Diesel Catalysts

Abstract: The first diesel catalysts, introduced in 1970s for underground mining applications, were simple oxidation catalysts designed for conversion of CO and HC. These catalysts gradually evolved into the modern diesel oxidation catalysts, optimized for PM emission reduction. Future requirements for NOx emission reduction from diesel engines call for new catalyst technologies, such as SCR, lean NOx catalyst, and NOx adsorber systems.

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Catalyst Technologies

Three-way catalyst (TWC) technology introduced in the 1980s became an integral part of the spark-ignited engine. The TWC catalyst, operating on the principle of non-selective catalytic reduction of NO_x by CO and HC, requires that the engine is operated at a nearly stoichiometric air-to-fuel (A/F) ratio [Eastwood 2000]. Modern catalyst systems for gasoline or natural gas engines include an oxygen sensor in front of the catalyst and a closed loop electronic control system. The electronic controller, based on a feedback system from the oxygen sensor, maintains the A/F ratio within a narrow range around the stoichiometric point, to assure maximum catalyst efficiency. In the presence of oxygen, the three-way catalyst becomes ineffective in reducing NO_x.

For this reason, three-way catalysts cannot be employed for NO_x control on diesel applications, which, being lean burn engines, contain high concentrations of oxygen in their exhaust gases at all operating conditions. Diesel emissions that can be controlled with high efficiency by today's catalyst technologies are CO and HC, including such HC material as the organic fraction of diesel particulates (SOF) or polynuclear aromatic hydrocarbons (PAH). Catalyst systems for the reduction of NO_x from diesel engines are either still under development or at early stages of commercialization, as summarized in Table 1.

The design target of early diesel oxidation catalyst (DOC) formulations was high removal efficiency of gas phase diesel pollutants, including carbon monoxide and hydrocarbons. At the time of their introduction, in the 1970s, carbon monoxide and hydrocarbon emissions from diesel engines were many times higher than they are in today's engines. The first diesel catalysts were used in confined space applications, such as in underground mining, where air quality was extremely important.

Introduction of fuels with reduced sulfur content (< 500 ppm S) made it possible to achieve small to moderate reductions of PM emissions with the DOC. In highway engine applications of modern diesel catalysts, the PM reduction became an important—in some cases the only important—catalyst function. Optimization of the PM performance of the diesel oxidation catalyst was the main objective of catalyst research in the late 1980s and early 1990s, both in the USA and in EU. These diesel catalysts have been commercialized on some heavy-duty diesel engines in the US and on light-duty diesel engines in the EU.

Future expectations focus on the NO_x reduction function of the diesel catalyst. Technologies for the reduction of NO_x from lean burn engines, both diesel and gasoline, have been researched for many years by catalyst manufacturers and research institutes worldwide. That research has produced some promising catalyst concepts, some of them being on the onset of commercialization.

Future emission standards for both highway (US 2010, Euro V, light-duty US Tier 2) and nonroad engines (US Tier 4, EU Stage IV) legislate NO_x emission levels that will require highly efficient NO_x emission aftertreatment. For example, the US 2010 NO_x limit of 0.2 g/bhp-hr represents an approximate 90% reduction relative to the 2004 standard. The regulators expect that NO_x reduction catalysts will mature to provide this magnitude of NO_x control on time. Indeed, the very future of the diesel engine may depend on technological developments in the catalytic reduction of NO_x under lean conditions.

Table 1
Diesel Catalyst Technologies

Catalyst Technology	Reaction Type	Reduced Emissions	Commercial Status
Diesel oxidation catalyst	Oxidation	CO, HC (incl. PAH), PM (SOF), odor	Established commercial technology
SCR	Selective catalytic reduction by ammonia/ urea	NO_x	Commercial technology for stationary and marine engines, under development for truck and car engines

DeNOx (lean NO$_x$) catalyst	Selective catalytic reduction by hydrocarbons	NO$_x$, CO, HC, PM (SOF)	Some commercial oxidation catalysts incorporate small NO$_x$ reduction activity (passive DeNOx)
NO$_x$ adsorbers	Adsorption (trapping) of NO$_x$ from lean exhaust, followed by release and catalytic reduction under rich conditions	NO$_x$, CO, HC	Technology under development, commercialized on lean burn gasoline engines

Diesel Oxidation Catalyst

The diesel oxidation catalyst, historically the first type of diesel catalyst, is still the only catalyst technology that demonstrated the required performance, robustness and durability and has been commercially established in a number of light- and heavy-duty applications.

DOC promotes a range of oxidation reactions utilizing oxygen which is in ample supply in diesel exhaust at all engine operating conditions. These reactions can convert virtually all emission components of chemically reducing character, such as CO, HC, and HC derivatives, into CO_2 and water vapor. The DOC chemistry is schematically shown in Figure 1.

At sufficiently high exhaust temperatures, diesel oxidation catalysts can provide very effective control of HC and CO emissions, with reduction efficiencies in excess of 90%. The DOC hydrocarbon activity extends to compounds such as polynuclear aromatic hydrocarbons or the SOF fraction of diesel particulates. The catalytic oxidation of SOF results in reduction of diesel PM emission. The PM conversion efficiency can range widely, depending on the SOF contents of the particulates and sulfur level in the fuel. In heavy-duty engines, it is usually between 15 and 30%. DOCs may be also effective in controlling diesel odor.
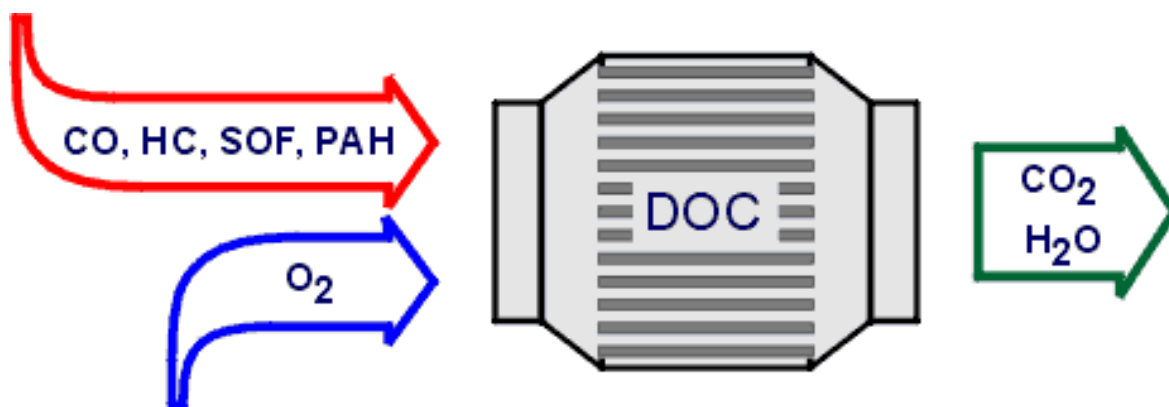
Figure 1. Conversion of Pollutants in Diesel Oxidation Catalyst

High conversion efficiencies for CO and HC are realized through the use of highly active, noble metal (e.g., platinum) based catalysts. Many DOCs

> Chemical reactions and DOC performance is discussed in **Diesel Oxidation Catalyst**.

developed in the 1990s for highway applications were optimized for PM emission reduction, as opposed to the abatement of CO or HC. In order to suppress undesired oxidation of sulfur compounds, these catalysts generally utilized formulations of reduced catalytic activity (e.g., through the use of base metals instead of platinum or the use of very low platinum loadings). It needs to be emphasized that CO and gas-phase HC conversion in these PM-optimized catalysts may be very low.

The diesel oxidation catalyst was introduced in the 1970s to protect the ambient air quality in underground mines. The objective of the catalyst was to reduce carbon monoxide emissions and odors from diesel-powered mining equipment. The use of the DOC extended into other enclosed space applications including construction, tunneling, and material handling. In most cases, there are no tailpipe emission regulations in these applications. Rather, the use of catalysts is driven by occupational health and safety standards which protect the ambient air quality at the workplace.

Early diesel catalysts, used throughout the 1970s and 1980s, were simple oxidation formulations, virtually the same as those developed for gasoline cars. Certain disadvantages of these catalysts, such as increased sulfate PM emissions, were gradually discovered by diesel research. As a result, the overall air quality benefit from using diesel oxidation catalysts in enclosed space applications had been questioned [Mogan 1987]. The introduction of emission standards for highway diesel engines in the 1990s stimulated catalyst research, which led to the development of next generation diesel oxidation catalysts. These new catalysts, when used with low sulfur fuels (< 500 ppm S), were able to control diesel particulate emissions in many diesel engine applications. Availability of the improved diesel catalyst technologies reinstated an endorsement for the use of diesel oxidation catalyst in underground mining and other enclosed space applications [MSHA 1998].

The first automotive application of diesel oxidation catalysts was the diesel-fueled Volkswagen Golf "Umwelt" (German for "environment") in 1989. The catalyst was designed to reduce CO and hydrocarbons emissions. The use of a catalyst was not necessary to meet German or European emission regulations at that time. Rather, it was introduced as a sign of an environmentally responsible attitude of the car maker. Since the introduction of the Euro 2 emission standards in the mid-1990s, the diesel oxidation catalyst has become a standard component in diesel fueled cars in Europe. The task of the catalyst is to reduce the emissions of particulates, as well as to provide some reduction in CO and HC emissions.

In the USA, the use of oxidation catalysts for highway heavy-duty engines was triggered in 1994, when the US EPA introduced a particulate matter emission standard of 0.1 g/bhp-hr for trucks and 0.05 g/bhp-hr for buses. Diesel oxidation catalysts were introduced on several truck and bus engines in order to meet that PM standard. However, the use of catalysts on US heavy-duty engines had been steadily decreasing, as the 0.1 g/bhp-hr PM standard could be achieved in more advanced, electronically controlled engines without the use of aftertreatment devices. The

reduction of particulate matter emission was the only purpose of the DOC; no reductions of gaseous HC or CO were necessary under the 1994 regulations. DOCs are being introduced again on certain heavy-duty engines meeting the 2004 emission standards, such as on the Caterpillar ACERT engines.

Oxidation catalysts have been also used in many diesel retrofit programs worldwide, mostly for heavy-duty engines. The US Urban Bus Retrofit/Rebuild program, which became effective in 1995, triggered retrofitting of pre-1994 urban bus engines with emission control devices, mostly diesel oxidation catalysts. DOCs were also used in the initial stage of the Swedish Environmental Zones program, and in diesel retrofits in a number of cities including Hong Kong and Tokyo.

NOx Reduction Catalysts

Reduction of NO_X in Lean Exhaust

Catalyst research has been increasingly focusing on catalysts for the reduction of oxides of nitrogen from lean exhaust gases. There is a need to reduce NO_X emissions from both heavy- and light-duty diesel engines significantly below levels which are currently achieved by means of engine design and calibration. Highly-efficient NO_X reducing catalysts would also allow to calibrate the diesel engine for maximum efficiency and fuel economy, which is currently being sacrificed for the sake of in-cylinder NO_X control.

NO_X reducing catalysts are needed not only for diesels, but also for lean burn spark ignited engines. Since the three-way catalyst remains the only commercially available, highly efficient NO_X control technology for mobile applications, today's gasoline engines are designed to operate at a stoichiometric air to fuel mixture. There is a significant fuel economy (and greenhouse gas emission) penalty associated with use of SI engines operating with stoichiometric A/F ratio. An impressive fuel economy improvement could be achieved by operating the gasoline engine at lean mixture. Catalysts that could bring nitrogen oxides emissions from lean-burn gasoline engines to the levels regulated in Europe and in North America would open the door for such engine technology.

The following catalytic approaches have been investigated for the control of NO_X in lean exhaust gases:

- NO decomposition catalyst
- Selective catalytic reduction with ammonia (SCR)
- Selective catalytic reduction with hydrocarbons (DeNOx or lean NO_X catalyst)
- NO_X adsorber-catalyst systems.

Decomposition of Nitric Oxide

Decomposition of nitric oxide to elements is described by the following equation:

$$2NO = N_2 + O_2 \tag{1}$$

The decomposition of NO is thermodynamically favored under pressures and temperatures found in diesel exhaust. However, the rate of the spontaneous reaction is practically zero. Catalysts have been researched to accelerate that process but no significant progress has been achieved. One of the best catalysts suggested for NO decomposition was a copper exchanged zeolite, Cu/ZSM-5. Copper exchanged zeolites were previously known to exhibit three-way catalyst activity for reducing NO_x in stoichiometric exhaust gas compositions [Ritscher 1981]. In a series of papers published in the late 1980s, Iwamoto and co-workers showed that Cu/ZSM-5, as well as other transition metal-containing molecular sieves, were able to catalytically decompose NO [Iwamoto 1991]. Although initially promising, catalytic decomposition of NO has proven difficult to realize. The decomposition of NO on Cu/ZSM-5 is subject to inhibition by water, is very sensitive to poisoning by SO_2, is effective only at low space velocities, and the catalyst activity and selectivity are not satisfactory.

Ammonia SCR Catalysts

Selective catalytic reduction (SCR) of NO_x can be realized if a reducing agent is injected into the gas upstream of the catalyst bed. SCR processes utilizing nitrogen containing reductants such as ammonia or urea are commercially available for stationary diesel engines and for industrial sources. Figure 2 schematically illustrates the SCR performance using ammonia as the reductant.
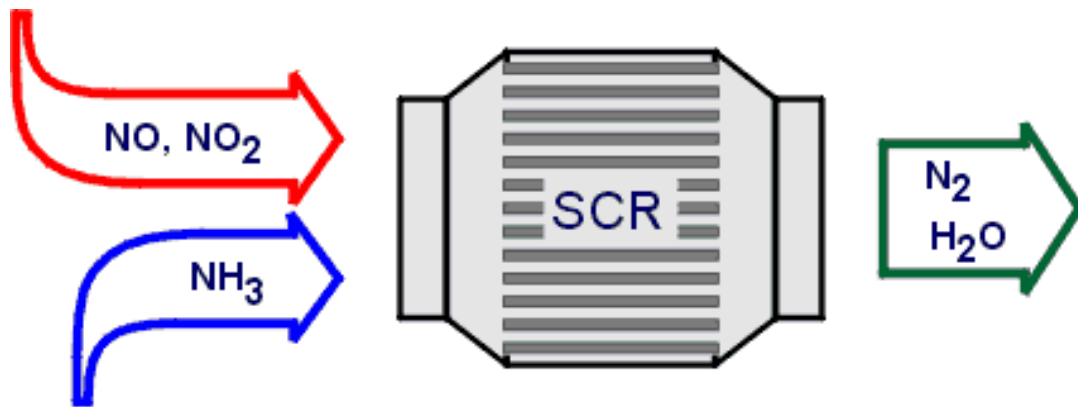

Figure 2. NO_x Reduction in SCR Catalyst

The primary selective reaction in this system is expressed by Equation (2). This reaction is promoted by the catalyst over the competitive reaction of NH_3 with oxygen, which is abundant in the system.

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \qquad\qquad (2)$$

The main advantage of SCR, which contributed to the widespread use of SCR in industrial (non-engine) applications, is its high NO_x conversion efficiency, reaching 90%. Disadvantages of SCR include high capital and operating cost, space requirements, generation of ammonia emissions (ammonia slip), and fouling of equipment with ammonium sulfate (hazardous waste).

SCR has been successfully adapted to control NO_x from large stationary diesel engines. It has been used on diesel power generation and cogeneration

> SCR technology for stationary and mobile diesel engines is presented in **Selective Catalytic Reduction**.

systems, primarily in Europe and Japan. SCR NO_x control systems have been introduced on large marine diesel engines.

Since the 1990s, there is ongoing interest in the application of SCR for mobile applications—trucks and diesel cars [Held 1990][Havenith 1997]. Since mobile applications of SCR would require a sophisticated, active catalyst system and the availability of a reductant (urea) fueling infrastructure, that technology is not the most attractive option for diesel trucks and cars. However, in the absence of more elegant NO_x reduction catalyst systems, SCR is an option for meeting future emission standards. Demonstration programs showed that NO_x emissions from existing heavy-duty Euro II engines (7 g/kWh) can be reduced by SCR to levels below 2 g/kWh, i. e., the Euro V standard [Fritz 1999]. Most heavy-duty engine manufacturers in Europe selected urea-SCR as the technology for meeting Euro IV/V emission standards. Stakeholders have been working on the implementation of the distribution network for aqueous urea solution, known under the trade name "AdBlue" [DMGK 2003]. SCR demonstration programs have been also conducted in the USA [Miller 2000]. The technology remains an option for meeting US 2010 NO_x emission standards for heavy-duty engines.

Lean NO_x Catalyst

One can substitute ammonia as the reducing agent in Equation (2) with hydrocarbons. By arbitrarily choosing propane as a representative HC, the reaction can be re-written as follows:

$$10NO + C_3H_8 = 5N_2 + 3CO_2 + 4H_2O \qquad\qquad (3)$$

Catalysts that promote the above reaction over the competitive, non-selective oxidation of hydrocarbons by oxygen are commonly referred to as *DeNOx* or *lean NO_x catalysts* (LNC). This selective DeNOx chemistry can be realized using either hydrocarbons emitted by the engine (so called "passive DeNOx" configuration) or else through the addition of extra hydrocarbons, such as diesel fuel, upstream of the catalyst ("active DeNOx"). Active DeNOx systems have higher NO_x conversion efficiency at a cost of increased system complexity and a fuel economy penalty.

> Selective catalytic reduction of NO_x by

It should be emphasized that the use of such terms as the "SCR" in reference to ammonia/urea based systems and "lean NO_x" or "DeNOx" in reference to

hydrocarbons is discussed in **Lean NO_x Catalyst**.

HC based catalysts is purely customary. Considering the nature of the chemical reactions, both processes represent selective catalytic reduction of NO_x. Both types of systems can be also described as lean NO_x catalysts, as determined by their capability to reduce nitrogen oxides under oxidizing, lean exhaust conditions. To complicate things even more, some authors use the term "DeNOx" in reference to any NO_x reducing catalyst technology, not necessarily limited to selective reduction by hydrocarbons. These terms should be used with caution to avoid confusion.

A combination of the lean NO_x catalyst with the diesel oxidation catalyst is sometimes called a *four-way catalyst*. The four-way catalyst is capable of simultaneous reduction of four diesel exhaust pollutants: CO, HC, PM, and NO_x.

Two different classes of DeNOx catalysts have been developed: (1) platinum-based catalysts and (2) base metal catalysts (Cu/ZSM-5). Each of these catalysts has its specific drawbacks, related primarily to narrow temperature windows, insufficient thermal durability and/or sulfur tolerance. More importantly, however, peak NO_x conversions of known DeNOx catalysts are in the range of 40-60%. Combined with relatively narrow temperature activity windows, these numbers translate to only about 10-20% NO_x conversions of passive systems on regulatory test cycles, such as the ECE/EUDC. Therefore, DeNOx catalysts are not currently seen as a technology capable of coping with the stringent future emission targets.

The ongoing research aimed at improving DeNOx catalysts has resulted in commercialization of this technology, primarily in the form of limited, passive NO_x removal functionality in oxidation catalysts. Several commercial diesel catalysts developed for the light-duty Euro 3 standard (year 2000) incorporate a passive DeNOx function and are capable of 5-15% NO_x reduction in addition to their main oxidation activity in respect to PM, CO, and HC [Kharas 1998].

NO_x Adsorber Catalysts

NO_x storage materials were first incorporated into DeNOx catalysts in an attempt to widen their temperature window. These compounds were supposed to adsorb NO_x during periods of low exhaust gas temperature, when the catalyst activity was low, and to release it at temperatures which would favor the selective reaction with hydrocarbons. This idea was then coupled with the three-way catalyst, producing nitrogen oxide *adsorber-catalyst systems*, also known as *NO_x traps*, which represent the newest concept in lean NO_x control research. First NO_x adsorbers have been commercialized on certain lean burn, DI gasoline engines in Japan and the EU. A huge amount of development work is being conducted worldwide to adapt this technology to the diesel engine. Laboratory experiments showed that NO_x adsorbers can achieve a 90% NO_x reduction efficiency

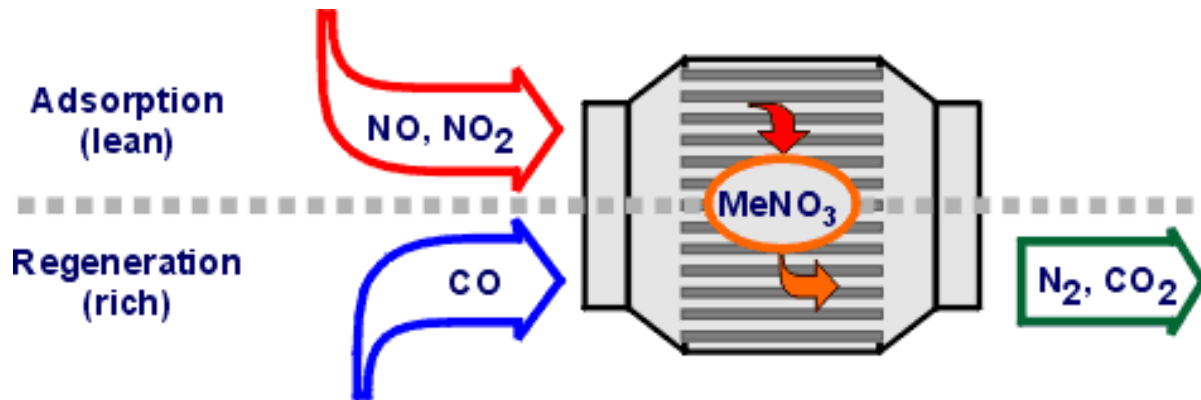over relatively wide temperature window.

Figure 3. Operation of NO_x Adsorber

These systems cycle through two stages of operation, including (1) storage (chemisorption) of NO_x in the catalyst washcoat during lean operation, and (2) regeneration of the trap through desorption and non-

> The application of NO_x traps to diesel engines is discussed in **NO_x-Adsorbers**.

selective catalytic reduction of NO_x during periods of rich operation. These phases of operation are schematically represented by the top and bottom parts of Figure 3, respectively. NO_x is stored in the form of a metal nitrate, shown as $MeNO_3$ in the schematic.

Regeneration of NO_x adsorbers involves reaction mechanisms virtually identical to those found in the gasoline three-way catalyst. A reductant, presumably carbon monoxide, reacts with NO_x in the absence of oxygen to form elemental nitrogen. Also the catalyst systems, such as the most common platinum/rhodium formulation, are very similar to the three-way catalyst. Since the regeneration requires periodic short pulses (say, a couple of seconds every minute) of rich A/F mixture, this technology requires extremely tight integration with the engine control system and is feasible only in conjunction with advanced electronic fuel injection systems. It also involves certain fuel economy penalty, which depends on the catalyst system, the required NO_x reduction, and on the quality of the regeneration algorithm.

The major stumbling block in the development of diesel NO_x adsorbers is their susceptibility to sulfur poisoning. Ultra low sulfur diesel (ULSD) fuels are the necessary condition for the commercialization of NO_x adsorbers. But ULSD alone is still not sufficient to solve sulfur deactivation and durability problems in NO_x adsorbers. Even if ultra low sulfur fuel is used, sulfur management strategies, including periodic desulfation, are required by this technology [Bailey 2000].

To conclude this overview, we should also mention a somewhat different NO_x adsorber concept

termed Selective NO_x Recirculation (SNR) [Krutzsch 1998]. In the SNR technique, two NO_x adsorbers are installed in parallel in the engine exhaust system. Control valves allow to switch the gas flow, so each of the adsorbers alternates between adsorption and desorption modes. While in the desorption mode, the NO_x carrying gas from the adsorber is recirculated to the engine intake air. This way, the desorbed NO_x can be reduced through in-cylinder reactions during regular combustion, through processes that appear to have something in common with the mechanisms on NO_x reduction by exhaust gas recirculation (EGR). The SNR technique eliminates the need for catalytic NO_x reduction, requiring a simpler catalyst system. Most likely, there is also less demand on the engine operating regime. However, SNR adsorber regeneration strategies still need to be demonstrated. In experiments involving feeding NO/NO_2 from bottles to the diesel engine air intake port (i.e., not accounting for the adsorber performance), the SNR achieved a NO_x reduction efficiency of 60%—much less than the adsorber-catalyst system.

It is common that commercial diesel catalysts incorporate a number of technologies into one catalytic device. Examples include oxidation and lean NO_x catalysts that incorporate hydrocarbon adsorbers/traps (see: Commercial Catalyst Technologies). Catalysts are also combined with non-catalytic devices to enhance their performance, the most prominent example being plasma assisted DeNOx catalyst (see: Plasma Exhaust Treatment).

Future Trends

As the emission standard deadlines approach, engine manufacturers must choose technologies for their future diesel engines. In Europe, urea-SCR became the technology of choice for meeting Euro IV and Euro V NO_x limits. From today's perspective, however, these standards—3.5 and 2.0 g/kWh, respectively—cannot be considered very stringent. Most likely, manufacturers will be able to meet them (certainly the Euro IV limit) using in-cylinder technologies, such as EGR, without the use of NO_x reduction catalysts. It is believed that two engine technologies will exist in parallel among Euro IV/V engines: urea-SCR and EGR.

More stringent NO_x limits have been adopted in the USA. Meeting the 2010 limit for heavy-duty engines of 0.2 g/bhp-hr or the light-duty Tier 2 (phase-in 2004-2009) Bin 5 limit of 0.07 g/mi is widely believed to require the use of NO_x aftertreatment. The same applies to the Tier 4 NO_x limit of 0.4 g/bhp-hr for nonroad engines, which becomes effective in 2014. The US EPA designed these low NO_x limits with the NO_x adsorber technology in mind. Contrary to European regulators, the US EPA has expressed reservations about urea-SCR technology, due to the urea infrastructure and regulatory enforcement issues.

On the other hand, several engine manufacturers would choose urea-SCR rather than NO_x adsorbers for NO_x control in future light- and heavy-duty diesel engines. NO_x adsorbers are still under development; their durability needs to be substantially improved before they become a

commercial technology. NO_X adsorbers are also believed to require larger and more expensive (noble metals) catalysts than SCR. Finally, the SCR path would allow many manufacturers to use the same or similar engine design in both European and North American markets.

A comparison of NO_X reduction technologies available to engine manufacturers, considering the state-of-the-art in 2003, was carried out by Ford [Lambert 2004]. The performance of urea-SCR, NO_X adsorber, and lean NO_X (HC SCR) catalyst on a light-duty engine is shown in Figure 4. It is clear that the urea-SCR catalyst provides an advantage over the NO_X adsorber, especially when tested over the FTP-75 cycle.
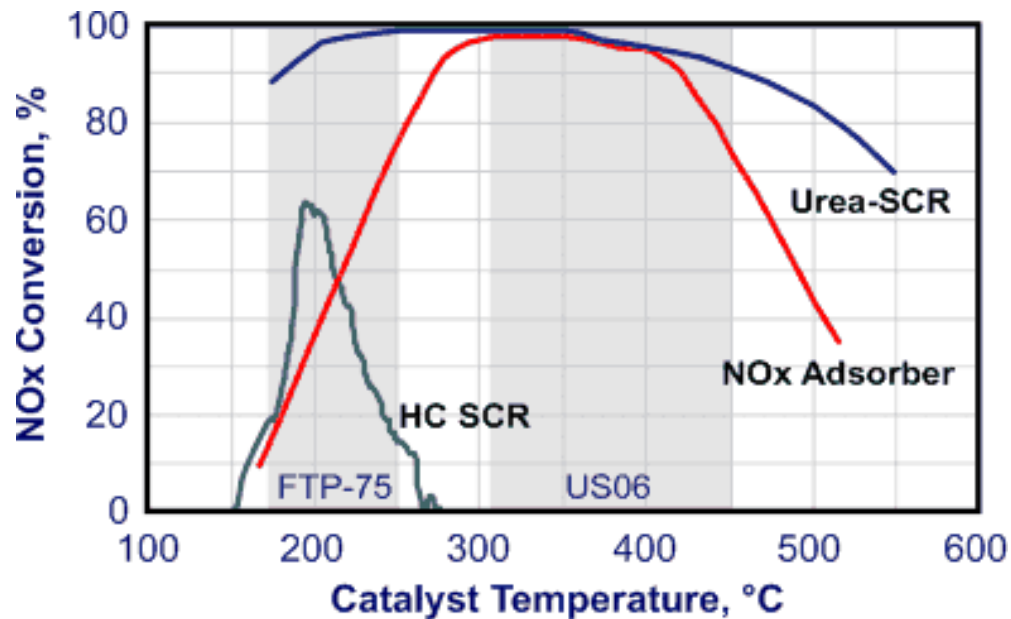

Figure 4. NO_X Conversion Using Different Catalyst Technologies

Slightly aged catalysts. Shaded areas indicate typical temperature ranges for underfloor converters over LD test cycles. SV = 30,000 1/h (catalyst volume about equal to the engine displacement).

The study examined, based on literature review and experiment, a number of other aspects related to the use of both technologies. It was concluded that urea-SCR can provide over 90% NO_X conversion, as required by future emission standards, with the following technical advantages over NO_X adsorbers:

- wider operating temperature window
- greater durability
- lower fuel economy penalty
- lower HC emissions
- lower greenhouse gas emissions

- lower system cost
- lower usage cost

These advantages are balanced by the known drawbacks of urea-SCR: (1) the necessity to establish and maintain urea infrastructure and (2) the long list of potential issues with urea replenishment (vehicle operators have a financial incentive not to replenish urea) [EC 2004]. And so, the choice of NO_x reduction technology in future diesel engines remains an open question, which is largely dependant on the progress in NO_x adsorber technology in the coming years.

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