the SOF would likely be good catalysts for the SO2 to SO3 reaction. Thus, a highly selective catalyst was required. Catalytic metals such as Pt and Pd were considered early because they have good low temperature activity for hydrocarbon conversion. However, they are also very active for the SO2 oxidation reaction. The most successful approach in North America was a monolithic catalyst composed of high surface area bulk CeO2 in combination with γ-Al2O3, which gives high conversions of SOF with some conversion of gaseous hydrocarbons and carbon monoxide, but with little formation of SO3 [54]. Diesel oxidation catalysts are now commonly used for medium to heavy duty trucks in the US [52], Japan [55] and Europe [56].

For a cooler running passenger car a higher metal loaded catalyst (10–40 g Pt/ft3) is preferred since little sulfate will form with all the benefits of good particulate, HC (odor) and CO reduction. The difficulty of cold start hydrocarbon emissions was solved by the addition of a specialized zeolite, which adsorbs and traps gas phase hydrocarbons. They are released at about 250 °C, which is above the lightoff temperature for the Pt component [57,58], which then converts them. Typical sizes are 3 in. × 5 in. oval (racetracks) 3–6 in. long. Cell densities vary from 200 to 400 cells per square inch (CPSI) depending on the nature and pressure drop requirements of the engine.

The unburned oils and their additives deposit within the catalyst structure under the cooler modes of operation. Unlike the organic portion of the oil the additives remain after the oil is catalytically oxidized. Thus, compounds of zinc, phosphorous and calcium accumulate (2–3%) on or within the catalyst [59] and represent the most significant cause for long term deactivation. Thus, the washcoat must be designed to be chemically inert to these types of poisons. Furthermore, the washcoat pore structure must be designed to tolerate large amounts of these metal oxides so
as to prevent pore blockage and the subsequent pore diffusion limitations that result. Field data indicates as little as 3–8% deactivation of the particulate removal function [52,56] up to almost 200,000 miles of operation for medium to heavy duty trucks weighing 19,500–33,000 lb. Deactivation of 13% for CO and 21% HC is not unexpected given the low Pt contents and the severity of the accumulation of inorganic ash. Clerc [52] has shown that the phosphorous content plays the largest role in deactivating gas phase activity.

6.2. Diesel particulate traps and fuel additives

One of the earliest attempts to treat diesel particulate emissions was the ceramic wall flow (cordierite) filter with each channel alternately plugged at each end to force flow through the highly porous wall which filters the particulate matter. Although this approach is still considered a possibility [51] with and without a catalyst [60,61] problems with reliable regeneration at modest exhaust temperatures and/or runaway temperatures during regeneration leading to substrate melting has plagued this technology. There are, however, a limited number of systems installed on trucks, buses and mining equipment giving up to 90% reduction in particulate with excellent durability [47,62].

The addition of metallo-organic fuel additives to the diesel fuel utilizes the same wall flow filter, but provides more reliable regeneration of the particulate matter accumulated. Copper, iron or cerium containing fuel additives can catalytically reduce the temperature for particulate burn off to considerably lower temperatures than the 600°C needed for thermal regeneration. For example, copper can initiate oxidation of the particulate at 250°C allowing for more frequent regeneration with less chance of particulate build up. The cerium metallo-organic fuel bound additive [51,63] coupled with exhaust gas recirculation (EGR) claims to simultaneously decrease particulate and NOx. Peugeot-Citroen plans to introduce diesel cars equipped with a system using cerium-based fuel additives which will decrease the temperature at which the particulate collected on the wall flow filter will regenerate [64]. Such systems are in an advanced state of testing, but still not commercially available at the time of this writing.

7. Natural gas engines

There is a growing use of lean-burn natural gas fueled vehicles currently in use primarily for service operations such as delivery trucks, buses, etc. Natural gas is used as a replacement for diesel fuel to more easily meet emission standards [65] especially for urban bus applications. These vehicles still need catalysts to control particulate emissions, primarily derived from lubricating oil, and specific gaseous hydrocarbon emissions, called reactive organic gases (ROGs) which participate with NOx and sunlight in the generation of smog. Catalysts for lean-burn engines are typically Pd and/or Pt supported on CeO2+γ-Al2O3 deposited on a ceramic monolith. The diameter can be as large as 10 in. with a length of 7 in. for an engine with a 10 l displacement. Methane is the major hydrocarbon in natural gas. It is non-reactive and does not participate in photochemical smog generating reactions and so in the US is unregulated. If it were to be required (CH4 is a greenhouse gas) a major breakthrough in catalyst technology would be needed [66,67] to pass the US FTP-test due to inhibition by sulfur oxides. For the European bus market a catalyst is successful for abating methane emissions because the R-49/13 test favors high temperature modes where the deactivation by oil has a minimum effect on the performance of the Pd catalyst.

8. Lean-burn engines (direct injected gasoline or diesel)

8.1. Full lean-NOx

More lean-burn fuel-efficient engines can accomplish decreased emissions of CO2 (greenhouse gas). For example European automobile companies such as Volkswagen have a goal of generating no more than 140 g/km of CO2 by 2008 [68]. Hence, the lean-burn diesel and direct injected gasoline engines are logical solutions since fuel economies of >20% can be realized. The problem is traditional TWC or diesel oxidation catalysts can not selectively reduce NOx in the presence of excess oxygen. Future emission standards will require significant reductions in NOx (NO and NO2) for which an ideal solution is a catalyst...
capable of decomposing it according to (17)

\[ \text{NO} \rightarrow \text{N}_2 + \text{O}_2 \] (17)

No such catalyst exists today so an alternative approach is to catalytically reduce \( \text{NO}_x \) selectively using hydrocarbons (18) derived from on-board fuel

\[ \text{HC} + \text{NO}_x + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 \] (18)

\[ \text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \] (19)

The undesirable reaction (19) consumes the hydrocarbon by reaction with the \( \text{O}_2 \) present in the exhaust. This reaction is dominant as the temperature is increased resulting in a decrease in conversion of the \( \text{NO}_x \).

To date the only two candidate materials are Pt supported on an Al\(_2\)O\(_3\) or a zeolite and Cu/ZSM-5 where the ZSM-5 is a pentasil zeolite with a Si/Al ratio of about 20 and pore size openings of about 5.5 Å. Literally 1000's of materials have been investigated, but none better have yet been found [69,70].

Given the lack of success with hydrocarbon lean-\( \text{NO}_x \) engine manufacturers are considering the use of selective catalytic reduction (SCR) with \( \text{NH}_3 \) as the reductant for \( \text{NO}_x \) for heavy duty trucks (3).

Urea is convenient for on board use as a liquid carrier for ammonia [62]. It hydrolyzes in the exhaust system according to reaction (20)

\[ \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2 \] (20)

The \( \text{NH}_3 \) then acts as a catalytically selective reductant for the \( \text{NO}_x \) (21) giving conversions ranging between 80 and 90%.

\[ \text{NH}_3 + \text{NO}_x + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \] (21)

For heavy-duty diesel applications, temperatures vary outside of the range of any one catalyst so it is necessary for a staged catalytic system for optimum reduction efficiency [3]. For an exhaust temperature between 200–300 °C \( \text{V}_2\text{O}_5 \) is preferred while above this temperature range a metal exchanged zeolite catalyst is required. At low temperatures (\(<200^\circ\text{C}\) the NO\(_x\) reduction with ammonia is desired (22) over the undesirable oxidation of ammonia to either N\(_2\) reaction (23) or NO reaction (24).

\[ 4\text{NH}_3 + 3\text{O}_2 \rightarrow \text{N}_2 + 6\text{H}_2\text{O} \] (23)

\[ 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \] (22)

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \] (24)

The lack of a refueling infrastructure, possible higher \( \text{N}_2\text{O} \) emissions, the need for on board diagnostics to control injection and ammonia slip are major issues that are being addressed.

9. Alternative catalytic technologies for automobile emissions

9.1. PremAir\textsuperscript{®} technology

Traditional approaches to pollution control have been to develop benign non-polluting processes or to abate emissions at the tailpipe or stack before emitting to the atmosphere. A new technology called PremAir\textsuperscript{®} catalyst systems takes a different approach and directly reduces ambient ground level ozone to oxygen through the following reaction (25)

\[ 2\text{O}_3 \rightarrow 3\text{O}_2 \] (25)

This technology can be applied to both mobile and stationary applications. For automotive applications, the new system involves depositing a catalytic coating on the car’s radiator or air conditioner condenser. Air passes over the radiator or condenser at a minimum of 70 °C and the catalyst converts the ozone [71–74].

This technology has been explored on a number of vehicles and radiator configurations and studies out of 100,000 vehicle miles have been completed on a number of base metal oxide technologies [74]. Both Volvo and Nissan have begun to implement this technology on their low emission vehicles [45,74]. Comparing the results of the PremAir\textsuperscript{®} strategy with the results of the VOC reduction strategy, it is possible to calculate on a “per vehicle” basis the VOC reduction that would have been needed to achieve the same ozone benefit as was achieved by the PremAir\textsuperscript{®} catalyst. In addition, this “equivalent VOC” reduction (expressed in g/mile) can be based on the relative effects of the PremAir\textsuperscript{®} catalyst on the 1 h peak ozone level or the 8 h peak ozone level. The effects on the 8 h peak ozone level are considered particularly informative since EPA promulgated the new 8 h ozone standard in 1997. The results for the southern California region show that the
ozone benefit from the PremAir® catalyst would be equivalent to what would be achieved by a VOC reduction from 0.01 to about 0.02 g/mile. This reduction is equivalent to the SULEV regulations and makes this technology a useful method to help achieve SULEV and lower emission requirements.

9.2. The fuel cell

Fuel cells hold promise as an alternative to combustion for power generation for stationary and/or mobile source applications in the near future. They are about twice as fuel efficient as the internal combustion engine and effectively produce no CO, HC or NO\textsubscript{x}. They operate on the basic principal of direct conversion of chemical energy into electrical energy, avoiding the mechanical steps and thermodynamic limitations of traditional combustion energy cycles. Hydrogen gas is electrocatalytically oxidized to hydrogen ions at the anode which pass through an electrolyte [75] to the cathode where they combine with electrocatalytically reduced O\textsubscript{2} (from the air) producing H\textsubscript{2}O. The electrons flow through the external circuit and do work.

The proton exchange membrane (PEM) fuel cell, which operates with H\textsubscript{2} as the anode fuel at about 80\textdegree{}C, is the most promising of all the fuel cell systems [76,77] for both stationary and vehicular applications. The proton selective membrane is a fluoro-carbon polymer of sulfonic acid. The anode and cathode are Pt containing electrocatalysts deposited on electrically conductive carbon carriers, which are deposited on the membrane. Hydrogen and air are distributed to the anode and cathode, respectively, through carefully machined conductive plates making a membrane electrode assembly. The cells are stacked in series to increase the voltage output. In a 50 kW fuel cell for a vehicle there will hundreds of cells comprising the “stack”.

Research will continue to focus on greater reductions of the precious metals in the electrocatalysts. A target is <0.025 mg/cm\textsuperscript{2} of Pt. Current Pt contents are about five times the target. The addition of other promoters such as Ru is used to reduce the tolerance to CO poisoning [78].

At the present time H\textsubscript{2} is the only fuel that can be electrocatalytically oxidized at the anode. There is considerable research in the direct electrochemical conversion of methanol, but success is not imminent. Although storage on-board would be a preferred method for providing the H\textsubscript{2} for the fuel cell the technology still requires significant breakthroughs in technology. In contrast to gasoline or natural gas, there is no infrastructure for obtaining hydrogen at the local gas station or in the home. The approach being taken by automobile companies is to reform liquid fuels such as gasoline to H\textsubscript{2} on board [79]. Consequently, there is considerable research in the development of cost effective, compact fuel processors [80].

Automobile companies such as Daimler-Benz Ballard, General Motors, Ford, Toyota, Honda, and Nissan are planning to produce fuel cells powered by on board methanol to H\textsubscript{2} by 2004. Daimler Chrysler executives estimate the current fuel cell costs about US$30,000 while a cost effective system must be about US$ 3000 [81]. The US initiative called the partnership for a new generation vehicles (PNGV) is a partnership between US industry, universities, and government with the goal of developing technologies that can be used to create cost effective full size sedans capable of obtaining 80 miles/gallon of fuel. The fuel cell is the predominant technology under consideration.

References
