INTEGRATED DIESEL ENGINE NOx REDUCTION TECHNOLOGY DEVELOPMENT

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INTRODUCTION

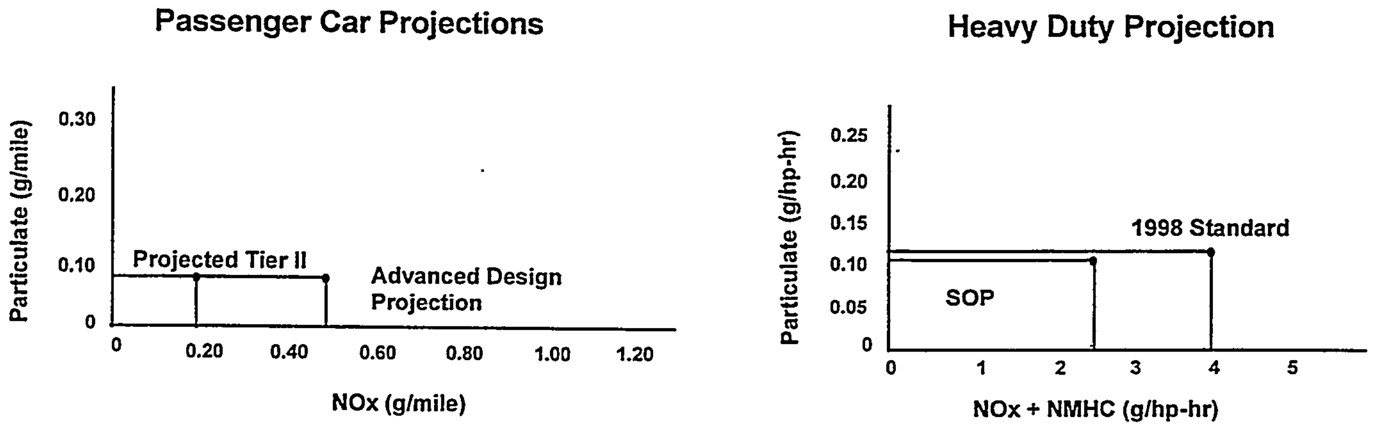
The primary purpose of current production diesel catalyst has been HC, CO, and SOF (soluble organic fraction) oxidation as typically needed for vehicles operating in congested urban areas and in underground mining operations. More stringent air quality standards will require significant NOx reduction as well. New lean NOx catalyst technology is being developed for this purpose.

Figure I illustrates that current production diesel engines require development to meet the projected environmental requirements. Passenger car and heavy duty diesel engines require a factor of two or more NOx reduction relative to existing production emission levels.

TECHNICAL APPROACH

Project activity flow is diagrammed in Figure 2. The interdependent systems include the engine, catalyst, and fuel. Key technologies and development interactions are also implied in the diagram. The primary thrust of in-cylinder management of NOx control is to reduce the peak temperature of combustion while minimizing fuel consumption penalties and/or particulate generation.

New catalyst formulations are developed at bench levels with simulated diesel exhaust before scaling to sizes required for engine assessment. Exhaust gas hydrocarbon speciation studies are aiding design of a reductant system which meets catalysis requirements. System design will ultimately be refined in full scale system testing.


Passenger Car Projections

Heavy Duty Projection

Figure 1 - Proposed NOx and Particulate Standards for HD and Passenger Car Engines

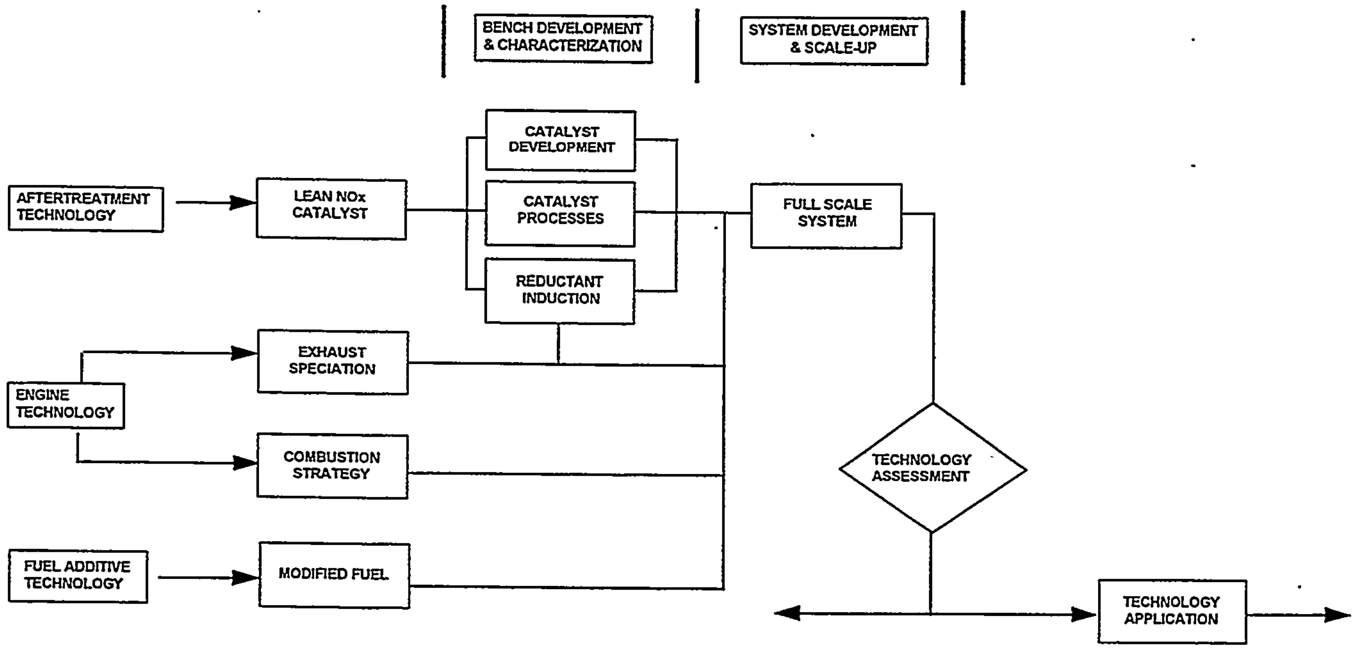


Figure 2 - Integrated Engine-Catalyst-Fuel Development Approach

Related fuel studies are a key feature of the integrated strategy. Production viability requires understanding of in-cylinder NOx forming chemi-stry but also whether and how intermediate spe-cies formation may facilitate NOx catalytic reduc-tion. Sulfur content is a significant challenge to the applicability of lean NOx catalyst systems. Sulfur removal is not so much a technical barrier, but a key variable of a complex technology-economics-infrastructure equation.

IN-CYLINDER MANAGEMENT - ANALYTICAL STUDIES

Analytical computational studies are contributing to better understanding of the complex combus-tion system interactions and their influence on real-time exhaust gas behavior. Computer assisted diesel combustion modeling continues to produce valuable development guidance. For engine-after-treatment systems, models provide insight to the complex balance of in-cylinder and aftertreatment mechanisms that influence the total emission signature. The use of super computer based KIVA modeling supports this need.

Figure 3, results from a KIVA study, are snapshots of in-cylinder temperature late in the power stroke. It is a three dimensional, one eighth segment with the apex of the 'pie slice' at the cylinder centerline. The piston is near bottom dead center. In the plan view, the segment is centered on an injector plume.

Given the direct correlation between temperature and NOx formation, knowledge of the temperature distribution provides valuable in-cylinder NOx reduction information which can be weighed against emission control strategies external to the combustion event. This iso-temperature profile provides the engine engineer with four-dimensional feed-back (including time) on potential changes to reduce local high temperature regions while maintaining the high mass average temperature ne-eded for then notorious high thermal efficiency of a diesel engine. Iso-thermal, iso-CO, and iso-NOx contours are illustrated in Figure 3.

A related mixing challenge is shown in the iso-CO contour. This indication of incomplete combustion suggests local regions in-cylinder during the cycle where the opportunity for HC and particulate management exist

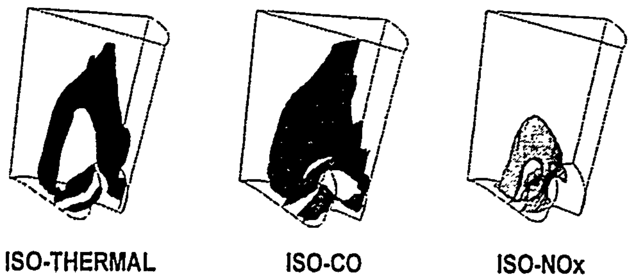


Figure 3 - Late Cycle In-cylinder Contours of Temperature, CO, and NOx

BASE ENGINE R&D STATUS

Figure 4 tracks progress that has been made in the past ten years for the high speed direct injection (HSDI) engine. Changes in the basic engine design description and Tier II emission requirements are included for context. Combustion strategies, shown as a key element of new designs, continue to be developed based on the direct injection (DI) system, with key features being refined in-cylinder airflow structure and more tightly controlled injection spray orifice designs. Increased injection pressure and rate shaping capabilities allow for exploration of advanced fuel-air mix strategies.

Hardware and software evolution of injection system technology has provided increased precision of injection patterns over a broader range of engine operating conditions. The combination of cooled EGR, variable valve timing, variable swirl, variable turbine geometry, and low turbine wheel inertia provide engine breathing improvements, and extend the benefits over a larger engine operating range. Similar technology mix and emission reduction progress has been achieved on the heavy duty engine.

In addition to the base engine improvement described above, the application of diesel catalysts may play a key role in achieving future emission control compliance. Lean NOx catalysts activities associated with this IER program are detailed below.

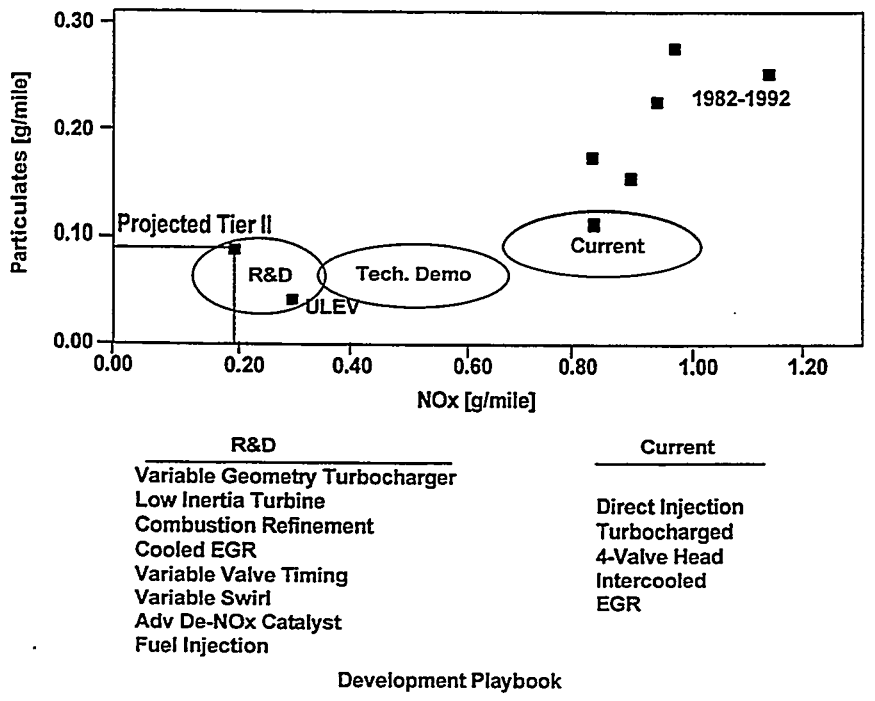


Figure 4 - HSDI Diesel Technology Advancements

LEAN NOx CATALYST DEVELOPMENT

Lean NOx catalysts may be categorized into two groups with respect to operating temperatures. We consider first the technology status of those catalysts designed for operating at higher temperatures (Figure 5). These catalysts usually exhibit onset of NOx conversion at temperatures greater than 300'C and the more intriguing ones continue to reduce NOx at temperatures over 500'C.

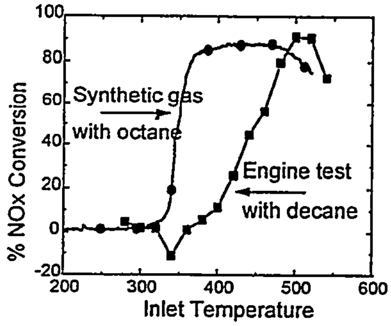
- Onset of NOx conversion occurs at 300-400°C.
- High NOx conversion achieved to temperatures > 500°C, given sufficient HC/NOx ratio.
- A wide variety of hydrocarbons including diesel fuel, paraffins, olefins, and oxygenates sustain NOx reduction.
- Durability has been demonstrated after high temperature catalysis.
- NOx conversion > 80% demonstrated both using synthetic gas and in engine tests.

Figure 5 - High Temperature Lean NOx Catalysts Characteristics

Concentrating on high temperature Allied Signal Environmental Catalysts (ASEC) R&D catalysts, there is ability to use a wide variety of hydrocar-bons as reductants. NOx reduction efficiency varies among the classes of hydrocarbons men-tioned, but encouragingly good performance is observed. With alcohols or heavy alkanes, broad temperature windows with NOx conversion > 90% at HC/NOx = 4 can be observed.

As will be shown, thermal durability under catalytic conditions is demonstrated for these catalysts.

In Figure 6, NOx conversion of ASEC LNX-28 catalysts is plotted as a function of catalyst inlet temperature. The octane-containing gas is made synthetically in a laboratory scale reactor system and contains 4000 ppm C_1 as octane, 1000 ppmv NOx, 300 ppmv CO, 20 ppmv $S0_2$, 12% 0_2, 8% H_20, 8% $C0_2$, and balance N_2. NOx reduction exhibits a sharp onset at temperatures of about 340°C.



Apparent lightoff on engine delayed, probably due to heat management issues

Figure 6 - LNX-28 Shows Interesting NOx Conversion Using Both Synthetic Exhaust and Engine Exhaust

NOx conversion is also plotted as a function of catalyst inlet temperature for a similar catalyst. These results were obtained using diesel exhaust from a 1.9 liter light duty diesel engine at constant speed and load. Temperature variation was introduced by passing the exhaust gas through a heat exchanger. Decane was introduced as a reductant at a constant rate using a Hewlett-Packard Liquid Chromatography pump/fuel injector assembly. The inlet NOx concentration was about 500 ppmv and inlet HC about 4500 ppm C_1.

The origins of the difference in NOx lightoff in the two environments were investigated. Issues relating to effective heating and vaporization of reductants injected into diesel exhaust are believed to account for part of the difference between the synthetic gas and the engine test results.

Catalytic performance of lean NOx catalysts is generally sensitive to the relative amount of HC present. This is specifically true for the current generation of LNX-28.

The left-hand panel in Figure 7 shows dynamometer data of the same catalyst for nominal HC I /NOx ratios of either 6 or 9. The catalyst shows better performance at the higher C/N ratio.

The right-hand panel in Figure 7 shows performance in a laboratory testing plant when octane is used as the reductant. We find that this catalyst reduces NOx over greater temperature ranges in a laboratory testing plant than it does over the dynamometer.

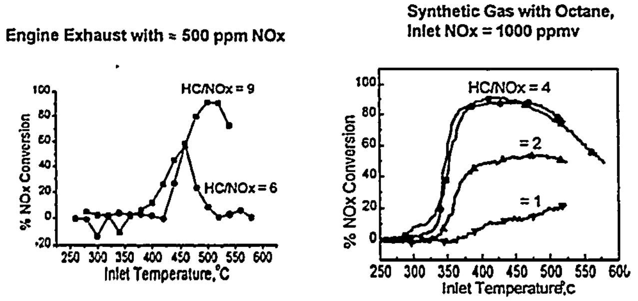


Figure 7 - NOx Reduction Performance is Sensitive to HC/NOx

Figure 8 demonstrates a degree of catalytic durability that is encouraging for a base metal catalyst. The data were acquired using a laboratory reactor system. A synthetic gas mixture was used that includes components that are often poisons or inhibitors for base metal catalysts, such as SO_2 and H_2O, which inevitably reside in diesel emissions. Aging conditions involved an inlet temperature of 550°C in a full complement of simulated exhaust gas. We have found that many other base-metal catalysts are more subject to thermal deactivation under catalytic conditions than under conditions that simply involve a stated temperature, air, and steam.

Benchmark lean NOx catalysts, such as CuZSM-5, degrade precipitously under these conditions. Generally speaking, catalysts susceptible to thermal degradation will show this susceptibility after short times on stream. LNX-28 shows no degradation after 50 hours onstream, leading to the expectation that this catalyst will provide good thermal durability for extended times. This is a necessary but only partial condition for demonstration as a practically useful catalyst.

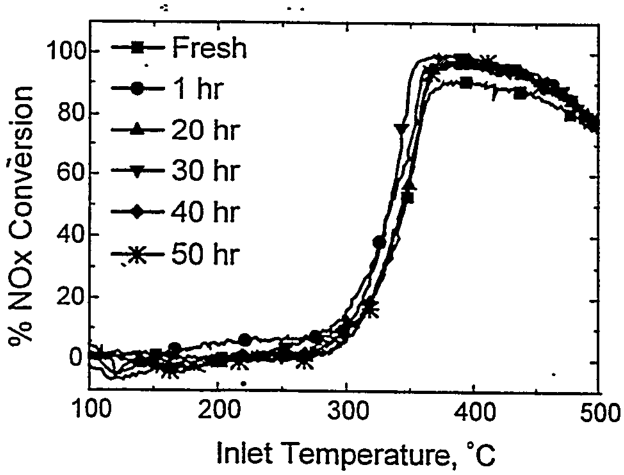


Figure 8 - LNX-28 Does Not Thermally Deactivate After Extended Catalysis

- Selective catalytic reduction using hydrocarbons
- Moderate NOx reduction activity at very low HC/NOx (<1 on average)
- Noble metal based
- Operating range below 150°C to about 300°C
- Low temperatures allow integration of hydrocarbon storage & release components with lean NOx reduction components
- Demonstrated NOx reduction on vehicles range from 20-35%

Figure 9 - Characteristics of Low Temperature Lean NOx Catalysts

As summarized in Figure 9, various catalysts employing noble metals, often platinum, can reduce NOx at lower temperatures between about 125-300°C. At temperatures below 100°C, these catalysts are not very active. At temperatures above 300°C these catalysts are quite active, and oxidize hydrocarbons very rapidly. But unfortunately, they have low selectivity for using HC species as the reductant, and the fraction of HC oxidized by atmospheric

02 *becomes high.* Hence, at higher temperatures, these catalysts cannot be considered to be lean NOx catalysts.

Noble metal catalysts can also contain a hydrocarbon storage and release component (or more than one such component) to help manage HC utilization, minimize HC breakthrough, and improve HC-NOx reactivity.

Demonstrated NOx reduction, exemplified here by use of the European test cycle, ranges frorn 20%35%, for advanced lean NOx catalysts, depending on the design of the overall vehicular emissions control system.

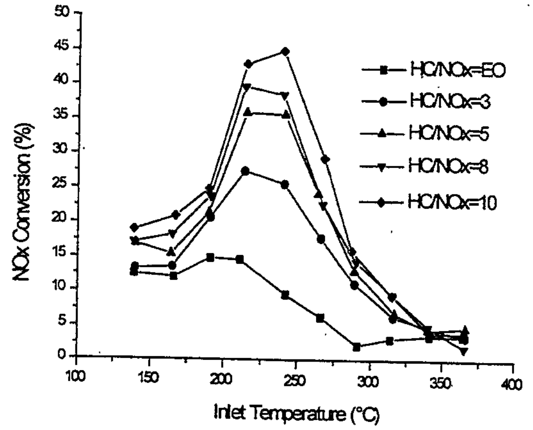


Figure 10 - Pt-Based Lean NOx Catalysts such as LNX-16.1B Utilize HC for the Reduction of NOx

As is the normal case for lean NOx catalysts, Pt-based catalysts such as ASEC LNX- 16.1 B exhibit sensitivity to the overall HC/NOx ratio. This sensitivity was assessed on a dynamometer, at various temperatures and steady state, and is shown in Figure 10. By operating at steady state, only catalytic efficiency is evaluated, and coupling between transient HC ad sorption/re lease is not probed.

Figure 11 shows tailpipe emissions of a diesel passenger car equipped with a similar ASEC Ptbased lean NOx catalyst. A fair HC, CO, NOx, and PM 4-way control is demonstrated. High degrees of HC conversion are obtained due in part to good HC storage/release management. The storage/release is well coupled with NOx reduction, leading to fair levels of NOx control in spite of very low HC/NOx values maintained over most of the evaluation. CO is adequately controlled. Only a portion of the PM is converted, but most of the unconverted PM occurs as solid, soot-like particulate that is not amenable to catalytic oxidation with flow-through devices. Very high levels of oxidation of the SOF portion of particulate are realized.

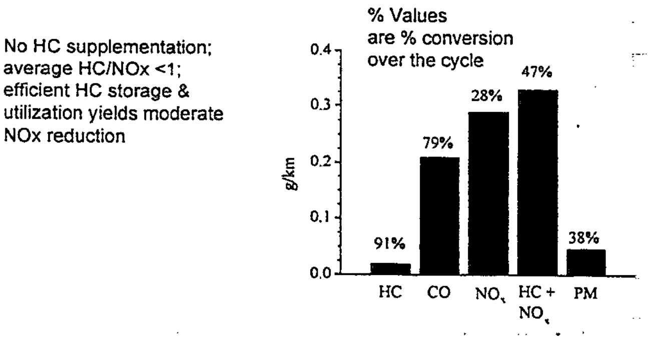


Figure 11 - Test Results Representing State-of-theArt Diesel Passenger Car Lean NOx Control

Several decision points regarding integration of catalyst and systems designs lie ahead, as outlined in Figure 12. It is not clear whether both high temperature and low temperature catalyst technologies will be needed for HD or LD NOx control. Many issues regarding method and strategy of HC provision, in-cylinder late injection versus in-exhaust injection, remain open and may be influenced by multiple catalyst technologies.

- Integration of catalyst and system designs
- Increased performance from both high tem-perature and low temperature catalysts
- Improved materials and systems designs will probably contribute

Figure 12 - Future Targets, Prospects

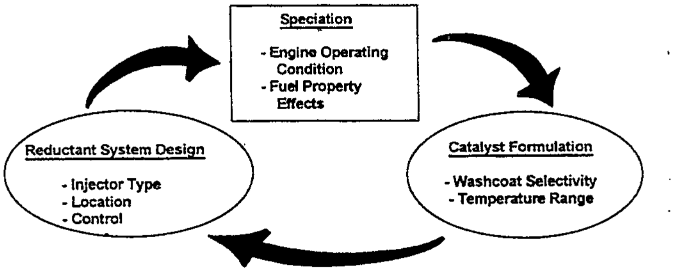
Desired levels of catalytic NOx control range from

30%-80%, depending on the nature of the engine-vehicle system and its intended application. Higher performance from low-temperature catalysts is needed, since moderate conversion levels of less than 50% require unacceptable fuel economy penalties. Although durable high temperature catalysts appear to offer high performance, this performance must be moved to lower temperatures. This is especially true since many engine-vehicle systems create a large fraction of total NOx emitted at catalyst inlet temperatures of 300-400'C

REDUCTANT SYSTEM DESIGN ENGINE/-CATALYST INTEGRATION

Although a number of reductants are more effective in the NOx reduction processes, diesel fuel is preferred. While there are many possible approaches to the system design, the system must deliver uniformly distributed, vaporized reductant of the preferred species to the catalyst. Oxidation of the reductant prior to the catalyst must be minimized to maintain superior diesel engine fuel economy. Control logic should integrate the other engine systems such as those being considered for advanced HSDI engines (Figure 4).

DDC has embarked on an exhaust gas speciation study to help verify reductant system design choice. The approach is detailed in Figure 13.



DDC - ORNL CRADA

Figure 13 - Exhaust Speciation

Independent variables in the matrix include engine design, reductant system design, reductant system control logic, and fuels. The effectiveness of an advanced lean NOx catalyst will be studied as the independent variables are changed. Major promoting and inhibiting HC species for NOx reduction will be identified. This study will provide valuable information for the final integrated NOx reduction system.

SUMMARY

The effectiveness of catalyst performance is a function of the inlet exhaust gas temperature, gas flow rate, concentration of NOx and oxygen, and reductant quantity and species. Given this interrelationship, it becomes immediately clear that an integrated development approach is necessary. Such an approach is taken in this project. As such, the system development path is directed by an engine-catalyst engineering team.

Of the tools at the engine engineer's disposal the real-time aspects of computer assisted subsystem modeling is valuable. It will continue to be the case as ever more subtle improvements are needed to meet competitive performance, durability, and emission challenges. A review of recent prototype engines has shown that considerable improvements to base diesel engine technology are being made. For example, HSDI NOx has been reduced by a factor of two within the past ten years. However, additional substantial NOx/PM reduction is still required for the future. A viable lean NOx catalyst would be an attractive solution to this end.

The results of recent high and low temperature catalyst developments were presented. High temperature base metal catalysts have been formulated to produce very good conversion efficiency and good thermal stability, albeit at temperatures near the upper range of diesel engine operation. Low temperature noble metal catalysts have been developed to provide performance of promising 4-way control but need increased NOx reduction efficiency.

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