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Catalysis in Diesel engine NO\textsubscript{x} aftertreatment: a review

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**Abstract** The catalytic reduction of nitrogen oxides (NO\textsubscript{x}) under lean-burn conditions represents an important target in catalysis research. The most relevant catalytic NO\textsubscript{x} abatement systems for Diesel engine vehicles are summarized in this short review, with focus on the main catalytic aspects and materials. Five aftertreatment technologies for Diesel NO\textsubscript{x} are reviewed: (i) direct catalytic decomposition; (ii) catalytic reduction; (iii) NO\textsubscript{x} traps; (iv) plasma-assisted abatement; and (v) NO\textsubscript{x} reduction combined with soot combustion. The different factors that can affect catalytic activity are addressed for each approach (e.g., promoting or poisoning elements, operating conditions, etc.).

In the field of catalytic strategies, the simultaneous removal of soot and NO\textsubscript{x} using multifunctional catalysts, is at present one of the most interesting challenges for the automotive industry.

**Keywords** Environmental catalysis, Air pollution, Diesel engine, NO\textsubscript{x} abatement, Nitrogen oxides

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**Introduction**

Air pollution from mobile sources, such as cars and trucks, contributes to a great extent to air quality problems and induces health risks in rural, urban, and industrialized areas in both developed and developing countries. About 60 million cars are produced every year and over 700 million cars are used worldwide. Moreover, the vehicle population is expected to grow to almost 1300 million by the year 2030.1

Most vehicle transport relies on the combustion of gasoline and Diesel fuels, and hence the emission of carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NO\textsubscript{x}), and particulates matter (PM) is of particular concern.2–4 The incomplete combustion of fuels causes the emission of partial oxidation products, such as alcohols, aldehydes. As a result of the thermal cracking reactions that occur in the flame, especially for incomplete combustion, hydrogen, as well as different hydrocarbons from those present in the fuel, are formed and emitted. Therefore, the total conversion of engine-out emissions into CO\textsubscript{2}, N\textsubscript{2}, and H\textsubscript{2}O using effective catalytic devices remains one of the most pressing challenges in the automotive industry.5–8

In the case of Diesel engines, the lean-burn conditions that are found in the combustion chamber lead to the following average composition of the emissions: CO\textsubscript{2}: 2–12%, H\textsubscript{2}O: 2–12%, O\textsubscript{3}: 3–17%, and N\textsubscript{2} balance. However, the features of the Diesel fuel itself, and of the Diesel engine operating conditions (air-to-fuel ratios greater than 22) lead to the formation of both gaseous (NO\textsubscript{x}, CO, HC) and solid/liquid (PM) pollutants.7 These Diesel engine emissions may originate from the incomplete combustion of fuel, from operating conditions that favor the formation of particular pollutants, or from the oxidation of nitrogen- and sulfur-containing compounds present in the fuel which are not hydrocarbons.3, 4 A common engine management strategy to control NO\textsubscript{x} emissions is Exhaust Gas Recirculation (EGR). In this strategy, part of the exhaust (with O\textsubscript{2}, N\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2}) is recycled back to the combustion chamber. In fact, since the heat capacity of CO\textsubscript{2} in the recirculated exhaust gas is about 20–25% higher than that of O\textsubscript{2} and N\textsubscript{2}, the energy released from the fuel combustion results in a lower temperature rise, and hence a lower peak cycle temperature, with consequent lower NO\textsubscript{x} levels. However, this strategy alone is not sufficient to meet the recent NO\textsubscript{x} regulations throughout the world.

The application of strict measures to control Diesel engine emissions has been the main reason for the reductions in emissions in western European countries. The introduction of new vehicle technologies (e.g. cooled EGR) and stringent inspection systems related to Euro standards (Table 1) have led to a progressive reduction in road traffic emissions, such as NO\textsubscript{x} since 1990, despite the increase in fuel consumption.6 Since NO\textsubscript{x} emission regulations have become more stringent over the last few years (Fig. 1), several catalytic DeNO\textsubscript{x} approaches have been investigated for lean-burn conditions, such as the direct decomposition of NO\textsubscript{x}, selective catalytic reduction (SCR) using different reducing agents (e.g. ammonia/urea, hydrocarbons), and NO\textsubscript{x} storage-reduction 10. 15. On the other hand, modern three-way catalysts cannot reduce NO\textsubscript{x} in the presence of excess oxygen, because high levels of oxygen suppress the necessary reducing reactions. Consequently, there is a strong driving force to develop multifunctional catalysts capable of reducing NO\textsubscript{x} to N\textsubscript{2} and of oxidizing PM, HC, and CO...
to CO₂ and H₂O under lean conditions. In the present paper, the role of aftertreatment catalysis in Diesel NOₓ abatement is discussed comprehensively.

### Direct catalytic NO decomposition

Engine-out NOₓ emissions mainly consist of NO (~90–95%) and, to a lesser extent, of NO₂. The main source of NO formation is the thermal (Zeldovich) mechanism. This mechanism takes place through a chain of high temperature reactions (greater than 1600 °C) and it is responsible for more than 90% of NOₓ emissions from road transport. During flame combustion, the reaction between N₂ and O₂ is thermodynamically favored (∆H°298 K = 180.6 kJ mol⁻¹), thus resulting in the formation of NO, according to the reaction:

\[
N₂ + O₂ \rightarrow 2NO
\]  

(1)

Direct NO decomposition (the reverse of equation (1)) has received considerable attention in the field of environmental catalysis, since the overall process is thermodynamically favored below 1000 °C, and the use of reducing agents is not required. In the catalytic decomposition of NO, the exhaust containing NO is made to flow over a solid catalyst, where the NO compound is split into its elements (2NO → N₂ + O₂). The main concern is to find a material that is both active and oxidation-resistant. Therefore, since the early 1990s, several materials have been investigated for direct NO decomposition.

### Noble metals

Direct NO decomposition is assumed to occur through four elementary steps:

\[
NO + \ast \leftrightarrow NO^* 
\]  

(2)

\[
NO^* + \ast \leftrightarrow N^* + O^* 
\]  

(3)

\[
N^* + N^* \leftrightarrow N₂ + 2\ast 
\]  

(4)

\[
O^* + O^* \leftrightarrow O₂ + 2\ast 
\]  

(5)

where NO*, N*, and O* are the adsorbed species on the catalytic active sites. Overall, the NO decomposition reaction consists of two parts: (i) adsorption and dissociation of the NO species (equations (2) and (3)); (ii) recombination and the removal of N₂ and O₂ from the catalyst surface (equations (4) and (5)).

Many studies have been conducted regarding NO decomposition over Pt–Al₂O₃ catalysts. Freund et al. have investigated the role of different adsorption and reaction sites on a structurally well-defined Pd/Al₂O₃ catalyst. They found that atomic nitrogen and oxygen species adsorb preferentially at sites in the vicinity of edges and defects of solid surfaces. The presence of these atomic species critically controls the NO dissociation activity. In other words, the direct decomposition of NO was found to be dominated by particle edges, steps, defects, and (100) sites rather than by (111) facets. Similarly, Ge and Neurock noted an exceptional low energy barrier for the dissociation of NO adsorbed on Pt (100) surfaces.

It has been shown that NO adsorption onto a solid surface is the kinetically controlling step, and the following kinetic equation has been proposed:

\[
r = N \cdot k \cdot (NO)/(1 + K \cdot (O₂)) 
\]  

(6)

where r is the reaction rate, N is the Avogadro number, k is the kinetic constant for NO adsorption, and K is the equilibrium constant for O₂ adsorption. This kinetic equation has been
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Cobalt oxide (Co$_3$O$_4$) is one of the most active compounds. Metal oxides have been studied as catalysts for direct NO decomposition, as can be seen in Table 2. Among these, cobalt oxide (Co$_3$O$_4$) is one of the most active compounds. The high activity of Co$_3$O$_4$ seems to be related to the relatively weak Co–O bonds, which lead to an easy desorption of lattice oxygen (O$_{l}$-species), especially at low temperature. Co$_3$O$_4$ shows a spinel structure with Co$^{2+}$ and Co$^{3+}$ cations. During the direct NO decomposition reaction, Co$^{3+}$ may partially oxidize to Co$^{2+}$ and form a Co$_2$O$_3$-like phase on the surface. The latter is not stable and decomposes to Co$_3$O$_4$ thus favoring NO dissociation.

Iwamoto et al. have found that promoting Co$_3$O$_4$ catalysts with small amounts of Ag results in a significant increase in the catalytic activity. Moreover, the decrease in the NO decomposition activity with an increase in the O$_{2}$ concentration was less marked when Co$_3$O$_4$ was doped with Ag. With the addition of either Ag or Na, the activity in fact enhances primarily due to the excess electron density on the surface.

The NO decomposition activity of metal oxides is closely related to the bond strength between the metal and the oxygen in the lattice. NO usually dissociates on the metal oxides, although NO dissociation depends on several factors, including the temperature, surface coverage, crystal planes, and surface defects. The catalytic activity of metal oxides towards the NO decomposition is usually lower than that of noble metals. Therefore, the operating temperature must be kept at quite high values (up to 1000 °C), which can lead to catalyst sintering, and is of no interest for Diesel exhaust applications. As a whole, the inhibiting effect of oxygen is lower for metal oxides than for noble metals. Moreover, the oxygen “self-poisoning effect” towards NO decomposition can be much lower on ceria-based materials, as a consequence of oxygen spillover phenomena.  

Table 2 Catalytic activity of metal oxides for the decomposition of NO. Reaction conditions: P$_{NO}$ = 2.0%; W/F = 0.5 g s cm$^{-3}$

| Catalyst          | Oxygen content (%) | Conversion of NO to N$_2$ (%) 500 °C | Conversion of NO to N$_2$ (%) 600 °C |
|-------------------|--------------------|--------------------------------------|--------------------------------------|
| Fe$_2$O$_3$       | 0                  | 3.8                                  | 11                                   |
|                   | 5                  | 0.2                                  | 1.8                                  |
| Co$_3$O$_4$       | 0                  | 25                                   | 77                                   |
|                   | 5                  | 2.0                                  | 39                                   |
| NiO               | 0                  | 3.5                                  | 15                                   |
|                   | 5                  | 3.7                                  | 1.9                                  |
| CuO               | 0                  | -                                    | 9.7                                  |
|                   | 5                  | 0.7                                  | 1.8                                  |
| CeO$_2$           | 0                  | 0.4                                  | 0.1                                  |
|                   | 5                  | 0.4                                  | 2.5                                  |
| Ag-Co$_3$O$_4$    | 0                  | 6.5                                  | 38                                   |
|                   | 5                  | 18                                   | 25                                   |

Source: Adapted from Ref.29

Frank et al. have observed good performances for Pt-Mo-based materials. Specifically, the catalyst with the best activity exhibited Pt-Mo-Co components, thus suggesting cooperation phenomena among several active centers. The latter catalyst decomposed ca. 60% NO at 150 °C (in the absence of CO). However, when CO was increased to 0.6%, the maximum NO conversion decreased to ca. 40% at 220 °C. The authors explained this catalytic behavior by showing that NO$_{abatement}$ begins when CO is fully oxidized and they argued that CO does not participate in NO$_{2}$ reduction.

Metal oxides

Several metal oxides have been studied as catalysts for direct NO decomposition, as can be seen in Table 2. Among these, cobalt oxide (Co$_3$O$_4$) is one of the most active compounds. The high activity of Co$_3$O$_4$ seems to be related to the relatively weak Co–O bonds, which lead to an easy desorption of lattice oxygen (O$_{l}$-species), especially at low temperature. Co$_3$O$_4$ shows a spinel structure with Co$^{2+}$ and Co$^{3+}$ cations. During the direct NO decomposition reaction, Co$^{3+}$ may partially oxidize to Co$^{2+}$ and form a Co$_2$O$_3$-like phase on the surface. The latter is not stable and decomposes to Co$_3$O$_4$, thus favoring NO dissociation.

Ver phenomena. Zhang et al. have performed studies on CeO$_2$–ZrO$_2$ mixed oxides, which exhibit interesting activities in NO$_{2}$ decomposition.

Perovskites

Perovskite-type catalysts have been widely investigated for the direct decomposition of NO, as reported in Table 3.

Mixed oxides with an ABO$_3$ chemical composition, in which the A cation is either a rare earth or an element of the II group (e.g. La, Sr, Ba, Y, etc.) and B is a transition 3d metal, belong to this category of catalysts. The substitution of A or B ions with other metals creates oxygen defects in the lattice, which are generally related to the catalytic activity, although the nature of these interactions has not yet been fully understood. However, it is known that oxygen-deficient perovskites adsorb large amounts of oxygen, and that the nature and reactivity of the adsorbed oxygen, which are more weakly bonded with metal cations, are quite different from the oxygen in the

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their sintering.44 Research should therefore be addressed to
ovskite-type oxides with low surface areas (<2 m² g⁻¹), due to
a high reaction temperature (>900 °C) and hence yield per-
used for the synthesis of perovskite-type materials, involve
reaction and co-precipitation methods, which are commonly
low surface areas and pore volumes. The ceramic solid–solid
decomposition activity. Other significant drawbacks are their
disadvantage of NO decomposition on perovskite catalysts is
removal of soot and for NO abatement. The most significant
fying exhaust gas from Diesel engines, particularly for the
oxygen, these materials should be good candidates for puri-
fishments of these materials toward several oxidation reac-
tions. Perovskites exhibit high thermal stability, compared to
metal oxides and metals, because of the presence of ions and
cations, which can assume a variety of charged states.
The effects of dopants in BaMnO₃ perovskites on the direct
NO decomposition activity have been investigated by Iwakuni
et al. The authors observed that the activity of NO decomposi-
tion increased by an order of Mg > Zr > Fe > Ni > Sn > Ta for
the Mn-site dopant, and La > Pr for the Ba site.
Teraoka et al. considered the effect of the preparation
method and catalyst composition on the activity toward NO
decomposition for several perovskites with a general formula
LaₓSr₁−ₓCoO₃ (X = Co, Cr, Mn, Fe, Ni and Cu).
Kim et al. observed that under realistic conditions,
LaₓSrCoO₃ catalysts exhibit higher NO-to-NO₂ conversions
than commercial Pt-based catalysts.
Complex perovskite-type catalysts have been prepared by
Monceaux et al. The authors have found that the substitu-
tion of a small quantity of Pt for Mn or Co makes it possible
to prevent sulfur poisoning and to increase the catalytic per-
migration of the reaction active sites, and the dealumination
deactivation, such as agglomeration of the active metal, the
It has been reported that the primary causes for the thermal
deactivation, such as agglomeration of the active metal, the
migration of the reaction active sites, and the dealumination
of zeolite support, can be obviously suppressed by the intro-
duction of a second metal.45 In particular, the addition of Ce
greatly improves the hydrothermal stability of the Cu/ZSM-5
catalysts, since Ce species stabilize the dispersion of CuO and
suppress the bulk-type CuO crystallites formation.31,52
As a whole, the NO decomposition over Cu/ZSM-5 pro-
cceeds via a redox-type mechanism.53 In other words, Cu⁺ ions
created through a thermal pre-treatment can be oxidized
to Cu²⁺ by gaseous oxygen. Thus, Cu²⁺ acts as an adsorption
center for NO, as follows:
\[ \text{Cu}^{2+} + \text{NO} \leftrightarrow \text{Cu}^{+} \text{NO}^+ \] (7)
NO molecules can be chemisorbed as NO⁺, NO³⁻, and NO₂⁻
species on the zeolite surface. A fraction of the Cu⁺ ions is
reduced to Cu⁺ through the desorption of O₂, whereas catalyst
re-oxidation with NO restores Cu⁺ sites, thus forming N₂.
The catalytic behavior of Cu/ZSM-5 is negatively affected by
the relatively high oxygen concentration in the feed, thus
limiting their use for applications in Diesel exhausts. For instance,
a maximum conversion rate of 6% has been obtained at 500 °C
for a feed similar to Diesel exhausts (1000 ppm NO and 10
vol.% O₂), which is far too low to be acceptable.53 Moreover,
this material is not stable in water vapor conditions for long
periods of time and it has proved to be sensitive to SO₂ poi-
sioning.54 As a whole, the presence of water vapor has an inhi-
bition (although reversible) effect on the decomposition of
NO, whereas SO₂ poisons the catalyst surface.
On the other hand, Weisweiler et al. have observed that
Pt/ZSM-5 catalysts may be able to adsorb NO under con-
trolled dynamic conditions (simulation of a driving cycle),
although real NO abatement cannot be attained at low tem-
peratures (below 180 °C).
Researchers are usually critical about the use of zeolite-type
catalysts for direct NO decomposition, since they have shown
low hydrothermal stability and low SO₂ resistance.54,55 On the

### Table 3: Catalytic activity of perovskite-type oxides for the decomposition of NO. Reaction conditions: P_NO = 2.0%;
W/F = 0.5 g s cm⁻³

| Catalyst            | Oxygen content (%) | Conversion of NO to N₂ (%) 500 °C | Conversion of NO to N₂ (%) 600 °C |
|---------------------|--------------------|----------------------------------|----------------------------------|
| SrFeO₃ₓ             | 0                  | 0.12                             |                                  |
| LaCoO₃              | 5                  | 3.8                              | 0.44                             |
| LaₓSr₁−ₓCoO₃        | 0.5                | 6.3                              | 0.49                             |
| YBaₓCu₉O₁₅₋ₓ        | 0                  | 1.5                              | 6.3                              |

Source: Adapted from Ref.29
other hand, since the operating temperatures of these catalysts are usually higher than those required for the catalytic reduction of NO, the decomposition route, even though very attractive, is actually not very interesting for application in aftertreatment exhaust devices.

**Selective catalytic reduction (SCR) of NO**

Since the ideal solution of direct catalytic NO decomposition has not been successful for the control of Diesel engine emissions, researchers have begun to investigate alternative approaches, such as the selective catalytic reduction (SCR) of NO.

The catalytic reduction of NO has been studied using a number of reductants, of which ammonia, urea, and hydrocarbons are the most frequently reported. Catalytic reduction with ammonia (or urea) is usually referred to as NH\textsubscript{3}-SCR, while reduction with hydrocarbons is often referred to as HC-SCR.

Several catalytic materials have been developed for the SCR of NO since the early 1970s. The first generation of commercial SCR catalysts for mobile applications was monoliths containing V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3}/TiO\textsubscript{2}, which were similar to the V\textsubscript{2}O\textsubscript{5}-based catalysts used for NH\textsubscript{3}-SCR in stationary applications. However, the stringent legislations on NO\textsubscript{x} based catalysts used for NH\textsubscript{3}-SCR in stationary applications. The reduction of NO with hydrocarbons is often referred to as HC-SCR.

Use of ammonia/urea as a reductant

The reduction of NO by using ammonia is a widely commercialized technology for large stationary combustion plants (e.g. power plants, heaters and boilers in the process industry). In Japan, USA, and Europe, large-scale applications of SCR have been introduced over the last few decades.

Ammonia is commonly used as a reductant agent in large commercial scale SCR. NH\textsubscript{3} is supplied to the SCR process using a gaseous solution (anhydrous form), an aqueous solution, or a solution of urea. The choice depends on the economic and safety issues involved in the handling of the preferred solution, that is, anhydrous ammonia. As a whole, a high efficiency of NO\textsubscript{x} removal can be obtained with the NH\textsubscript{3}-SCR process (namely 70–98%). The uniqueness of this reaction with NH\textsubscript{3} is that it can occur in the presence of excess O\textsubscript{2}. Thus, this technology has received a great deal of attention for Diesel-engine vehicles.

The overall NH\textsubscript{3}-SCR reaction is:

4NO + 4NH\textsubscript{3} + O\textsubscript{2} ↔ 4N\textsubscript{2} + 6H\textsubscript{2}O “Standard SCR reaction” (8)

The role of oxygen is to donate one electron to the redox process. Thus, oxygen enhances the rate of the NO–NH\textsubscript{3} reaction. A complex reaction network can be observed on the catalyst surface. The main prevailing reactions are:

6NO + 4NH\textsubscript{3} ↔ 5N\textsubscript{2} + 6H\textsubscript{2}O

4NO + 4NH\textsubscript{3} + O\textsubscript{2} ↔ 4N\textsubscript{2} + 6H\textsubscript{2}O

6NO\textsubscript{2} + 8NH\textsubscript{3} ↔ 7N\textsubscript{2} + 12H\textsubscript{2}O “NO\textsubscript{2}-SCR reaction”

2NO\textsubscript{2} + 4NH\textsubscript{3} + O\textsubscript{2} ↔ 3N\textsubscript{2} + 6H\textsubscript{2}O

NO + NO\textsubscript{2} + 2NH\textsubscript{3} ↔ 2N\textsubscript{2} + 3H\textsubscript{2}O “Fast SCR reaction”

These reactions are inhibited by water, which can be present in the exhaust gases. However, other reaction pathways may occur and, as a result, undesired products can be formed. These reactions may include a partial reduction of NO\textsubscript{x} which leads to N\textsubscript{2}O (equations (14)–(16)), or the direct oxidation of NH\textsubscript{3}+, which forms NO (equations (17)–(18)):

8NO\textsubscript{2} + 6NH\textsubscript{3} ↔ 7N\textsubscript{2}O + 9H\textsubscript{2}O

4NO\textsubscript{2} + 4NH\textsubscript{3} + O\textsubscript{2} ↔ 4N\textsubscript{2}O + 6H\textsubscript{2}O

2NH\textsubscript{3} + 2O\textsubscript{2} ↔ N\textsubscript{2}O\textsubscript{3} + 3H\textsubscript{2}O

4NH\textsubscript{3} + 3O\textsubscript{2} ↔ 2N\textsubscript{2} + 6H\textsubscript{2}O

4NH\textsubscript{3} + 5O\textsubscript{2} ↔ 4NO + 6H\textsubscript{2}O

Particular temperature conditions (100–200 °C) may lead to the formation of NH\textsubscript{4}NO\textsubscript{3} which is explosive and deposits in the cavities of the catalytic material, causing temporary deactivation. One possible way of reducing the ammonium nitrate or other byproducts is to tailor the reductant injection with different amounts rather than stoichiometric with respect to NO\textsubscript{x}:

2NH\textsubscript{3} + 2NO\textsubscript{2} + H\textsubscript{2}O ↔ NH\textsubscript{4}NO\textsubscript{3} + NH\textsubscript{4}NO\textsubscript{2} (19)
The DOC oxidizes the NO to NO\textsubscript{2}, and this compound is more reactive and extends the operating temperature window for the SCR process. In this way, the catalyst can take advantage of the “fast SCR” (equation (13)) to significantly enhance the DeNO\textsubscript{x} efficiency at low temperatures\textsuperscript{10, 14}. The SCR catalyst can be fouled and deactivated due to the deposition of ammonium sulfate and disulfate, resulting from the oxidation SO\textsubscript{2}, with the subsequent formation of H\textsubscript{2}SO\textsubscript{4} in the DOC, and the reaction with NH\textsubscript{3} in the SCR. The SCR deactivation occurs at temperatures below 250 °C; hence, at low temperatures (150–250 °C), the urea injection can be interrupted to prevent SCR catalyst deactivation. Urea has mainly been selected as the best ammonia source, due to its low toxicity, safety, availability, and low cost. However, 32.5% urea solutions have freezing temperatures of −11 °C, which is not acceptable for winter conditions in cold climates. Thus, the use of ammonium formate (HCO\textsubscript{2}NH\textsubscript{4}) has been proposed for SCR applications in cold climates (a 40% aqueous solution of HCO\textsubscript{2}NH\textsubscript{4} has a freezing point of −35 °C), but it has a lower NH\textsubscript{3} content than urea. An alternative reductant supply method is to use solid urea rather than aqueous solutions.

An interesting approach has been introduced by Tarabulski et al.\textsuperscript{65} in which urea, or another reducing agent, is employed in the SCR process in a solid state (Fig. 3). Aqueous solutions of urea or other reagents are not required in the Tarabulski process. The solid reagent is fed to a gas generator that produces a reactant gas through heating; the latter gas is rich in NH\textsubscript{3}, and can therefore be added to the exhaust gas on an as-needed basis.

The layout of an SCR process for mobile Diesel engines, fueled with urea, is generally structured as an open-loop control, namely the amount of injected urea follows a pre-determined route of the NO\textsubscript{x} emissions as a function of the engine operating conditions. This technology has been shown to yield above 80% conversion of the engine-out NO\textsubscript{x}.\textsuperscript{14} The urea solution is injected into the exhaust line upstream from the SCR catalyst. The atomization allows the solution that has been tailored to obtain a good mixing with the exhaust gasses to evaporate quickly, a process that can be assisted through the use of static mixers. A uniform distribution of the flow in the catalytic converter is necessary to reach high conversion efficiencies.\textsuperscript{64} The SCR is usually placed after the Diesel oxidation catalyst (DOC), which is used to oxidize CO, HC, and part of the NO (Fig. 2).

![Figure 3 Experimental plant developed by Tarabulski et al. to test solid urea as a reducing agent for NO\textsubscript{x} abatement\textsuperscript{65}](image-url)
basis for NO\textsubscript{x} abatement. Using urea or another solid reducing agent can cause nozzle plugging and fouling of the catalyst. This technology offers several advantages, including the realization of significant savings in energy, which would otherwise be necessary to vaporize the water, and savings on the cost of antifreeze additives. The temperature that must be reached for urea gasification is about 400 °C and, to reduce the vessel volume, it is possible to use solid catalysts, such as platinum, palladium, oxides of vanadium, titanium, and chromium. However, the SCR systems that have been proposed for dosing solid urea appear more complex than those that utilize urea water solutions, which are now the most common applications for Diesel engines.

Platinum, vanadium oxide and zeolites

Two important features of an SCR catalyst are that the material is active as an oxidation catalyst, and that materials which are effective in partial oxidation, when supported on TiO\textsubscript{2} (namely anatase), are usually good SCR catalysts.\textsuperscript{2} Such materials can be based on V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3} on TiO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5}–MoO\textsubscript{3} on TiO\textsubscript{2}, although other materials (e.g. zeolites) have been considered. The main reason for such dominance is that they offer excellent performances, yet at the same time they are very tolerant toward poisons in the flue gasses.\textsuperscript{2,4} The anatase form of TiO\textsubscript{2} is the preferred support, mainly because SO\textsubscript{2} poisoning has a lower influence on the TiO\textsubscript{2} surface.\textsuperscript{4}

The first SCR technology that was developed was based on a Pt-containing catalyst. However, NO\textsubscript{x} reduction over the Pt surface is only effective at temperatures below 250 °C (Fig 4).\textsuperscript{2} In fact, at temperatures between 225 and 250 °C, the oxidation of NH\textsubscript{3} to NO and H\textsubscript{2}O (equation (18)) becomes dominant and, as a result, poor selectivity toward N\textsubscript{2} can be achieved/observed. On the other hand, low temperatures (150–200 °C) may lead to the above-mentioned NH\textsubscript{4}NO\textsubscript{3} formation, which entails a very narrow range of available working conditions.\textsuperscript{2} Moreover, Pt catalyzes the reduction of NO\textsubscript{x} to N\textsubscript{2}O, which is a powerful greenhouse gas. Pt has the benefit of generally being insensitive to SO\textsubscript{2} and possesses good thermal stability, but it may favor the formation of SO\textsubscript{4}\textsubscript{2}−.

Vanadium oxide catalysts act well in a wider and upper temperature range, from 260 °C up to 450 °C, with the best SCR performances taking place between 300 and 400 °C.\textsuperscript{7} This range is optimal for both light-duty (lower limit) and high duty (upper limit) applications. Catalytic materials, such as V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2}, are capable of NO\textsubscript{x} reduction in excess of 90%, and they are most probably the best candidates to meet severe NO\textsubscript{x} reduction goals.\textsuperscript{14} Despite discrepancies concerning the detailed nature of the active centers, there is general consensus in experimental analyses that the SCR reaction involves both Brønsted (V–OH) and Lewis (V=O) acidic sites, and hence the presence of water has significant effects on the SCR process.\textsuperscript{14} The terminal V\textsuperscript{5+}=O groups of V\textsubscript{2}O\textsubscript{5} appear to be essential in carrying out this reaction, since they are the energetically favored sites and, in addition, are accessible for the formation of Bransted acidic sites. Thus, ammonia can readily adsorb on V\textsuperscript{4+}–OH species to form an NH\textsubscript{4}+ intermediate, which subsequently reacts with co-adsorbed NO to form the adsorbed (NH\textsubscript{3}–NHO)\textsuperscript{+} intermediate. The N–H bond in the ammonium intermediate is broken as it reacts with NO (from the gas-phase). The proton which transfers from the NH\textsubscript{4}+ to the V\textsubscript{2}O\textsubscript{5} surface during this initial step is subsequently transferred back to the NO molecule from the V\textsubscript{2}O\textsubscript{5} (redox cycle). Ultimately, V\textsuperscript{5+}=O groups can be restored via proton transfer. This produces gas-phase NH\textsubscript{2}NO, which can be converted into N\textsubscript{2} and H\textsubscript{2}O through subsequent reactions over V\textsubscript{2}O\textsubscript{5}.\textsuperscript{1,17}

Several studies have confirmed an Eley–Rideal-type mechanism (ER) for the SCR reaction, where ammonia adsorbs onto the V\textsubscript{2}O\textsubscript{5} surface and NO molecules react from the gas-phase (or as weakly adsorbed species) on the solid surface. Although ER is the prevalent mechanism in most of the operating conditions, at low temperatures (<200 °C), the reaction seems better described as a Langmuir–Hinshelwood-type mechanism (LH), thus suggesting that the SCR process takes place between adsorbed NH\textsubscript{4}+ and NO species on the solid surface.\textsuperscript{2} Moreover, Dumesic et al.\textsuperscript{9} proposed an SCR catalytic cycle, which consists of two cycles interacting with each other (namely acid-base and redox cycles), thus confirming the complexity of this catalytic system. V-species can in fact act simultaneously as Lewis/Brønsted acidic and redox centers (Fig. 5).

Over the last few years, reports on health issues concerning vanadium emissions from SCR catalysts in mobile applications,\textsuperscript{18} V\textsubscript{2}O\textsubscript{5} having been classified as possibly carcinogenic
to humans (group 2B),71 have limited its further exploitation for mobile systems.

Therefore, zeolites containing transition metal ions (Cu, Fe, Cr, Mn, Ni, Ce, etc.) have been investigated extensively for mobile applications.19 Zeolite-type catalysts have been considered for special applications, in particular for low-sulfur fuels. Unfortunately, however, zeolites are relatively expensive and thus are not suitable for extruded monoliths, although they are suitable for coated monoliths.3

Zeolitic materials have a relatively wide temperature range of application (300–450 °C), and the most frequently studied material for the SCR reaction is Cu-exchanged ZSM-5.14, 15, 29, 30 This catalyst does not oxidize NH₃ to NO₂ at high temperatures, and the upper temperature limit for the SCR process depends on its structural stability.72

Low-temperature zeolites have also been synthesized, with the aim of widening the temperature range at which they are operative, and moderate NOₓ to N₂ conversion efficiencies of between 200–400 °C have been reached.73 Metal-exchanged zeolites have been found to adsorb considerable amounts of NH₃ under certain operating conditions, and this results in rather slow responses to temperature variations or changes in NOₓ concentration. The NH₃ adsorption capacity of catalysts depends to a great extent on the temperature; unwanted ammonia slip occurs for the increases of fast temperature.65

Moreover, it has been observed that the SCR reaction shows considerable sensitivity to the nature of the support, and hence comparative studies on different zeolite supports (ZSM-5, A, beta, FAU, ferriette, CHA, Linde type L) have been performed. From these studies, it emerged that Fe- or Cu-exchanged ZSM-5 zeolite showed good activity and selectivity for N₂ production.14 However, they demonstrate a lack of hydrothermal stability at temperatures above 700 °C. In particular, Cu-CHA catalysts have become the state of the art in NH₃-SCR catalysis for Diesel vehicles, due to their excellent low temperature activity and high hydrothermal stability,74, 75 which makes it a valuable candidate in the functionalization of DPFs with NH₃-SCR catalysts, in order to increase the operating temperatures of the SCR catalysts by being close-coupled with the DOC instead of in underfloor position, in the so-called “SCR on filter” concept. Indeed, compared to ZSM-5 or beta-type zeolites, the chabazite zeolite contains small-sized pores and can coordinate isolated Cu²⁺ species, which are more resistant to hydrothermal aging.76

Many other NH₃-SCR catalysts have been investigated over the years. Among these, it is worth mentioning Fe₂O₃, Fe-containing mixed oxides, and Fe-exchanged materials that may show good SCR performances.10, 77 Similarly, Mn-oxides have received much/ a great deal of interest for the SCR reaction because of their low-temperature activity, although they exhibit low selectivity for N₂ production. In particular, MnCr₂O₄ spinel-Oxide Catalysts have shown promising catalytic results, as they can reach an NO conversion of 96% and selectivity to N₂ of 97% at 125 °C.78

Use of hydrocarbons as reductants

An alternative to the use of ammonia as a reductant agent is the employment of hydrocarbons, namely the HC-SCR process. The latter is also known as DeNOₓ or lean-NOₓ process. According to this approach, the hydrocarbons can be oxidized by the oxygen present in NOₓ as follows:

\[ \text{NO} + \text{hydrocarbon} + \text{O}_2 \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \] (23)

The reaction of equation (23), which leads to N₂, CO₂, and H₂O, is not the only path involved in the NO reduction, since undesired products, such as N₂O, can also be obtained.

It is thought that the HC-SCR reaction proceeds competitively with the combustion reaction of hydrocarbons, and the selectivity to N₂ determines the feasibility of the HC-SCR process. The selectivity can be defined as the ratio between the amount of hydrocarbon oxidized by NO, with subsequent N₂ formation, and the total reacted hydrocarbon. Thus, the HC promoted SCR reaction of the NO reduction and the simple HC combustion are10:

\[ \text{C}_x\text{H}_y + (2x + 1/2y)\text{NO} \leftrightarrow (x + 1/4y)\text{N}_2 + 1/2y\text{H}_2\text{O} \] (24)

\[ \text{C}_x\text{H}_y + (x + 1/4y)\text{O}_2 \leftrightarrow x\text{CO} + 1/2y\text{H}_2\text{O} \] (25)

Consequently, catalyst selectivity is the key parameter that has to be optimized using suitable catalytic materials, as well as a suitable reducing agent, HC/NOₓ ratio, temperature range, and so on.

As highlighted by/in Zelenca et al.,77 the research should be conducted in three main directions:

- Choice, characterization, and improvement of suitable catalytic materials, which should be industrially available;
- Determination of the most efficient hydrocarbon through the injection of different hydrocarbon compounds into the synthetic gas ahead of the catalyst to increase NOₓ conversion rates;
- Optimization of the different parameters that affect the catalyst performance, in order to improve its use with vehicles.

An important parameter for NOₓ abatement is the HC to NOₓ ratio; generally, a two to fourfold surplus of hydrocarbons (expressed as ppm-HC) relative to the NOₓ concentration (ppm-NOₓ) is necessary to reach ca. 80% NOₓ conversion.78–80 As such a surplus of hydrocarbons is not usually present in Diesel exhaust gases, hydrocarbons or Diesel fuel would have to be added to the Diesel exhaust gases.81–83 There are two main possibilities of HC enrichment, that is, low or high pressure injection of Diesel fuel ahead of the catalyst (“active DeNOₓ”) and utilization of unburned HC emissions directly from the engine exhaust gas (“passive DeNOₓ”). In “active DeNOₓ,” systems, the increase in the HC amount, and the control of their concentration to optimize the SCR catalyst can be realized by two means: the injection of hydrocarbons, preferably Diesel fuel, into the exhaust system upstream of/from the catalyst, or late in-cylinder injection in a common rail fuel system. The DOC system, which has a classical CO/HC emission reduction function, can be positioned downstream from the DeNOₓ system, in order to also undertake the role of preventing possible HC emissions.

On the other hand, “passive DeNOₓ” should be a simpler and cheaper option, since no additional injection equipment would be necessary. However, since the HC concentration in the exhausts is dependent on the engine points and it is
somewhat limited, low conversion efficiencies can be reached. In order to achieve the necessary HC concentrations, engine modifications should be undertaken, in order to obtain higher hydrocarbon emissions. As a result, active DeNO_{x} systems offer higher NO\textsubscript{x} conversion efficiency, but at the cost of increased system complexity and a fuel economy penalty.

A wide variety of metal oxides, alumina-based catalysts, zeolites, and perovskites have so far been tested for this promising technology. The first catalyst screening, which shows the catalytic behavior of several metals (Pt, Au, Cu, Co and Ag) supported on Al\textsubscript{2}O\textsubscript{3} and ZSM-5, was published by Obuchi et al. Then, Ag/alumina have been found to be promising catalysts for the selective catalytic reduction of NO\textsubscript{x} to N\textsubscript{2}, by hydrocarbons in laboratory tests as well as in full-scale diesel engine operation.

The addition of small amounts of H\textsubscript{2} can promote the HC-SCR activity of Ag-based catalysts for low temperature NO\textsubscript{x} reduction. Over the years, several explanations have been proposed for this beneficial “H\textsubscript{2}-effect”, including the enhancement of the partial oxidation of the reducing agent, the formation of reactive N species (NCO-like groups or gas phase radicals) from the reducing agent, the easier formation of active cationic Ag clusters, and the destabilization of surface nitrates blocking active Ag sites. Hence, H\textsubscript{2} promotes the HC-SCR activity of Ag-based catalysts through multiple roles, involving morphological, chemical, and kinetic changes.

Appropriate reductants, such as C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, CH\textsubscript{3}OH and C\textsubscript{2}H\textsubscript{5}OH (which are efficient reductants), were used. The catalytic performances for each catalyst are summarized in Table 4. The most promising materials are based on platinum, although the high emission of N\textsubscript{2}O is a difficult problem to solve. For this reason, the most suitable catalyst seems to be the Co/Al\textsubscript{2}O\textsubscript{3} one, with the addition of an oxidation catalyst downstream to prevent the leakage of non-reacted or incompletely oxidized reductants. De Soete has published an interesting work that shows the reduction rate expressions of NO to N\textsubscript{2} in the HC-SCR reaction over Cu/ZSM-5. The author has found that C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{5}OH, when used as reductants, show different catalytic behavior: the reaction order in C\textsubscript{2}H\textsubscript{6} is negative, whereas it is positive for C\textsubscript{2}H\textsubscript{5}OH. In fact, ethylene is less active in NO reduction than n-hexane, although HC oxidation is lower.

Many studies have shown that hydrocarbons do not participate directly in the reduction of NO, but they are first partially oxidized to active intermediates (e.g. aldehydes) which then can react with NO to form N\textsubscript{2} and O\textsubscript{2}. On the other hand, Bell et al. reported that, for HC-SCR over Co- M\textsubscript{n}-Fe- and Pd-ZSM-5, the highly active species are CN groups which react with NO\textsubscript{x} to form N\textsubscript{2} and CO\textsubscript{2}.

### Zeolite-type catalysts

As a whole, the HC-SCR activities of zeolite-type catalysts are better than those of metal oxides, such as alumina. The crystalline structure seems to contribute to the high activity of the zeolites. Thus, several zeolite-related compounds, such as metallo-silicates and silicoaluminophosphates, have been reported to be active for the HC-SCR reaction. Interestingly, lanthanum co-exchange resulted in an improvement in the NO adsorption capacity of the zeolite, both in the absence and in the presence of water.

Pt-ZSM-5 is more stable than Cu-ZSM-5: Iwamoto et al. investigated the long-term stability of Pt-ZSM-5 under simulated and actual exhaust conditions, and found that its activity did not decrease in the presence of water vapor or SO\textsubscript{2} in the reactant stream. Moreover, they observed that the catalyst activity barely changes after 1000 h exposure to water vapor. On the other hand, the catalytic performances of Cu-exchanged zeolites are affected by the presence of SO\textsubscript{2} (Fig. 6).

Falley et al. have prepared a new catalytic material, based on a zeolite chosen from between β-Zeolite Y-Zeolite and ZSM-5, in which Cu, Co, and Fe have been incorporated as active species. They observed that a combination of these three metals tends to lower the temperature at which a Cu-containing

| Catalyst  | Reductant | Catalytic performances | Note                        |
|-----------|-----------|------------------------|-----------------------------|
| Cu/ZSM-5  | C\textsubscript{2}H\textsubscript{6} | Maximum conversion: 33% (370 °C) | No production of N\textsubscript{2}O |
| Co/Al\textsubscript{2}O\textsubscript{3} | CH\textsubscript{3}OH | Maximum conversion: 40% (370 °C) | No production of N\textsubscript{2}O but CH\textsubscript{3}OH emissions |
| Ag/Al\textsubscript{2}O\textsubscript{3} | C\textsubscript{2}H\textsubscript{5}OH | Maximum conversion: 31% (460 °C) | N\textsubscript{2}O and aldehydes produced from 370 °C |
| Pt/Al\textsubscript{2}O\textsubscript{3} | C\textsubscript{2}H\textsubscript{6} | Maximum conversion: 41% (215 °C) | High N\textsubscript{2}O production |
| Pt/ZSM-5  | C\textsubscript{2}H\textsubscript{6} | Maximum conversion: 33% (240 °C) | High N\textsubscript{2}O production from 240 °C |

Source: Adapted from Ref.85
catalyst reaches its optimum NO\textsubscript{x} conversion rate (Fig. 7), particularly after aging (Fig. 8). This trimetallic-based system lends stability to the catalytic material, so that NO\textsubscript{x} conversion rates after an accelerated ageing cycle are higher than those of comparative materials.

Although Cu is the exchange metal chosen for most studies, many other metals have been tested, either alone or as co-cations: interesting tests were carried out using Gallium and Cerium. Gallium exchanged ZSM-5 was tested in SCR with 1000 ppmv of NO and C\textsubscript{3}H\textsubscript{6} by Yogo \textit{et al.}\textsuperscript{96} who found that this catalyst exhibits similar catalytic behavior to that of Cu-based systems.

Over the last few years, new multicomponent catalysts have been designed to expand the lean NO\textsubscript{x} reduction capacity of zeolite-type catalysts. For instance, Deeba \textit{et al.}\textsuperscript{102} reported interesting NO\textsubscript{x} conversions over new four-way catalysts, which were active over a temperature range of between 150 and 320 °C. These materials allow hydrocarbons to be activated and stored; these hydrocarbons then reduce NO\textsubscript{x} selectively. Moreover, synergistic phenomena (e.g. cooperative adsorption) in the HC-SCR reaction can be observed for zeolite-type catalysts when different hydrocarbons (e.g. CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8}) are used as reductant agents\textsuperscript{103, 104}.

**Supported noble metals**

Due to the low hydrothermal stability of zeolitic materials, several researchers have addressed their efforts to the development of noble metal catalysts.\textsuperscript{105–108} An interesting work on the catalyst choice for the HC-SCR process was conducted by Nakatsuji \textit{et al.}\textsuperscript{105} and remarkable results were shown for the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst. This catalyst can be active at 300 °C and exhibit good catalytic stability in the presence of SO\textsubscript{x}, which is further improved by the addition of WO\textsubscript{3}, MoO\textsubscript{3}, and Pt. The authors observed that catalyst activity can be improved by adding the aldehydes that form from the injected fuel in the exhaust gas. Thus, they tried to partially oxidize fuel in a catalytic oxidizing reactor before injecting it into flue gas. The results obtained using this system are very interesting: at 450 °C, the engine bench test exhibited an NO\textsubscript{x} conversion of 75%.

Several works have been published on platinum-group metals, mainly due to their relatively high surface stability.\textsuperscript{107, 108} Bamwenda \textit{et al.}\textsuperscript{109} studied platinum-group metals (Pt, Pd, Rh and Ir) deposited on different supports (TiO\textsubscript{2}, ZnO, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}) for the SCR of NO in the presence of C\textsubscript{3}H\textsubscript{6}. They found that the alumina supported catalysts showed both the highest activity for NO conversion and the highest selectivity toward N\textsubscript{2} formation. The catalytic activities followed the Pt/Al\textsubscript{2}O\textsubscript{3} > Rh/Al\textsubscript{2}O\textsubscript{3} > Pd/Al\textsubscript{2}O\textsubscript{3} > Ir/Al\textsubscript{2}O\textsubscript{3} order, whereas Rh/Al\textsubscript{2}O\textsubscript{3} was found to have the highest selectivity toward N\textsubscript{2} formation\textsuperscript{110}.

Other studies have been carried out for Ag supported on Al\textsubscript{2}O\textsubscript{3}\textsuperscript{110–116} or saponite.\textsuperscript{108} Miyadera \textit{et al.}\textsuperscript{110} have shown that 2 wt.% Ag/Al\textsubscript{2}O\textsubscript{3} can reduce NO with ethanol (a higher molar ratio of C\textsubscript{2}H\textsubscript{5}OH/NO, than 1.25), even in the presence of water vapor, although several byproducts may appear (e.g. N\textsubscript{2}O, NH\textsubscript{3}, CH\textsubscript{3}CN and HCN). Cyanide is the dominating byproduct below 400 °C (the typical exhaust temperature of a Diesel engine), although its concentration decreases at higher temperatures.
The influence of the reducing agents (C$_x$-C$_y$ hydrocarbons) on the HC-SCR of NO in a Ga$_2$O$_3$-Al$_2$O$_3$ system has been studied by Miyahara et al.$^{108}$: the most efficient NO abatement was achieved with C$_3$ hydrocarbons, whereas C$_2$ hydrocarbons were less selective for N$_2$ production. Thus, it has been proposed that only one carbon atom per molecule is used for/in the HC-SCR process, and the other carbons are consumed by the combustion reaction. However, under wet conditions, the NO conversion on the Ga$_2$O$_3$-Al$_2$O$_3$ catalyst decreased for all the hydrocarbons. The decrease in NO conversion caused by the presence of water is due to the preferential adsorption of water, which inhibits the HC adsorption on the catalyst surface (competitive adsorption).$^{110}$ Noble metals should be added to avoid the retarding effect of water vapor. For instance, Haneda et al.$^{109}$ have studied the catalytic behavior of an Indium supported catalyst (5 wt.% In/TiO$_2$-ZrO$_2$) for the SCR of NO with C$_3$H$_6$ with or without the presence of water: a decrease in NO conversion occurred under wet conditions. However, the authors observed that small amounts of Pd (0.005–0.02 wt.%) may improve the ‘resistance’ of In/TiO$_2$-ZrO$_2$ against the presence of water (up to ca. 400 °C).

Highly dispersed Au catalysts have been studied for the HC-SCR of NO in recent years.$^{111}$ These catalysts are active in the reduction of NO with C$_x$H$_y$ in the presence of O$_2$ and moisture. The catalytic behavior of Au-species depends on the metal oxide support. In fact, an activity scale has been drawn up: α-Fe$_2$O$_3$ < ZnO < MgO < TiO$_2$ < Al$_2$O$_3$. The highest conversion to N$_2$ (around 70%) at 427 °C has been achieved over a 0.1–0.2 wt.% Au/Al$_2$O$_3$ catalyst.$^{111, 112}$ It is worth noting that the conversion of NO to N$_2$ over Au/Al$_2$O$_3$ was increased slightly by the presence of water: a decrease in NO conversion occurred under wet conditions. However, the authors observed that small amounts of Pd (0.005–0.02 wt.%) may improve the ‘resistance’ of In/TiO$_2$-ZrO$_2$ against the presence of water (up to ca. 400 °C).

NO$_x$ traps

NO$_x$ traps (or NO$_x$ adsorbers) constitute an interesting NO$_x$ control technology for gasoline direct injected engines and for Diesel engines. NO$_x$ traps are also referred to using different terms: Lean NO$_x$ traps (LNT), NO$_x$ adsorbers catalysts (NAC), DeNO$_x$ traps (DNT), NO$_x$ storage catalysts (NSC), NO$_x$ storage/reduction (NSR) catalysts.

NO$_x$ traps, which are incorporated into the catalyst washcoat, chemically bind the NO$_x$ species and convert them into solid species (metal bonded nitrates). NO$_x$ accumulation is carried out during lean conditions, and proceeds until the adsorber capacity is saturated. Then, the NO$_x$ trap is regenerated, and the released NO$_x$ species are reduced to N$_2$ when a rich air-to-fuel mixture is injected.$^{114}$

Since the rich mode of operation is not feasible for Diesel engines, periodic fuel injections are necessary. The amount of fuel and the periodicity of the injections, as well as the storage capacity of the materials, are the main parameters that need to be optimized to reduce the fuel penalty associated with this technology.

Among the main drawbacks, it should be pointed out that the supply of additional fuel to either the cylinder or directly to the exhaust pipe, causes PM, CO, and HC emissions, whose concentration must comply with the current legislation limits. Moreover, the regeneration step must be carried out as efficiently as possible in order to prevent it from having too much of an impact on the fuel economy of the vehicle. Finally, NO$_x$ adsorbers can be poisoned by sulfur compounds,$^{2, 115, 116}$ thus requiring both the use of low sulfur Diesel fuels and the development of efficient desulfation strategies. Therefore, low sulfur fuels favor NO$_x$ conversion levels and reduce the frequency of the desulfation step.

Operating principles

During operating conditions, the NO$_x$ reduction takes place according to a two-stage mechanism, as shown in Fig. 9. The NO$_3$ trap combines the effect of an oxidation catalyst (e.g. platinum), an adsorbent material (e.g. BaO), and a reduction catalyst (e.g. rhodium).

The exhaust is rich in NO (a thermodynamically stable species at high-temperatures), but traps are more effective toward NO$_x$ entrapment. Therefore, the step immediately before NO$_x$ adsorption should be the NO oxidation to NO$_3$ step. This operation is performed by means of an oxidation catalyst, such as a Pt-containing system, which is able to operate at the low exhaust temperatures of light-duty Diesel engines, as follows$^{60, 117}$:

$$\text{NO} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{NO}_2$$ (26)

The NO$_2$ formed on the solid surface is trapped on an adsorbent (BaO) in the form of a nitrate (e.g. Ba(NO$_3$)$_2$), which is chemically stable at the operating conditions. Thus, the following reaction steps can occur$^{10, 60}$:

$$\text{BaO} + \text{NO}_3 \leftrightarrow \text{BaO} - \text{NO}_2$$ (27)

$$\text{Ba(NO}_3)_2 \leftrightarrow \text{BaO} + \text{NO}$$ (28)

$$\text{BaO}_2 + 2\text{NO}_2 \leftrightarrow \text{Ba(NO}_3)_2$$ (29)

The adsorption capacity of an NO$_3$ trap depends on the accessibility of the BaO sites, which must be regenerated when a certain NO$_x$ concentration is attained at the exit of the converter. During the regeneration process, the oxygen concentration decays to almost zero, and redundant conditions for NO abatement are thus achieved.

The first regeneration step consists of the decomposition of the Ba(NO$_3$)$_2$ and the recovery of the BaO active phase (equation (30)). In this step, NO is released and hence a suitable amount of fuel has to be dosed in order to reduce the released NO.$^{60}$

$$\text{Ba(NO}_3)_2 \leftrightarrow \text{BaO} + 2\text{NO} + \frac{3}{2}\text{O}_2$$ (30)

NO reduction is carried out by means of a reducing catalyst, such as an Rh-based system, incorporated in the catalyst formulation.$^{118}$ This reduction step is similar to that which occurs in a conventional three-way converter for the treatment of the exhausts from gasoline fueled engines. When the engine is switched to a fuel-rich condition, HC, CO, and H$_2$ react with the
The operating temperature of these NOx traps has a lower limit, which is determined by the Pt activity toward the NO oxidation, as well as the NO release and reduction in the regeneration step; on the other hand, the upper limit is related to the stability of the NOx species, which undergo thermal decomposition at high temperatures, even under lean conditions.

It is worth noting that several complex phenomena may appear on the surface of NOx traps, since they are multicomponent materials which have different functionalities. For instance, BaCO3 and Ba(OH)2 coexist with BaO on the catalyst surface. Moreover, NOx release and reduction may not occur as consecutive steps, but, as a first step, it could appear via a direct nitrate reduction, without thermal decomposition of the adsorbed NOx species. Therefore, it is very difficult to investigate the NOx storage/release mechanisms of these catalytic materials.

NOx adsorbents are sensitive to sulfur species: sulfur is a poison for Pt-sites and, in the form of SOx, it is competitive with NOx in the formation of barium salts (e.g. BaSO4), thus causing a loss of activity toward the adsorption of NOx (= competitive adsorption). BaSO4 is more stable than the corresponding nitrate, and hence its decomposition occurs at higher temperatures. Finally, the possibility of having parasitic reactions that lead to undesired products (e.g. NH3, NOx, H2S) reduces the NOx trap efﬁciency, and a careful control of the secondary emissions is also necessary.

**Multifunctional catalysts**

NOx traps are multifunctional catalysts that display adsorbent, oxidation, and reduction functionalities. These materials consist of alkaline earth metals (Ba, Ca, Sr, Mg), alkali metals (K, Na, Li, Cs), and rare earth metals (La and Y). As a whole, they appear in the form of binary oxides, mixed oxides (perovskites), and metal-containing zeolites. In particular, alkali metals, such as potassium, show the highest NOx conversion efficiency among these metal groups: the inclusion of K, Na, and Cs-based oxides in the adsorbent oxides increases the NOx reduction to between 350 and 600 °C. Another remarkable advantage of alkali metals is their good resistance to sulfur poisoning: their inclusion in Ba-containing materials leads to a better performance; however, this in turn leads to a lower NOx conversion, due to the hydrocarbons, which makes the adsorbent catalyst more fuel demanding.

Finally, alkali-based materials exhibit low performances and give rise to leaching effects in the presence of water vapor. It is therefore necessary to find a trade-off between the good NOx reduction activity at high temperatures of alkali metal oxides and their excessive mobility, in order to include them in Ba-based systems.

NOx traps for light-duty Diesel engines, which operate at lower temperatures, may eliminate the necessity of using alkali metals.

A washcoat is usually obtained using γ-Al2O3. Washcoats are often employed due to their high surface area (> 100 m2 g⁻¹); this allows high dispersion of the active sites. Ba and Al mixed oxides are designed to limit BaO sintering in the 700-800 °C temperature range. Another washcoat component is TiO2, whose acidity gives a lower sulfur affinity, although it also reduces the stability of nitrates. CeO2 can be considered a good washcoat component as it prevents Pt-sintering. However, its high oxygen storage capacity (OSC) can cause a higher fuel penalty during rich fuel conditions, since some of the hydrocarbons react with the released oxygen. The effects of BaO loading on the trapping capacity of NOx and on the overall conversion performance of NOx are summarized in Fig. 10. In this work, the catalyst consisted of Pt (2.20 wt.%) and BaO (16.3 wt.%) over Al2O3, and it showed a mean NO conversion of 85% over cycles lasting 60 s, with injection of C3H6 every 10 s. The complete cycle involves a fuel penalty which can be kept under 4% with an overall NO conversion above 80%. The regeneration strategy is closely related to the nature of the reductant species. The regeneration step is constituted by a short pulse of a reducing agent, such as H2, CO, or HC, to convert the stored nitrates. The activity of a complex multicomponent catalyst toward NOx reduction is reported in the work by Takahashi et al.; the catalyst consisted of an Al2O3-based washcoat of CeO2–ZrO2 oxygen storage materials, with Ba and K oxides as the NOx storage compounds and with Pt and Rh as the supported noble metals. Figure 11 reports a schematization of the adsorption capacity of the fresh/regenerated catalyst: the capacity of the reductant species to restore the BaO sites is considered. “Lean 1” is the inlet composition of the gas fed (namely at 250 °C), and represents a gas model for the exhausts; when the lean atmosphere is switched on, the outlet NOx concentration gradually increases with time, up to reach a constant level.
of the trap, in the so-called Di-Air system. The fundamental finding of this phenomenon is that a high-frequency injection of hydrocarbons might considerably improve the NO\textsubscript{x} regeneration phase, at high temperatures, with a very moderate fuel penalty (<2%).

The combination of different catalytic functionalities could also be implemented to achieve synergies that increase the overall NO\textsubscript{x} abatement efficiency. A relevant example is the embodiment of an SCR catalytic functionality in a NO\textsubscript{x} trap. This system was presented by Ford in 2004, and widely studied by the group at the University of Houston (see the general concept in\textsuperscript{130}). The concept is based on the fact that, in the presence of H\textsubscript{2} during the rich pulses of the NO\textsubscript{x} trap regeneration, NH\textsubscript{3} can be formed by direct reaction with the previously stored NO\textsubscript{x}\textsuperscript{131}; CO instead leads to NH\textsubscript{3} formation through intermediate isocyanate species, in water-assisted reaction. The water gas shift reaction makes both pathways to co-exist, due to the presence of CO\textsubscript{2} and H\textsubscript{2}O in the exhausts.\textsuperscript{131} The suitable proportion of the SCR and NO\textsubscript{x} trap catalysts in the overall formulation is determined by the amount of NH\textsubscript{3} generated in the NO\textsubscript{x} trap during its regeneration, which should be utilized by the SCR adsorption sites. Since it was found that only the neighboring SCR catalyst concurs in adsorbing the NH\textsubscript{3} produced in the NO\textsubscript{x} trap in the reduction stage, a dual-layer configuration (two layers with different composition) outperforms the dual-brick (consecutive washcoat formulations along the axial length), largely because the NH\textsubscript{3} generated in the NO\textsubscript{x} trap layer is better utilized in an adjacent SCR layer.\textsuperscript{130} The optimal configuration in terms of relative thickness of the layers depends on the operating temperatures and SCR site density.

**Plasma-assisted catalytic NO\textsubscript{x} reduction**

Non-thermal, atmospheric pressure plasma has been widely studied for the removal of VOC from waste gas streams for almost 20 years.\textsuperscript{132}

Non-thermal plasma (NTP) discharges in exhaust gas have been investigated as a potential technology to reduce NO\textsubscript{x} and PM emissions in Diesel exhaust as well as NO\textsubscript{x} and cold start hydrocarbons in lean gasoline exhaust.

NTP is generated, by means of an electrical excitation, to induce thermodynamically unstable NO\textsubscript{x} species; the latter should decompose into N\textsubscript{2} and O\textsubscript{2}.\textsuperscript{133–135} On the other hand, oxidative NO\textsubscript{x} reactions dominate the subsequent kinetics, converting most flue gas NO to NO\textsubscript{2} and HNO\textsubscript{3}\textsuperscript{133–135} through reactions with plasma-produced oxygen and hydroxyl (equations (33) and (34)).

\[
\text{O} + \text{NO} \leftrightarrow \text{NO}_2 \quad (33)
\]

\[
\text{OH} + \text{NO}_2 \leftrightarrow \text{HNO}_3 \quad (34)
\]

Several other byproducts can be produced, including N\textsubscript{2}O, N\textsubscript{2}O\textsubscript{3}, N\textsubscript{2}O\textsubscript{4}, HONO, and HONO\textsubscript{2}, and the selectivity of the plasma aftertreatment therefore remains an important drawback, as does the large power requirement. The electric power supply has similar characteristics for each experimental setup: the ΔV range is from 5 to 35 kV and the frequency is about 1 kHz. Park \textit{et al.} investigated NO\textsubscript{x} abatement for Diesel...
removal efficiency. Thus, lower temperatures can be used in the removal of NO to NO\textsubscript{2} rather than NO.\textsuperscript{137–140} This means that the NTP reduction achieves a higher conversion of NO to N\textsubscript{2}O\textsubscript{5} (vide supra); hence, NTP can oxidize NO without depleting the number of hydrocarbons available for the reduction of NO\textsubscript{2} to N\textsubscript{2}.\textsuperscript{142} This means that the function of SCR catalysts could be greatly simplified by focusing on the reduction of NO\textsubscript{2} by hydrocarbons.

A different approach has been studied by Bittenson et al.,\textsuperscript{143} who proposed generating atomic nitrogen in an electric discharge external to the exhaust stream, followed by rapid injection and mixing into exhaust gas to achieve an NO\textsubscript{2} chemical reduction.

\[ \text{N} + \text{NO} \leftrightarrow \text{N}_2 + \text{O} \] (35)

This approach leads to the elimination of the generation of very reactive oxygen and hydroxyl species by the discharge, thus preventing contact between soot and wet particles and allowing for lower pressure drops. In this case, the electrical power supply has a larger frequency: 40–60 kHz.

**Simultaneous NO\textsubscript{x} and soot removal systems**

The stringent regulation limits on both NO\textsubscript{x} and PM are forcing the automotive industry, one hand, to maximize engine control to reduce pollutant emissions, and on the other hand to design reduction systems that are cost-effective. In this context, Diesel particulate traps appear to be necessary. Our research group has been involved in several European R&D programs (e.g., CATATRAP, DEXA-cluster, TOP-Expert, ATLANTIS) for several years, with the aim of developing novel multifunctional catalytic traps.\textsuperscript{144} The simultaneous removal of soot and NO\textsubscript{x} in a single catalyzed filter (single brick solution) represents the most ambitious strategy in this field, in view of the considerable advantages in terms of both investment costs and pressure drop reduction.

The possibility of obtaining a contemporary reduction in NO\textsubscript{x} and soot from Diesel engine exhausts has clearly been pointed out in several kinetic studies (Fig. 13).\textsuperscript{14, 15, 145–149} Fino et al.\textsuperscript{145} studied the kinetics of a soot-NO\textsubscript{x} reacting system over perovskite-type catalysts and formulated two reaction mechanisms (Fig. 14). In mechanism 1, soot combustion leads to the formation of two oxygen vacancies on the catalytic surface, which become active centers for the chemisorption of NO\textsubscript{x} and/or hydrocarbon supplies for fixed conversion efficiency. Similarly, the HC-SCR process occurs via oxidation of NO, followed by the reduction of NO\textsubscript{x} with hydrocarbons (vide supra); hence, NTP can oxidize NO without depleting the number of hydrocarbons available for the reduction of NO\textsubscript{2} to NO\textsubscript{3}. This system is presented to be active for this technology.\textsuperscript{135–139}

As a whole, plasma reactors are pulsed corona-type reactors and the catalyst is generally placed after the plasma device (Fig. 12).\textsuperscript{135} Although plasma aftertreatment favors oxidation over reduction, a useful synergism can be observed when it is combined with a catalyst.\textsuperscript{135} The reducing capability of some catalysts is enhanced considerably when NO\textsubscript{x} is presented to catalytic surfaces as NO\textsubscript{2} (peroxyl radicals favor the conversion of NO to NO\textsubscript{x}) rather than NO.\textsuperscript{137–140} This means that the NTP technology may significantly improve catalyst selectivity and removal efficiency. Thus, lower temperatures can be used in NO\textsubscript{x} reduction with plasma-catalyst technology than with NTP. An increase in temperature improves catalytic activity but the function of SCR catalysts could be greatly simplified by focusing on the reduction of NO\textsubscript{2} by hydrocarbons.

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lower the reaction rate by filling up the oxygen vacancies over the oxidation catalysts.154–156 On the other hand, according to mechanism 2, carbon plays a role in the reduction of NO through the formation of C(N,O) adducts. The latter are formed through the combination of reactive free carbon (C\text{f}) and the NO molecule adsorbed on the catalyst surface (NO\text{ads}). Finally, N\text{2} can be formed through the reaction of C(N,O) with further NO\text{ads} (LH-type kinetics) or directly with a gaseous NO molecule (ER-type kinetics). However, it is also possible for N\text{2} to be formed through the decomposition of C(N,N) adducts. According to this mechanism, the promoting effect of oxygen can be ascribed to the formation of active centers for NO chemisorption on C\text{f} as a consequence of carbon combustion. The other beneficial effect is the easy formation of N\text{2} which is much more active than NO for the reduction of soot. Thus, the presence of soot has a beneficial effect in a combined SCR + CSF at low temperature, since it may promote the reduction of NO\text{X} (via the “fast SCR reaction”). On the other hand, the NO\text{X}/NO ratio has to be kept close to one for effective SCR + CSF systems.

**DeSoot-DeNO\text{X} Catalysts**

La-K-Cu-V-based perovskites have shown their potential application as active catalysts for the simultaneous removal of NO\text{X} and soot. The role of vanadium species in the perovskite lattice has been found to be prevalent in obtaining outstanding NO\text{X} abatement efficiencies. Nevertheless, several other complex reaction pathways involving reaction intermediates, either present on the catalyst surface or on that of the carbon particulate itself, could take place. On the other hand, nanostructured spinel-type oxide catalysts, that is, AB\text{2}O\text{4} (where A = Co and Mn, B = Cr and Fe) have proved to be particularly active in the simultaneous removal of soot and NO\text{X} in the 350–450 °C temperature range.145, 146 The best compromise between soot and NO abatement below 400 °C has been shown by the CoCrO\text{3} catalyst. The relevant activity of chromite catalysts could be explained by their higher amount of suprafacial, weakly chemisorbed oxygen (α-species), which contributes actively to soot combustion through spillover in the 300–500 °C temperature range. Similarly, nanostructured perovskite-type lanthanum ferrites, that is, La\text{1−x}Fe\text{x}B\text{2}O\text{4} (where A = Na, K, Rb and B = Cu) have displayed high catalytic activity toward carbon combustion and NO conversion in the same temperature range. Other multicomponent catalysts, characterized by the highest possible α-oxygen type concentration, have been prepared by our group over the last few years, with careful attention being paid to their compatibility with the substrate material or to the poisoning components present in the Diesel exhaust gas (e.g. sulfur oxides). Using a standard protocol on an engine bench, promising results have been obtained with the La\text{0.9}K\text{0.1}Cr\text{0.9}O\text{3−δ}+1 wt% Pt catalyst over a wall-flow SiC trap.150 The presence of Pt in fact aids the oxidation of NO and therefore allows more NO:NO\text{2}-NO cycles before it leaves the catalyst (the efficiency of NO\text{2} utilization can be as high as 140% on average). Li et al.151, 152 and Kotarba et al.153 have reported that K-promoted CoMgAlO\text{2} hydrotalcite can favor soot combustion, but can also lead to a 30% conversion of NO\text{X} under “real” conditions. Lin et al.154 have shown high catalytic activity of BaAl\text{2}O\text{4} systems for the simultaneous removal of soot and NO\text{X} under “loose” contact conditions.

It is worth noting that ceria-based catalysts have received a great deal of attention because CeO\text{2} alone, or in combination with other metals/metal oxides, may exhibit promising oxidation activity under either O\text{2} or in a NO/O\text{2} atmosphere.155 Thus, zirconium and many rare earth elements (e.g. La, Pr, Sm, Y, Gd, Tb, Lu, Hf and Nd) have been introduced into the ceria framework to improve the oxidation activity (OSC and redox properties) of CeO\text{2} mixed oxides and their structural stability. The redox behavior and the availability of chemisorbed oxygen (α-species) are important features for these materials.156–158 Atribak et al.149 have reported interesting results with Ce–Zr mixed oxides for soot combustion under NO/O\text{2} atmosphere. The different mixed oxides, Ce\text{1−x}Zr\text{x}O\text{2} provided the best performance.159 The same authors observed that the most active mixed oxides are those which combine high surface areas

![Figure 13](image-url)  
**Figure 13** Reaction mechanisms proposed for the soot/NO\text{2}/O\text{2} reacting system over perovskite-type catalysts  
Source: Adapted from Ref.142

![Figure 14](image-url)  
**Figure 14** Simultaneous abatement of NO\text{X} and soot over different solid catalysts: 1 = mobile catalyst; 2 = catalyst promoting oxygen spillover; 3 = catalyst coupling a NO → NO\text{2} functionality148
with a homogeneous distribution of cerium and zirconium throughout the particles (Ce/Zr surface ratio about 3:2).\textsuperscript{149}

The number of soot-catalyst contact points also plays a significant role in complex solid–solid–gas systems, just as the overall activity for NO\textsubscript{x} and soot removal depend on the interaction between the two solids and the gas mixture.\textsuperscript{150, 161} Nanostructured CeO\textsubscript{2},-based materials, or other mixed oxides, are particularly interesting because of their small-featured size, which endows them with size- and shape-dependent properties due to the high surface-to-volume ratio (= higher number of coordinated unsaturated sites), and their unique electronic features (quantum size effects).\textsuperscript{152-156} Moreover, the effects of cooperation between active sites (or between different phases) are favored, thus leading to a simultaneous NO\textsubscript{x} and soot abatement.

**Some issues pertaining to Diesel NO\textsubscript{x} aftertreatment catalysts**

One of the main current issues for NO\textsubscript{x} aftertreatment catalysts is that no material seems to ensure a high NO\textsubscript{x} abatement throughout the whole Diesel exhaust temperature range (i.e. 200–500 °C).\textsuperscript{2, 4, 8, 14, 10} As reported above, many multicomponent catalysts have been designed over the years to increase their NO\textsubscript{x} abatement activity and to cover a broader temperature range. This is often possible since synergistic (beneficial) effects may arise through phase-cooperation (namely, the structural relations among atoms/ions/electrons) and spillover phenomena.\textsuperscript{160, 161} Moreover, solid catalysts must be active and stable during operating conditions. As far as the former aspect is concerned, catalytic materials are usually tested under laboratory conditions, which can be sometimes be different from real operating conditions. For instance, researchers may perform the activity tests with relatively low GHSV or O\textsubscript{2} concentrations; however, high values of these parameters are known to adversely affect NO\textsubscript{x} abatement. Similarly, two features of Diesel exhausts can be critical for catalyst stability, that is, the sulfur content and the presence of water vapor associated with high temperatures. Sensitivity to sulfur poisoning can also be a major problem for metal-exchanged zeolites.\textsuperscript{95} Feeley \textit{et al.}\textsuperscript{152, 156} have found that long-term exposure of Cu-ZSM-5 to SO\textsubscript{2} leads to its permanent deactivation. Conversely, Pt-based catalysts may exhibit good resistance to poisoning by SO\textsubscript{2}.\textsuperscript{54} Nevertheless, these catalysts favor the oxidation of SO\textsubscript{2} and thus cause an increase in the total mass of the particulate emitted. Moreover, phosphorous from lubricating oil can cause a decline in catalyst performance.

In the case of low-temperature DeNO\textsubscript{X} catalysts, a further problem still has to be solved, that is, the formation of N\textsubscript{2}O instead of N\textsubscript{2}, with a subsequent negative environmental impact, due to the fact that N\textsubscript{2}O is a greenhouse gas.\textsuperscript{159}

Sensitivity to water vapor is a very critical limitation for the hydrothermal stability of catalysts, several methods have been proposed over the years, but none of them seems so far to have completely solved the problem. On the other hand, as previously mentioned, Pt-ZSM-5 (Pt nanoparticles dispersed on the zeolite surface) is more resistant to water vapor.\textsuperscript{170} Nevertheless, the low selectivity, and hence the relatively high amounts of N\textsubscript{2}O formed in the presence of this catalyst are important issues that still need to be solved. Nanostructured mixed metal oxides, on the other hand, can be considered suitable candidates for NO\textsubscript{x} abatement, due to their unique electronic features and (usually) high hydrothermal stability.

This analysis is consistent also in the case of the use of biofuels: as far as emissions are concerned, biodiesel produces substantially smaller amounts of CO, hydrocarbons (HC), and soot, which has been reported to dramatically decrease by 50, 70, and 50%, respectively, for pure biodiesel and to moderately decrease by 12, 20, and 12% for a diesel with a 20% biodiesel content.\textsuperscript{171} These are average values, but a more than 80% particulate matter emission reduction was recorded in tests with pure biodiesel\textsuperscript{172} with respect to fossil one. These emission reductions are reached at the price of a modest 10% emission increase in nitrogen oxides (NO\textsubscript{x}) for pure biodiesel, which is close to zero for a 20% biodiesel content,\textsuperscript{173} therefore not entailing radically different catalytic formulations.

Moreover, as in the case of innovative biofuels like farnesane, which often require a recalibration of the engine map to achieve combustions efficiencies comparable to the ones of conventional diesel, beneficial results in terms of emissions can be achieved at the same time, thus eliminating the problem of increased pollutant emissions.\textsuperscript{173}

**Conclusions**

The progressive requirements for fuel-efficient diesel cars highlight the problem of the necessity of removing NO\textsubscript{x} under lean-burn conditions in order to satisfy current legislation. Since direct NO decomposition cannot be applied successfully to control Diesel engine emissions, researchers have begun to investigate alternative approaches, such as the selective catalytic reduction of NO\textsubscript{x} by means of ammonia/urea or hydrocarbons. The SCR of NO\textsubscript{x} by ammonia/urea has become a key technology for the aftertreatment of exhaust emitted from Diesel and other lean-burn engines. In fact, a high efficiency of NO\textsubscript{x} removal can be obtained with NH\textsubscript{3}-SCR (namely 70–98%).
The uniqueness of this technology is that the reaction can occur in the presence of excess O₂. Thus, the NH₃-SCR approach has received a great deal of interest for Diesel-engine vehicles. On the other hand, the HC-SCR of NOx has been investigated extensively since the early 1990s, and many catalysts have been tested. Although promising results have been obtained with this technology (more than 80% NOx conversion), most of the research was conducted in the absence, or low presence, of sulfur. Moreover, it has been revealed that the narrow activity temperature range and the poor activity below 300 °C are relevant drawbacks for the application of HC-SCR catalysts.

Recently, growing interest has been shown in the adsorption of NO (NO traps) from lean exhaust, followed by release and catalytic reduction under rich conditions. This strategy has been shown to achieve ca. 70–90% NOx reduction, and seems the most promising approach for NOx abatement in diesel engines, since it does not require a reducing agent. NTP has been proposed as a promising technology to reduce NOx and PM emissions in Diesel exhaust. At present, however, this approach appears more complicated than other advanced technologies for NOx abatement.

The stringent regulation limits for both NOx and PM emissions are forcing the automotive industry to pile up a number of costly catalytic converters, which results in rather high pressure drops, sophisticated control systems, inefficiency linked to considerable weight and space consumption and hence elevated costs. Therefore, the simultaneous removal of soot and NOx in a single filter catalyzed represents the most ambitious strategy, in view of the great advantages that can be obtained in terms of both investment costs and pressure drop reduction. In this scenario, synergistic effects play a key role in catalytic converters. This means that it is necessary to obtain more detailed knowledge of the surface phenomena (reaction mechanisms, cooperative effects, etc.) in order to be able to develop effective catalytic systems.

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