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Catalytic converters: state of the art and perspectives

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Abstract

This paper gives an overview of the advanced technologies currently used for abating emissions from the gasoline and diesel internal combustion engines. The challenges towards the end of the 20th century into the 21st century will also be presented. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In 1995 we celebrated the 20th year for which catalysts were widely used for the abatement of unburned hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO_x) from the internal combustion engine. At the inception the automobile manufacturers believed that catalysts would only provide a short term solution since engine technology with electronic controls was advancing at an accelerated pace. Now more than 20 years later we continue the use of advanced catalysts in conjunction with sophisticated engine management systems and onboard diagnostics. The catalyst is now at the heart of an emission control system.

The demands of a catalyst to function in the hostile environment of the automobile exhaust (and in some cases the abusive treatment of the driver) has resulted in the development of materials never before needed in catalysis [1]. We have seen the widespread use of an entirely new structure: the ceramic and metallic monolithic substrate to carry the catalytic washcoat. It allows high conversion efficiencies at high gaseous throughput, provides a high geometric surface area with lower pressure drop, excellent high temperature and thermal shock resistance and can be conveniently oriented in the exhaust train in any number of directions. The carrier material, most notably γ-Al₂O₃, has been modified by the use of oxide stabilizers, i.e. La, Si, Ba, etc., to maintain high surface areas after experiencing the varying temperatures up to 1100°C in the high H₂O content of the automobile exhaust. The dispersion of the catalytically active precious metal components has been stabilized against sintering by using rare earth metal oxides in the catalyst formulation. The zirconia based electrochemical O₂ sensor in the exhaust provides computer controlled feed back from the combustion process to maintain the engine air to fuel ratio within a narrow window for efficient three way catalysis. CeO₂, in combination with ZrO₂, plays an integral role in providing oxygen storage which broadens the conversion efficiency for all the three pollutants during the rich/lean perturbations associated with the feedback control system. Truly, the automobile catalyst has resulted in the

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development of materials durable under extreme environments previously thought impossible in conventional catalytic processes. Further improvements, however, are still required to meet ever more stringent emission standards worldwide.

The value of the automobile catalyst experience extends well beyond the gasoline vehicle. The great success of this technology has provided a strong basis of confidence in using catalysts for many other applications in the vital role of cleaning our environment. Today we routinely use catalysts for abating emissions from diesel and alternative fueled engines, i.e. natural gas, chemical manufacturing and power plants, restaurants and food processing facilities, commercial aircraft and small engines, converting toxic wastes to benign products.

This paper gives an overview of the advanced technologies currently used for abating emissions from the gasoline and diesel internal combustion engines. The challenges for the late 1900s into the 21st century will also be presented.

2. Modern three way catalysts and engine control systems

Late in the 1970s it was discovered that certain precious metal combinations, most notably Pt and Rh, could simultaneously oxidize CO and HC and reduce NO_x provided the air to fuel ratio was maintained near stoichiometric. This so-called three way catalyst (TWC) gave a conversion profile versus air to fuel ratio shown as Fig. 1. The key to advancing this new TWC technology was to control the air to fuel ratio at all times within a narrow "window" of about ± 0.05 around the stoichiometric air to fuel ratio point of about 14.6 (wt basis). This became possible by the development of the O2 or lambda sensor which is positioned immediately before the catalyst in the exhaust manifold. The sensor is composed of an electrically conductive solid electrolyte of stabilized zirconia with electrodes of high surface area Pt. One electrode is located directly in the exhaust stream and senses the O2 content relative to the concentration on the reference electrode side positioned outside of the exhaust in the natural air. The electrode is a catalyst that converts the HC and CO at its surface when excess O₂ is present. If the exhaust is hydrocarbon-rich, the

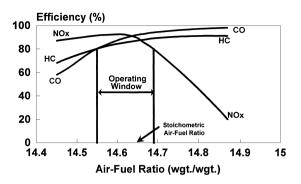


Fig. 1. Three way catalyst: simultaneous conversion of CO, HC and NO₂.

 O_2 content at the electrode surface is quickly depleted. For the condition of a lean exhaust, O_2 remained unreacted and the electrode senses its relative high concentration [1]. The voltage generated across the sensor is strongly dependent on the O_2 content and is represented by the Nernst equation:

$$E = E_0 + \text{RT}/nF\ln\left(\text{PPO}_2\right)_{\text{ref}}/(\text{PPO}_2)_{\text{exhaust}}.$$
 (1)

The voltage signal generated is fed back to a control computer which adjusts the air to fuel ratio, at a frequency of 0.5 or 1 times per second. Fig. 2 shows the response of the oxygen sensor. This relatively simple device controls the air to fuel ratio within the narrow window that allows simultaneous conversion of all the three pollutants [2]. TWC technology was first installed on vehicles in 1979. Even today, this is the state of the art in air to fuel ratio control in the gasoline internal combustion engine and is critical for efficient use of the TWC.

The primary precious metals for a TWC were Pt and Rh with the latter being mostly responsible for reduction of NO_x [3] and the former for oxidation of CO and HC. The oscillatory nature of the air to fuel ratio in the exhaust means that the catalyst will see slightly rich and slightly lean conditions alternatively, approximately 0.5 or 1 times per second. Thus, when operating rich there is a need to provide a small amount of O_2 to consume the unreacted CO and HC. This was accomplished by the development of the O_2 storage component (OSC) which liberates or adsorbs O_2 during the air to fuel perturbations. CeO_2 was found to have this property and is the most commonly used O_2 storage component in modern three way catalytic

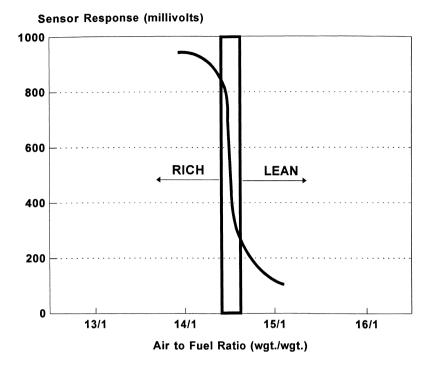


Fig. 2. Voltage response from an O2 sensor.

converters [4,5]. It is essential to deposit some of the precious metal onto the OSC component to significantly decrease the temperature for the above reactions to occur [6–8]. The reactions (2) and (3) are indicated below:

$$Rich\ condition: CeO_2 + CO \rightarrow Ce_2O_3 + CO_2 \qquad (2)$$

Lean condition:
$$Ce_2O_3 + 1/2O_2 \rightarrow CeO_2$$
 (3)

Another benefit of CeO_2 is its catalytic activity for steam reforming (4) in the rich mode, generating H_2 which reduces a portion of the NO_x to N_2 .

CO or HC +
$$H_2O \xrightarrow{CeO_2} H_2 + CO_2$$
 (4)

It also stabilizes the Pt against sintering [9]. The kinetics of CO oxidation on Pt/CeO₂ are positive order in CO as opposed to the negative order or inhibition for Pt/Al₂O₃.

The OSC effectiveness of the CeO₂ is greatly enhanced by combining it with ZrO₂, forming solid solutions [10]. It is postulated that incorporation of ZrO₂ into the framework of the CeO₂ structure promotes oxygen mobility, enhancing the exchange rate

of O₂ [11]. The ZrO₂ imparts thermal stability to the CeO₂ which alone is highly unstable. The kinetics of CO oxidation for Pt/CeO₂/ZrO₂ are also enhanced relative to Pt/CeO₂, especially after high temperature exposure [12].

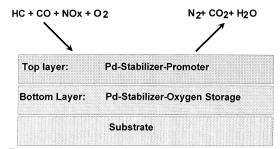
Three way catalysts are primarily composed of about 0.1-0.15% precious metals at a Pt to Rh ratio of 5-1, and varying concentrations of bulk high surface area CeO2 or CeO2/ZrO2 admixed with the $\gamma\text{-}Al_2O_3$ washcoat. The $\gamma\text{-}Al_2O_3$ is stabilized with 1-2% of La₂O₃ and/or BaO. This composite washcoat is then deposited on a ceramic honeycomb with 400 cells per square inch (cspi) with wall thicknesses of 0.006 in. Recently 400 cpsi metallic monoliths with wall thicknesses of 0.002 in. with open frontal areas approaching 90% have found use for specialty applications where pressure drop must be kept to an absolute minimum, as for example in high performance vehicles. Typically, the washcoat loading is about 1.5-2.0 g/in.3 or about 10-15% of the weight of the finished honeycomb catalyst. The size and shape of the final catalyst configuration varies with each automobile company but typically they are about 5-6 in. in

diameter and 3 in. long with multiple honeycomb catalysts.

Within the family of precious metals Pd is usually significantly less expensive than either Pt or Rh. Palladium, however, is less resistant to deactivation by poisons such as Pb and S versus Pt and Rh. Research over the last few years has concentrated on preparation of Pd/Rh [13,14], and high Pd containing catalysts [15]. With improved fuel quality (reduced levels of Pb, reformulated fuel), better engine control of the air to fuel perturbations, higher catalyst operating temperatures and improved catalyst formulations it has now been demonstrated that Pd, promoted with certain proprietary base metal oxides, can indeed be used to meet tighter future emission regulations at higher operating temperatures [16,17]. From a fundamental understanding of the positive and negative interactions that occur in multicomponent catalysts some catalyst manufacturers have developed segregated or layered washcoat structures, adding great flexibility to optimizing the chemistry of the washcoat.

A high Pd loaded catalyst with small amounts of Pt and Rh is prepared in two layers. Undesirable deactivation by alloy formation is accomplished by locating the Pd and Rh in separate layers. Furthermore, the Rh NO_x function is maintained by segregating it from the CeO_2 . Some of the Pd interacts with the OSC to enhance the OSC and CO oxidation function while the remainder of the Pd is free, allowing better NO_x and HC oxidation [15]. Reduced generation of H_2S is also realized by reacting the CeO_2 with ZrO_2 , minimizing the formation of $Ce(SO_4)_2$ which reduces to H_2S .

A catalyst in which the only precious metal present is Pd is promoted with various metal oxides and its washcoat is designed for optimum performance. It is highly desirable to deposit Pd directly on the OSC component to enhance the oxygen exchange kinetics and capacity and to promote the CO oxidation and water gas shift reactions. Separating the Pd from the CeO_2 results in better NO_x reduction and HC oxidation. Thus, a washcoat is formulated in two distinct layers (see Fig. 3), permitting the positive aspects of each function to be preserved [18]. The same authors have recently found that the addition of certain oxides including Nd and La promotes enhanced NO_x reduction and imparts greater tolerance of the Pd towards deactivation by SO_x [19].



Features:

Top Layer: Efficient Pd Species to Give High NOx/HC Activity. Bottom: Pd-OSC Interaction Provides High Temperature Performance.

Fig. 3. Advanced TWC with multilayered washcoat functionality.

3. Future challenges for the gasoline catalytic converter and system

One of the key problems identified in the US FTP test as well as the European (MEG) test cycle is the liberation of unburned non-methane hydrocarbons (NMHC) from the exhaust during the cold start mode. The catalyst does not reach its HC light-off temperatures (about 300°C) until about 2 min after the start of the test. Consequently, up to 50–80% of the total unburned hydrocarbons are emitted during this period, resulting in a failure to meet future regulations, especially in California for their ultra-low emission vehicle (ULEV) standards of 0.04 g/mile of NMHC. The close coupled or manifold mounted catalyst appears to be the most promising technology for meeting future emission standards although other technologies are still under consideration.

3.1. Close coupled catalyst

Catalysts mounted close to the exhaust ports of the engine, as shown in Fig. 4, will benefit from the hot exhaust and thus will reach hydrocarbon light-off temperatures within 10 s [20]. The primary function of this catalyst is to oxidize the hydrocarbons during the first 2 min of the test. A larger TWC catalyst is located downstream in an underfloor position to function during other driving modes. The close couple design, however, exposes the catalyst to hotter overall temperatures, increasing the likelihood of carrier and/or metal sintering. One preparation selectively oxidizes the HC with minimal CO oxidation to avoid high temperatures during rich engine excursions and high

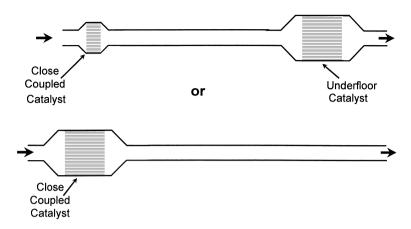


Fig. 4. Location of close coupled and underfloor catalyst in exhaust manifold.

CO concentrations. This novel catalyst has temperature stability to 1050°C. Proprietary metal oxides are added to stabilize the Al₂O₃ and Pd against excessive sintering. This technology has had significant success in vehicle tests [20], some typical data of which are shown in Fig. 5.

Disadvantages of the close couple are space requirements and heat management in underhood location. Therefore, this approach, although potentially a solution, is not without drawbacks. Furthermore, more stringent test cycles (US 06 modification to the US FTP to include aggressive driving modes of high speed and load) will add additional high temperature stress to close coupled catalysts.

3.2. Electrically heated catalyst

An alternative to decreasing the time required for HC light-off is to heat electrically a small pre-catalyst

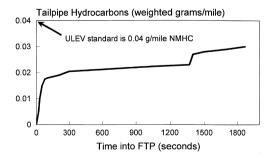


Fig. 5. Hydrocarbon emissions from a vehicle equipped with a close couple/underfloor combination catalyst system.

supported on a metal substrate [21]. This can bring the temperature to light-off in less than 15 s. A TWC catalyst is located downstream to complete the emission reductions for all the three pollutants. This approach has been shown to be feasible but long term durability, power requirements and cost issues of the metal substrate and system will not place this approach in a favorable position relative to other solutions although its use is anticipated for specialty vehicles where close couple is not satisfactory by itself.

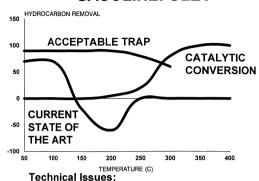
3.3. Hydrocarbon trap

The concept of the trap is to store the unburned HC in a material upstream of the main catalyst during the early portion of the cold start test. Once the catalyst reaches light-off, the HCs are released and converted downstream. Unfortunately no materials (e.g. zeolites) capable of retaining the HCs to a high enough temperature have been found. The performance of an ideal trap material relative to light-off conversion is shown in Fig. 6.

3.4. Exhaust gas igniter

The principle is to use a choke strategy to increase the HC concentration in the exhaust and to ignite it up stream of the catalyst. This raises the catalyst temperature to light-off in about 15 s. This system is getting serious attention, especially in Europe [22].

HYDROCARBON TRAPS FOR GASOLINE: ULEV



1) Adsorption and retention of hydrocarbons to 300 C for 100,000 miles in 10% H₂O and CO₂

Fig. 6. Ideal hydrocarbon trap relative to light-off profile of an oxidation catalyst.

3.5. Chemically heated catalyst

Hydrogen can be catalytically oxidized by precious metals essentially at room temperature. It is generated by rich operation of the engine and stored on-board in hydrides. By injecting it into the catalyst, its oxidation liberates sufficient heat to initiate light-off [23]. The complexity and expense of such a system is likely to limit its commercial use.

3.6. Catalytic converter/system technologies

Regulations will soon require that the driver be informed as to when the converter is not efficiently working. The law requires that a signal on the dash board informs the driver that maintenance to the catalyst is necessary. Current thinking is to use O_2 sensors before and after the catalyst as shown conceptually in Fig. 7. The difference in voltage response between the two sensors will indicate the amount of O_2 slip. The theory is that if the catalyst is not working, the O_2 will exit the monolith unreacted. This will generate a signal on the sensor similar to the sensor at the inlet to the converter. Thus, the voltage comparison will be calibrated for catalyst effectiveness. This approach is generally satisfactory for meeting LEV but is not satisfactory for ULEV [24].

This represents a major challenge for the catalysts and the entire system of emission control. The need for a sensor for detecting small amounts of HC for ULEV

Dual oxygen sensor OBD must report HC activity of catalyst

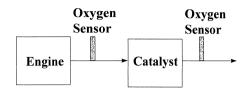


Fig. 7. Dual O₂ sensors for on-board diagnostics.

standards is a preferred solution. Research continues in this area.

3.7. Direct injected gasoline engines

Toyota, Honda, Mazda and other manufacturers have reported that full lean burn engines are possible; however, the lean operation decreases the effectiveness of the TWC for NO_x conversion. The challenge to emission control companies is to develop NO_x reduction catalysts that function in the presence of large excesses of O_2 . Such technology is available for stationary engines when NH_3 is the reductant; however, it is more practical to use on-board derived fuel to perform the reduction. The feasibility of selectively reducing NO_x with HC has been reported [25] and will be further discussed below in the section on diesel engines.

New engine technology with improved fuel economy and lower generation of green-house gases, e.g. CO_2 , is aggressively being pursued by engine manufacturers especially in Japan. A full lean burn vehicle with a direct injected gasoline engine operates with A/F>14.7 delivering fuel economy savings up to 25% compared to stoichiometric engines. The engine operates in a region of instability of fuel combustion which results in slip of hydrocarbon into the exhaust and this hydrocarbon can be used as a reductant for NO_x . A catalyst capable of abating NO_x in the presence of large excesses of O_2 continues to be a limiting technology. This is further discussed in the Diesel section of this paper.

3.8. Catalysts for partial lean burn engines

Toyoto has pioneered a new engine/catalyst hybrid system which operates lean during cruise conditions,

PARTIAL LEAN BURN: NOx REMOVAL

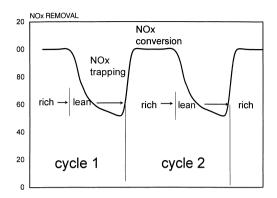


Fig. 8. Conversion profiles for a partial lean-NO_x strategy.

resulting in 5–6% fuel economy savings. The NO_x generated is stored in an alkaline metal oxide compound, such as BaO, incorporated into a TWC. Periodically the engine goes rich of the stoichiometric point for a short time during which the stored NO_x is reduced on the TWC catalyst [26] as shown in Fig. 8. This system is commercially available in Japan, where low sulfur containing fuels are used. For the US and Europe, the higher concentration of acidic sulfur oxides present in the exhaust compete for the same sites as the NO_x . Some adsorbed sulfur oxides are desorbed during the rich pulse but at a slower rate than the NO_x , this resulting in permanent deactivation of the NO_x storage function. Alternative materials and approaches are therefore necessary.

4. Diesel emission control

In the early 1990s the diesel engine manufacturers, being aware of the successes of the catalytic converter for the gasoline engine, considered a catalyzed flow-through monolith for controlling emissions from their engines. The exhaust, however, comprises particulates composed of solid dry carbon or soot, and liquid fuel and oil called the soluble organic fraction or SOF. Furthermore, the gaseous exhaust contained significant amounts of SO₂ which, over most oxidation catalysts, would be converted to SO₃ (H₂SO₄) which is obviously an unfavorable secondary emission and indeed contributes to the total particulates. Thus, the challenges for catalysts was quite demanding and

different from that for its gasoline counterpart. The general idea was for the catalyst to oxidize the liquid or SOF component of the particulates to CO₂ and H₂O. Diesel engines operate lean and therefore are much cooler than modern stoichiometrically operated gasoline engines. The catalyst would therefore have to function at much lower temperatures than in the gasoline counterpart and would be required to treat liquids rather than 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 oxidation. Fortunately, the larger hydrocarbon molecules that make up the SOF, i.e. >C₁₆, can be oxidized with the proper catalyst, at lower temperatures than needed for 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. The design of the catalyst had to include hydrocarbon adsorption and storage by an organo-philic surface with the proper pore size to promote condensation. Another very important catalytic property was that it must have a low activity for the oxidation of the gaseous SO₂ to SO₃; the latter quickly forms sulfate particles, adding to the particulate load. This is shown in Fig. 9 where an acceptable and unacceptable catalyst are contrasted. For such a system to function, the dry soot had to be further reduced by engine strategies to prevent clogging the channels of the monolithic honeycomb.

Catalyst formulations comprised of bulk CeO₂ admixed with Al2O3 are now used for the effective oxidation of the liquid portion of the particulates (the SOF) without generation of SO₃ particulates. Durabilities of over 180 000 miles for medium-heavy duty trucks have been routinely accomplished in the US since 1994 [27]. Engine technology is sufficiently advanced that no abatement of CO or HC is necessary to meet US Heavy Duty truck standards. Since 1996, diesel passenger cars in Europe have to abate CO and HC emissions and the preferred catalyst consists of a small amount of Pt supported on Al₂O₃ with additions of bulk CeO₂ and a zeolite [27]. The zeolite effectively stores the unburned HCs during cold conditions and releases them to the Pt for light-off as the temperature increases in the exhaust. All of these formulations are deposited on ceramic monoliths.

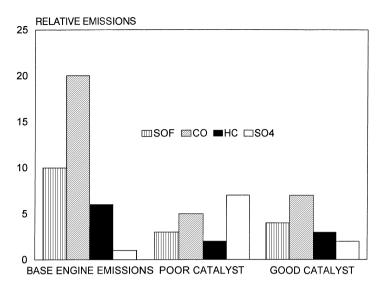


Fig. 9. Comparison of an acceptable and unacceptable diesel oxidation catalyst.

4.1. New challenges for diesel emissions

The desire for improved fuel economy, and for lower emissions of green-house gases such as CO_2 , is projected to increase the demand for diesel engines throughout the world. It is therefore of great importance to develop catalyst technology that will allow NO_x reduction in lean environments for truck and passenger car applications by either decomposition of NO_x directly into N_2 and O_2 or reduction using onboard hydrocarbons, e.g. diesel fuel.

Due to the lack of success in developing feasible NO_x decomposition catalysts, the alternative approach of NO_x reduction using diesel fuel derived HC is now under intensive investigation by engine manufacturers, catalyst companies, and universities throughout the world [25,28]. The relatively low HC/ NO_x ratio in the exhaust of a lean burn engine is the reason it is necessary to add additional HC, derived from the fuel, to raise this ratio to permit adequate NO_x reduction.

Literally thousands of catalyst have been studied over the last 10 years but to date the only active ones are Pt and Cu/ZSM-5 [29]. Catalyst formulations containing Pt are the most active for hydrocarbon/ NO_x reduction between 200°C and 300°C while Cu/ ZSM-5 formulations are less active but convert NO_x above 350°C. The conversion for Pt reaches a maximum at about 250°C but then quickly drops to zero as

the hydrocarbon reaction with O₂ becomes dominant and consumes all the hydrocarbon:

$$C_3H_6 + 2NO_x + 7/2O_2 \rightarrow N_2 + 3CO_2 + 3H_2O$$
 (5)

$$C_3H_6 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O$$
 (6)

The catalyst to be used for lean- NO_x reduction in diesel engine exhausts must have good low temperature activity and selectivity for NO_x reduction but have low activity for oxidation of SO_2 to SO_3 at elevated temperatures. The most serious limitation for Pt technology is the narrow temperature range in which they are active for reducing NO_x and the high selectivity to N_2O rather than N_2 [30].

Catalysts based on Cu/ZSM-5 are active at temperatures above about 350°C and can function in hotter exhaust temperatures. Unfortunately, like Pt based catalysts, non-selective combustion dominates over NO_x reduction above 400°C and conversion again begins to fall. However, unlike Pt, N₂ is the dominant product with only small amounts of N₂O formed. A most serious disadvantage with Cu/ZSM-5 based catalysts is their vulnerability to deactivation due to sulfur oxide poisoning [31]. The origins of the sulfur are both the fuel and the engine oil and thus sulfur containing molecules will be realistic exhaust constituents for which improvements in catalyst tolerance must be made. Another disadvantage is the generally

poor hydrothermal stability of the Cu/ZSM-5 catalysts in the diesel exhaust. Thus, major challenges face Cu and zeolites for lean-NO $_x$ applications. In summary, Pt based catalysts are the most promising materials currently available for lean-NO $_x$ reduction using onboard hydrocarbons. They retain their activity for NO $_x$ reduction after high temperature laboratory and diesel engine aging. Furthermore, they are generally resistant to sulfur oxide poisoning and are hydrothermally stable. The major improvement requirements are:

- 1. broadening of the NO_x reduction temperature window of operation;
- 2. an improvement in selectivity for the NO_x reduction reaction over the hydrocarbon combustion reaction:
- 3. decreased selectivity for SO₂ oxidation to SO₃;
- 4. decreased production of N₂O.

It must also be emphasised, however, that the lean- NO_x solution will be that of a engine/catalyst system which will deliver the proper type and amount of hydrocarbon needed to obtain high-efficiency, cost-effective NO_x reduction along with reductions in particulate, CO and unburned hydrocarbons [32].

Decomposition catalysts, or as a second choice, lean- NO_x catalysts using on-board derived hydrocarbons as the reductant giving better than 80% conversion remain a major goal for catalyst and engine manufacturers. This continues to be a challenging problem and a solution will represent a major breakthrough in catalyst technology.

In the absence of either NO decomposition or HC reduction catalysts, engine manufacturers are re-considering the possible use of urea as a source of NH_3 to carry out SCR. This technology is widely practiced in stationary power plants and engines [33]. However, it is not desirable since it requires another fuel to be carried on-board and the injection must be closely controlled with the NO_x to avoid slippage of NH_3 to the environment. This requires an additional feedback control system and a rapid response NO_x sensor adding to the system complication.

5. Lean burn-natural gas fueled vehicles

The transportation industry is experiencing continued growth in the use of compressed natural gas fueled

lean burn engines in US and Europe. Because of their relatively low particulate make, these engines are a viable approach to meeting particulate standards in urban environments where they substitute for dieselpowered buses and other fleet vehicles. In spite of their relatively low emissions, Pt, Pd monolithic catalysts are installed on many vehicles to convert any unburned non-methane hydrocarbons, CO and particulates. The methane component, which comprises the largest component of the hydrocarbon emissions, does not contribute to photochemical smog and is thus not subject to regulations. It is, however, a powerful green-house gas and its abatement would thus be preferred. Too date, the only catalyst capable of oxidizing methane at any appreciable rates is Pd but only when the exhaust exceeds about 300-350°C. The US Heavy Duty test cycle emphasizes the relatively low temperature of the driving cycle, indicative of stop/go urban driving, and methane emissions are not abated to any significant effect. A recent study has identified that traces of S (<1 ppm) present in the fuel and oil selectively adsorb onto the Pd, significantly decreasing its activity for methane [34]. Discovering a low temperature SO_x-tolerant methane oxidation catalyst represents a challenge for the future. It is interesting to note that methane emission standards can be met for European Heavy Duty trucks by virtue of the higher temperature modes of the standardized test (R-49) where the sulfur inhibited Pd catalyst retains sufficient activity.

6. Conclusions

The automobile gasoline catalytic converter has now found successful commercial use for over 20 years, converting CO, HC and NO_x. New material requirements, along with a more fundamental understanding of the function of various components, is now allowing more precisely defined washcoats with less expensive metals and enhanced performance for 100 000 miles (160 000 km). Future needs for meeting ULEV standards and on-board diagnostics will continue to be a challenge into the 21st century. Fuel economy improvements with lean burn gasoline engines still face a major hurdle in the abatement of NO_x. Catalysts that can decompose NO_x in a lean environment are the ideal solution. In the absence of

this, new catalyst materials which can selectively reduce NO_x over a broad temperature range using on-board derived hydrocarbons is most desirable.

Liquid particulates (SOF), CO and HC emissions are now abated from diesel fueled trucks and passenger cars with new monolithic catalysts but NO_x reduction continues to be a major challenge for new catalytic materials. Further reductions in dry soot, especially those with particle sizes below 2.5 microns, will also be required for future standards.

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