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Catalysis in Diesel engine NO_x aftertreatment: a review

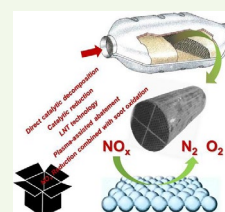
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Abstract The catalytic reduction of nitrogen oxides (NO_x) under lean-burn conditions represents an important target in catalysis research. The most relevant catalytic NO_x abatement systems for Diesel engine vehicles are summarized in this short review, with focus on the main catalytic aspects and materials. Five aftertreatment technologies for Diesel NO_x are reviewed: (i) direct catalytic decomposition; (ii) catalytic reduction; (iii) NO_x traps; (iv) plasma-assisted abatement; and (v) NO_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_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_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_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 CO₂, N₂, and H₂O 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: CO₂ 2–12%, H₂O 2–12%, O₂ 3–17%, and N₂ 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_x, CO, HC) and solid/liquid (PM) pollutants.² 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_x emissions is Exhaust Gas Recirculation (EGR). In this strategy, part of the exhaust (with O₂, N₂, H₂O and CO₂) is recycled back to the combustion chamber. In fact, since the heat capacity of CO₂ in the recirculated exhaust gas is about 20–25% higher than that of O₂ and N₂, the energy released from the fuel combustion results in a lower temperature rise, and hence a lower peak cycle temperature, with consequent lower NO_x levels. However, this strategy alone is not sufficient to meet the recent NO_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_x, since 1990, despite the increase in fuel consumption.⁹ Since NO_x emission regulations have become more stringent over the last few years (Fig. 1), several catalytic DeNO_x approaches have been investigated for lean-burn conditions, such as the direct decomposition of NO_x, selective catalytic reduction (SCR) using different reducing agents (e.g. ammonia/urea, hydrocarbons), and NO_x storage-reduction^{10–16}. On the other hand, modern three-way catalysts cannot reduce NO_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_x to N₂ and of oxidizing PM, HC, and CO

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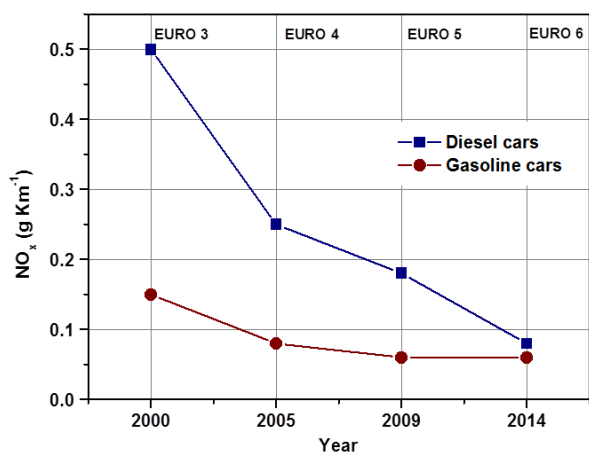
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Table 1 European emission standards for passenger cars, g/km

Tier	Date	CO	HC	VOC	NO _x	HC + NO _x	PM
Diesel cars							
Euro 1 ^a	July 1992	2.72 (3.16)	–	–	–	0.97 (1.13)	0.14 (0.18)
Euro 2	January 1996	1.0	–	–	–	0.7	0.08
Euro 3	January 2000	0.64	–	–	0.50	0.56	0.05
Euro 4	January 2005	0.50	–	–	0.25	0.30	0.025
Euro 5	September 2009	0.50	–	–	0.180	0.230	0.005
Euro 6	September 2014	0.50	–	–	0.080	0.170	0.005
Gasoline cars							
Euro 1 ^a	July 1992	2.72 (3.16)	–	–	–	0.97 (1.13)	–
Euro 2	January 1996	2.2	–	–	–	0.5	–
Euro 3	January 2000	2.3	0.20	–	0.15	–	–
Euro 4	January 2005	1.0	0.10	–	0.08	–	–
Euro 5	September 2009	1.0	0.10	0.068	0.060	–	0.005 ^b
Euro 6	September 2014	1.0	0.10	0.068	0.060	–	0.005 ^b

^aValues in brackets are conformity of production (COP) limits.


Figure 1 Trend of the European emission NO_x limits for both Diesel and gasoline cars

to CO₂ and H₂O under lean conditions. In the present paper, the role of aftertreatment catalysis in Diesel NO_x abatement is discussed comprehensively.

Direct catalytic NO decomposition

Engine-out NO_x 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 NO_x emissions from road transport.⁹ During flame combustion, the reaction between N₂ and O₂ is thermodynamically favored ($\Delta H_{298\text{K}} = 180.6 \text{ kJ mol}^{-1}$), thus resulting in the formation of NO, according to the reaction:

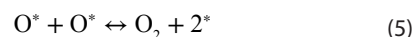
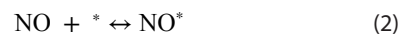


Direct NO decomposition (the reverse of equation (1)) has received considerable attention in the field of environmental catalysis, since the overall process is thermodynamically favored below 1000 °C, and the use of reducing agents is not required.^{17,18} In the catalytic decomposition of NO, the exhaust 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.¹⁹ 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 steps¹⁸:



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.^{17, 20, 21} Freund *et al.*²⁰ 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 Neurock²¹ 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:

$$r = N k (\text{NO}) / (1 + K (\text{O}_2)) \quad (6)$$

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

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	–	1.9
CuO	0	3.7	9.7
	5	0.7	1.8
CeO ₂	0	0.4	0.1
	5	–	–
Ag-Co ₃ O ₄	0	45	38
	5	18	25

Source: Adapted from Ref.²⁹

used to describe the catalytic behavior of several noble metal-containing catalysts. The main problem related to the use of noble metals for direct NO decomposition is likely that such materials are easily oxidizable and therefore not very active in the presence of oxygen. In fact, the high *K* value takes into account the inhibiting effect of oxygen on the kinetics of this reaction.²²

The results obtained by Hamada *et al.*²³ with Pt, Rh, Pd, and Ru on Al₂O₃ (noble metal content = 0.5 wt.%) had shown that the NO decomposition activity increased with a decrease in the affinity of the metals toward oxygen. Thus, Pt is the most active metal, and this is followed by Rh, Pd, and Ru. Ogata *et al.*²⁴ observed that Pd exhibits more activity when it is dispersed on oxides containing Mg²⁺ ions (e.g. MgAl₂O₄, MgO, Mg₂Si₃O₈, MgZrO₃) than when it is supported on Al₂O₃. The Pd–Mg interactions significantly increase the catalytic activity, since the two components are in intimate contact with each other on an atomic scale.²⁵ Thus, interactions among active sites may lead to beneficial effects (synergies) for catalysis.

On the other hand, Wu *et al.*²⁶ have shown the beneficial effect of small amounts of Au or Ag on the catalytic activity of Pd/Al₂O₃ catalysts (namely 0.5% Pd - 0.03% Au/Al₂O₃ and 0.5% Pd - 0.06% Ag/Al₂O₃) obtained by co-precipitation, due to an easier reducibility of the active phase.

Frank *et al.*^{27,28} 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.²⁷ 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_x conversion decreased to ca. 40% at 220 °C. The authors explained this catalytic behavior by showing that NO_x abatement begins when CO is fully oxidized and they argued that CO does not participate in NO_x reduction.

Metal oxides

Several metal oxides have been studied as catalysts for direct NO decomposition, as can be seen in Table 2.²⁹ Among these, cobalt oxide (Co₃O₄) is one of the most active compounds. The high activity of Co₃O₄ seems to be related to the relatively weak Co–O bonds, which lead to an easy desorption of lattice oxygen (β-species), especially at low temperature. Co₃O₄ shows a spinel structure with Co²⁺ and Co³⁺ cations. During the direct NO decomposition reaction, Co²⁺ may partially oxidize

to Co³⁺ and form a Co₂O₃-like phase on the surface. The latter is not stable and decomposes to Co₃O₄, thus favoring NO dissociation.³⁰

Iwamoto *et al.*³¹ have found that promoting Co₃O₄ 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 O₂ concentration was less marked when Co₃O₄ 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.³⁰

The NO decomposition activity of metal oxides is closely related to the bond strength between the metal and the oxygen in the lattice.¹⁷ NO usually dissociates on the metal oxides, although NO dissociation depends on several factors, including the temperature, surface coverage, crystal planes, and surface defects.^{17,20,30} The catalytic activity of metal oxides towards the NO decomposition is usually lower than that of noble metals.^{29,30} Therefore, the operating temperature must be kept at quite high values (up to 1000 °C), which can lead to catalyst sintering, and it 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.^{18,29,30} Moreover, the oxygen “self-poisoning effect” towards NO decomposition can be much lower on ceria-based materials, as a consequence of oxygen spillover phenomena.^{32,33} Zhang *et al.*³⁴ doped La₂O₃ catalysts with Sr (namely 4% Sr/La₂O₃), thus promoting NO decomposition activity under different operating conditions. Other authors³⁵ have performed studies on CeO₂–ZrO₂ mixed oxides, which exhibit interesting activities in NO_x decomposition.

Perovskites

Perovskite-type catalysts have been widely investigated for the direct decomposition of NO, as reported in Table 3.²⁹ Mixed oxides with an ABO₃ 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.³⁶ 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

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 N ₂ (%) 500 °C	Conversion of NO to N ₂ (%) 600 °C
SrFeO _{3-x}	0	0	0.12
	5	–	–
LaCoO ₃	0	1.5	3.8
	5	–	0.44
La _{0.8} Sr _{0.2} CoO ₃	0	1.6	6.3
	5	–	–
YBa ₂ Cu ₃ O _{7-x}	0	–	0.49
	5	–	–

Source: Adapted from Ref.²⁹

lattice.¹⁷ The order of the desorption temperature for oxygen is correlated to the NO decomposition activity: the weaker the adsorption of oxygen on the catalyst surface, the greater the mobility of the oxygen, and hence the greater the activity toward NO decomposition.³⁷ This suggests that surface oxygen species may act as catalytic active sites.³⁸ On the other hand, oxygen-deficient compounds, such as the YBa₂Cu₃O_{7-x} perovskite, have been proved to be active for NO decomposition,³⁹ especially when supported on MgO. In perovskites, the complexity of surface defects (e.g. oxygen vacancies) is at least one order to magnitude higher than that of binary 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.*⁴⁰ The authors observed that the activity of NO decomposition 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.*⁴¹ considered the effect of the preparation method and catalyst composition on the activity toward NO decomposition for several perovskites with a general formula La_xSr_{1-x}XO₃ (X = Co, Cr, Mn, Fe, Ni and Cu).

Kim *et al.*⁴² observed that under realistic conditions, La_{1-x}Sr_xCoO₃ catalysts exhibit higher NO-to-NO₂ conversions than commercial Pt-based catalysts.

Complex perovskite-type catalysts have been prepared by Monceaux *et al.*⁴³ The authors have found that the substitution of a small quantity of Pt for Mn or Co makes it possible to prevent sulfur poisoning and to increase the catalytic performances of these materials toward several oxidation reactions. Perovskites exhibit high thermal stability, compared to metal oxides, and do not suffer to any great extent from the oxygen “self-poisoning effect.” Since they can easily desorb oxygen, these materials should be good candidates for purifying exhaust gas from Diesel engines, particularly for the removal of soot and for NO abatement. The most significant disadvantage of NO decomposition on perovskite catalysts is the high reaction temperature required to achieve a high NO decomposition activity. Other significant drawbacks are their low surface areas and pore volumes. The ceramic solid–solid reaction and co-precipitation methods, which are commonly used for the synthesis of perovskite-type materials, involve a high reaction temperature (>900 °C) and hence yield perovskite-type oxides with low surface areas (<2 m² g⁻¹), due to their sintering.⁴⁴ Research should therefore be addressed to the development of new preparation techniques, aimed at obtaining perovskite structures with better textural properties.

Zeolites

Several types of metal-ion-exchanged zeolites, including X- and Y-faujasite, mordenite, ferrierite, and ZSM-5-type zeolites with different Si/Al molar ratios, have been studied for direct NO decomposition.^{45,46} Among zeolite-based catalysts, the Cu/ZSM-5 catalyst has been paid much attention, due to its superior activity and N₂ selectivity in a wide temperature range.⁴⁷ However, the Cu/ZSM-5 has been found to deactivate readily during high temperature hydrothermal treatment.⁴⁸ 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 introduction of a second metal.^{49,50} 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.^{51,52}

As a whole, the NO decomposition over Cu-ZSM-5 proceeds via a redox-type mechanism.³⁰ 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:



NO molecules can be chemisorbed as NO⁺, NO⁻, and NO₂⁻ species on the zeolite surface. A fraction of the Cu²⁺ ions is reduced to Cu⁺ through the desorption of O₂, whereas catalyst re-oxidation with NO restores Cu²⁺ 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.²⁹ Moreover, this material is not stable in water vapor conditions for long periods of time and it has proved to be sensitive to SO₂ poisoning.²⁹ As a whole, the presence of water vapor has an inhibition (although reversible) effect on the decomposition of NO, whereas SO₂ poisons the catalyst surface.

On the other hand, Weisweiler *et al.*⁵³ have observed that Pt-ZSM-5 catalysts may/are able to adsorb NO under controlled dynamic conditions (simulation of a driving cycle), although real NO abatement cannot be attained at low temperatures (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

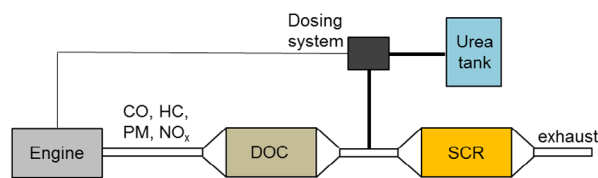


Figure 2 Schematization of DOC and SCR systems in Diesel vehicles

Source: Adapted from Ref.¹⁰

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.

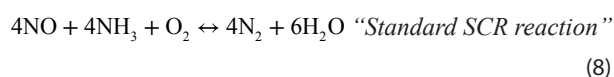
The catalytic reduction of NO has been studied using a number of reductants, of which ammonia, urea, and hydrocarbons are the most frequently reported.^{4,16} Catalytic reduction with ammonia (or urea) is usually referred to as NH₃-SCR, while reduction with hydrocarbons is often referred to as HC-SCR.

Several catalytic materials have been developed for the SCR of NO_x since the early 1970s.⁵⁶ The first generation of commercial SCR catalysts for mobile applications was monoliths containing V₂O₅/WO₃/TiO₂, which were similar to the V₂O₅-based catalysts used for NH₃-SCR in stationary applications.² However, the stringent legislations on NO_x emissions, the necessity of new materials to extend the temperature operation window, and the toxicity of vanadium have driven the research toward the development of more effective catalysts.³⁰

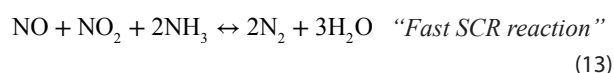
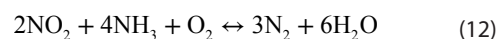
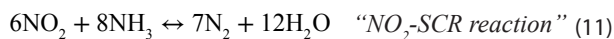
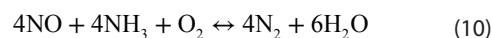
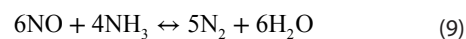
Use of ammonia/urea as a reductant

The reduction of NO_x 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.^{57–59} Ammonia is commonly used as a reductant agent in large commercial scale SCR. NH₃ 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_x removal can be obtained with the NH₃-SCR process (namely 70–98%).³ The uniqueness of this reaction with NH₃ is that it can occur in the presence of excess O₂. Thus, this technology has received a great deal of attention for Diesel-engine vehicles.

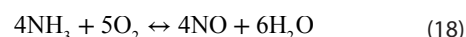
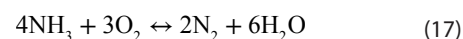
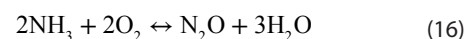
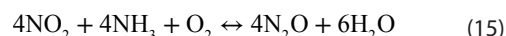
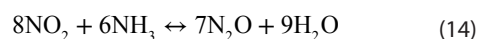
The overall NH₃-SCR reaction is⁶⁰:



The role of oxygen is to donate one electron to the redox process.¹⁷ Thus, oxygen enhances the rate of the NO–NH₃ reaction.⁵⁷ A complex reaction network can be observed on the catalyst surface. The main prevailing reactions are⁶⁰:



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_x, which leads to N₂O (equations (14)–(16)), or the direct oxidation of NH₃, which forms NO (equations (17)–(18))⁶⁰:



Particular temperature conditions (100–200 °C) may lead to the formation of NH₄NO₃, which is explosive and deposits in the cavities of the catalytic material, causing temporary deactivation.⁶¹ 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_x⁶⁰:



The molar ratio of ammonia to NO_x is set below one (sub-stoichiometric) to minimize ammonia slip. The typical SCR process operates using/with an oxidation catalyst (e.g. V₂O₅–WO₃/TiO₂) downstream from the SCR, which prevents the unreacted ammonia from leaving the reactor. The oxidation catalyst may also favor the oxidation of CO and HC emissions.⁶⁰ On the other hand, an increase in N₂O and NO in the exhaust gases may occur due to the oxidation of ammonia.⁶³ Similarly, the catalyst may enhance SO oxidation and hence cause an increase in sulfate emissions. Since ammonia poses health and practical problems (NH₃ is a toxic gas that has to be stored under

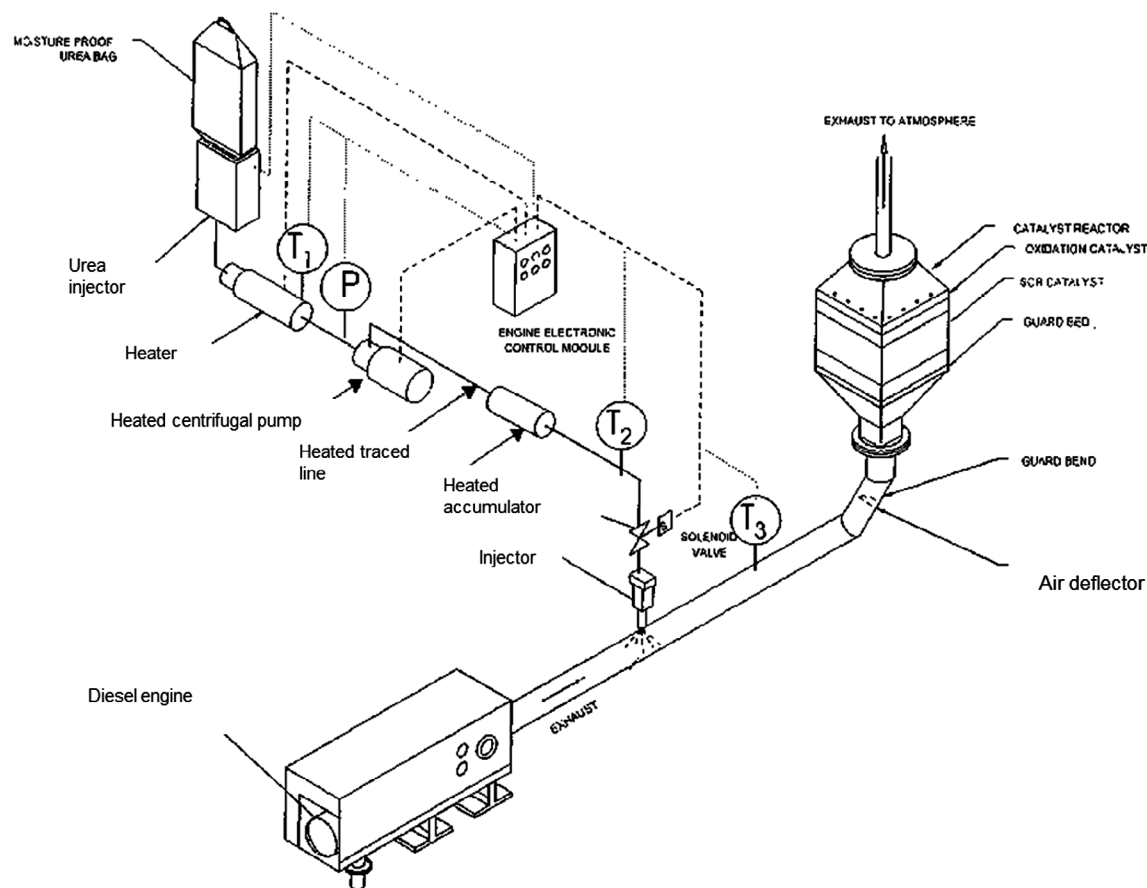
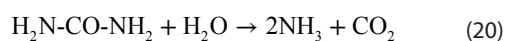


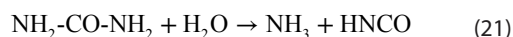
Figure 3 Experimental plant developed by Tarabulski et al. to test solid urea as a reducing agent for NO_x abatement⁶⁵

pressure), an alternative source of NH₃ has been developed, in the form of urea, especially for non-stationary Diesel engines.^{14, 30} Urea, which is a solid that is highly soluble in water, can be injected, as an aqueous solution, into the exhaust gases, where it decomposes, according to equation (20), at about 200 °C:

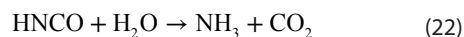


Equation (20) is the result of the following two steps⁶²:

(i) Thermal decomposition (hydrolysis)



(ii) Isocyanic acid reaction with water



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_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_x.^{2, 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.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).

The DOC oxidizes the NO to NO₂, 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_x efficiency at low temperatures.^{10, 14} The SCR catalyst can be fouled and deactivated due to the deposition of ammonium sulfate and disulfate, resulting from the oxidation SO₂ with the subsequent formation of H₂SO₄ in the DOC, and the reaction with NH₃ 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 (HCO₂NH₄) has been proposed for SCR applications in cold climates (a 40% aqueous solution of HCO₂NH₄ has a freezing point of –35 °C), but it has a lower NH₃ 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.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 NH₃ and can therefore be added to the exhaust gas on an as-needed

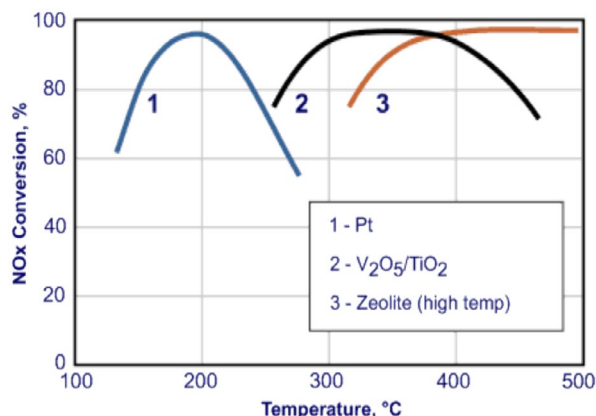


Figure 4 Operating temperature windows for different NH₃-SCR catalysts

Source: Reprinted with permission from Ref.⁶⁶

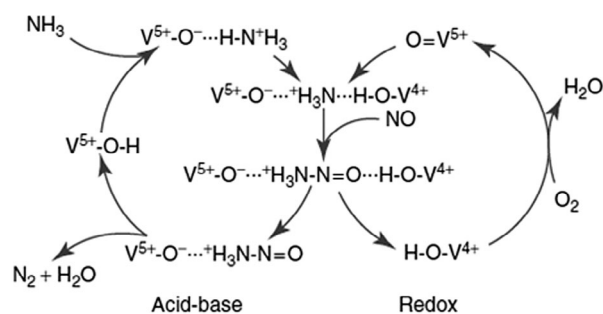


Figure 5 Catalytic cycle of the SCR reaction over a V₂O₅/TiO₂ catalyst

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basis for NO_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 TiO₂ (namely anatase), are usually good SCR catalysts.³ Such materials can be based on V₂O₅-WO₃ on TiO₂ or V₂O₅-MoO₃ on TiO₂, 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.²⁻⁴ The anatase form of TiO₂ is the

preferred support, mainly because SO₂ poisoning has a lower influence on the TiO₂ surface.⁶⁸

The first SCR technology that was developed was based on a Pt-containing catalyst. However, NO_x reduction over the Pt surface is only effective at temperatures below 250 °C (Fig 4).² In fact, at temperatures between 225 and 250 °C, the oxidation of NH₃ to NO and H₂O (equation (18)) becomes dominant and, as a result, poor selectivity toward N₂ can be achieved/observed. On the other hand, low temperatures (150–200 °C) may lead to the above-mentioned NH₄NO₃ formation, which entails a very narrow range of available working conditions.² Moreover, Pt catalyzes the reduction of NO_x to N₂O, which is a powerful greenhouse gas. Pt has the benefit of generally being insensitive to SO₂ and possesses good thermal stability, but it may favor the formation of SO₃.²

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.⁶⁷ This range is optimal for both light-duty (lower limit) and high duty (upper limit) applications. Catalytic materials, such as V₂O₅/TiO₂ or V₂O₅-WO₃/TiO₂, are capable of NO_x reduction in excess of 90%, and they are most probably the best candidates to meet severe NO_x reduction goals.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.¹⁴ The terminal V⁵⁺=O groups of V₂O₅ 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 Brønsted acidic sites. Thus, ammonia can readily adsorb on V⁴⁺–OH species to form an NH₄⁺ intermediate, which subsequently reacts with co-adsorbed NO to form the adsorbed (NH₃–NHO)⁺ 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 NH₄⁺ to the V₂O₅ surface during this initial step is subsequently transferred back to the NO molecule from the V₂O₅ (redox cycle). Ultimately, V⁵⁺=O groups can be restored via proton transfer. This produces gas-phase NH₂NO, which can be converted into N₂ and H₂O through subsequent reactions over V₂O₅.^{3,17}

Several studies have confirmed an Eley–Rideal-type mechanism (ER) for the SCR reaction, where ammonia adsorbs onto the V₂O₅ 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 NH₃ and NO species on the solid surface.³ Moreover, Dumesic *et al.*⁶⁹ 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,⁷⁰ V₂O₅ 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.¹⁴ 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, 50} This catalyst does not oxidize NH₃ to NO_x 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 NO_x 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 NO_x 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.⁶¹

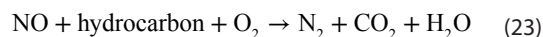
Moreover, it has been observed that the SCR reaction shows considerable sensitivity to the nature of the support, and hence comparative studies on different zeolite supports (ZSM-5, A, beta, FAU, ferrierite, CHA, Linde type L) have been performed. From these studies, it emerged that Fe- or Cu-exchanged 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.⁷²

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.^{30, 73} 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.⁷⁶

Use of hydrocarbons as reductants

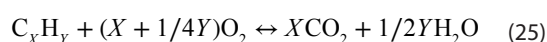
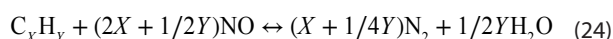
An alternative to the use of ammonia as a reductant agent is the employment of hydrocarbons, namely the HC-SCR process. The latter is also known as DeNO_x or lean-NO_x process.

According to this approach, the hydrocarbons can be oxidized by the oxygen present in NO, as follows:



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 are⁶⁰:



Consequently, catalyst selectivity is the key parameter that has to be optimized using suitable catalytic materials, as well as a suitable reducing agent, HC/NO_x 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 NO_x conversion rates;
- Optimization of the different parameters that affect the catalyst performance, in order to improve its use with vehicles.

An important parameter for NO_x abatement is the HC to NO_x ratio; generally, a two to fourfold surplus of hydrocarbons (expressed as ppm-HC) relative to the NO_x concentration (ppm-NO_x) is necessary to reach ca. 80% NO_x 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 DeNO_x”) and utilization of unburned HC emissions directly from the engine exhaust gas (“passive DeNO_x”). In “active DeNO_x” 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 DeNO_x system, in order to also undertake the role of preventing possible HC emissions.

On the other hand, “passive DeNO_x” 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

Table 4 Catalytic performances of several materials towards the HC-SCR reaction

Catalyst	Reductant	Catalytic performances	Note
Cu/ZSM-5	C ₃ H ₆	Maximum conversion: 33% (370 °C) Conversion higher than 20% (320–450 °C)	No production of N ₂ O
Co/Al ₂ O ₃	CH ₃ OH	Maximum conversion: 40% (370 °C) Conversion higher than 20% (>290 °C)	No production of N ₂ O but CH ₃ OH emissions
Ag/Al ₂ O ₃	C ₂ H ₅ OH	Maximum conversion: 31% (460 °C) Conversion higher than 20% (>370 °C)	N ₂ O and aldehydes produced from 370 °C
Pt/Al ₂ O ₃	C ₃ H ₆	Maximum conversion: 41% (215 °C) Conversion higher than 20% (200–270 °C)	High N ₂ O production
Pt/ZSM-5	C ₃ H ₆	Maximum conversion: 33% (240 °C) Conversion higher than 20% (220–270 °C)	High N ₂ O production from 240 °C

Source: Adapted from Ref.⁸⁵

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_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.⁸⁴ The first catalyst screening, which shows the catalytic behavior of several metals (Pt, Au, Cu, Co and Ag) supported on Al₂O₃ and ZSM-5, was published by Obuchi *et al.*⁸⁵ Then, Ag/alumina have been found to be promising catalysts for the selective catalytic reduction of NO_x to N₂ by hydrocarbons in laboratory tests as well as in full-scale diesel engine operation.⁸⁶

The addition of small amounts of H₂ can promote the HC-SCR activity of Ag-based catalysts for low temperature NO_x reduction. Over the years, several explanations have been proposed for this beneficial “H₂-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, H₂ promotes the HC-SCR activity of Ag-based catalysts through multiple roles, involving morphological, chemical, and kinetic changes.^{87,88}

Appropriate reductants, such as C₃H₆, CH₄, CH₃OH and C₂H₅OH (which are efficient reductant agents), 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 N₂O is a difficult problem to solve. For this reason, the most suitable catalyst seems to be the Co/Al₂O₃ one, with the addition of an oxidation catalyst downstream to prevent the leakage of non-reacted or incompletely oxidized reductants. De Soete⁸⁹ has published an interesting work that shows the reduction rate expressions of NO to N₂ in the HC-SCR reaction over Cu/ZSM-5. The author has found that C₂H₄ and C₆H₁₄, when used as reductants, show different catalytic behavior: the reaction order in C₂H₄ is negative, whereas it is positive for C₆H₁₄. In fact, ethylene is less active in NO reduction than n-hexane, although HC oxidation is lower.

Many studies^{82,89} 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 N₂ and O₂. On the other hand, Bell *et al.*^{90–93} reported that, for HC-SCR over Co-, Mn-,

Fe- and Pd-ZSM-5, the highly active species are CN groups which react with NO₂ to form N₂ and CO₂.

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.^{14,30,46}

Many ion-exchanged zeolites, such as Cu-, Fe-, Pt-, Co-, Ga-, Ce- and H-exchanged zeolites, have been found to be active for this reaction. In particular, Cu- and Co-ZSM-5 have received a great deal of attention over the last few decades.^{2,3,11,17,46} Several studies have revealed/pointed out the key role of reductant agents toward selectivity to N₂. It has been observed, for Cu-ZSM-5, that some hydrocarbons (namely C₂H₄, C₃H₈, C₄H₈, and alcohols) behave as selective reductants, while other reductants (i.e. H₂, CO and CH₄) are non-selective toward N₂ production.⁹⁴ Conversely, CH₄ has been shown to be a selective reductant over Co-ZSM-5 and Ga- or In-ZSM-5 catalysts.^{95,96} Erkfeldt *et al.*⁹⁷ established that a C–C bond in the reducing agent is required for lean NO_x reduction over Cu-ZSM-5. The influence of the hydrocarbon concentration on the activity of a Cu-ZSM-5 catalyst has been investigated by Konno *et al.*,⁸¹ who reported that the reduction rate increases with the hydrocarbon concentration up to an HC/NO molar ratio of ca. 8. The presence of some co-exchanged cations (Ca, Sr, Fe, Co and Ni) had the effect of expanding the temperature range over which a Cu-ZSM-5 can be active for the HC-SCR process.^{42,98} 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.⁹⁹

Pt-ZSM-5 is more stable than Cu-ZSM-5: Iwamoto *et al.*⁹⁴ 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 SO₂ in the reactant stream. Moreover, they observed that the catalyst activity barely changes after 1000 h exposure to water vapor.¹⁰⁰ On the other hand, the catalytic performances of Cu-exchanged zeolites are affected by the presence of SO₂ (Fig. 6).

Falley *et al.*¹⁰¹ 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

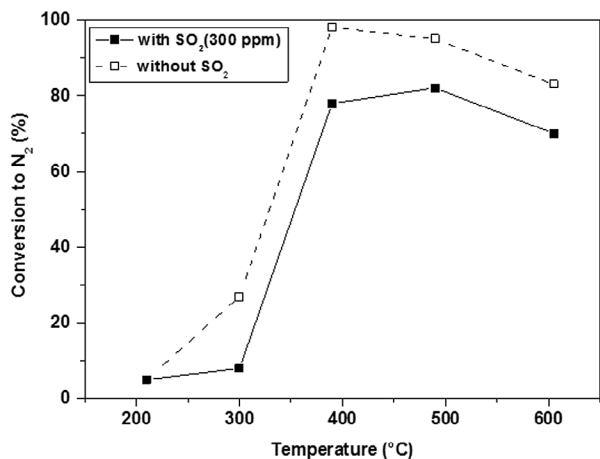


Figure 6 Conversion of NO + O₂ + C₃H₆ system into N₂, with and without SO₂. Catalyst Cu-MFI. Without SO₂: P_{NO} = 500 ppm, P_{O₂} = 1.0%; P_{C₃H₆} = 990 ppm, W/F = 0.1 g cm⁻³; With SO₂, P_{NO} = 530 ppm, P_{O₂} = 1.0%; P_{C₃H₆} = 1000 ppm, W/F = 0.1 g cm⁻³, P_{SO₂} = 300 ppm
Source: Adapted from Ref.⁹⁴

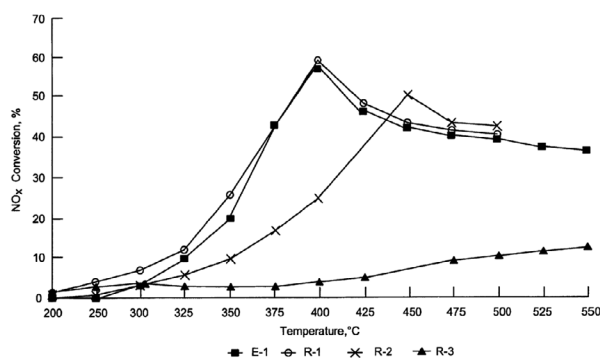


Figure 7 NO_x conversion vs. temperature obtained using fresh ZSM-5-based catalytic material, with the addition of small amounts of Cu, Co and Fe: E-1 3.31% Cu, 2.27% Fe, 0.72% Co; R-1 3.22% Cu, 1.96% Fe; R-2 3.17% Cu, 3.13% Co; R-3 3.3% Co, 1.98% Fe
Source: Adapted from Ref.⁹⁴

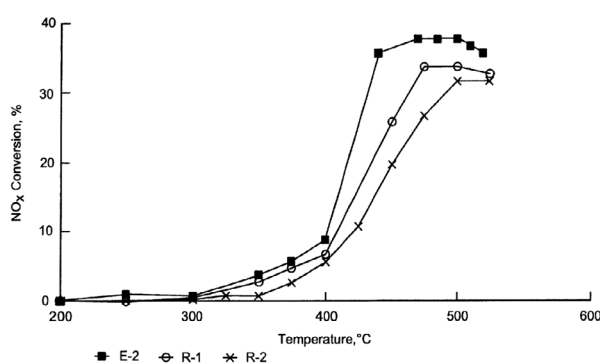


Figure 8 NO_x conv. vs. T obtained using an aged (through exposure to a mixture of 10% steam in air for 5 h at 700 °C) ZSM-5-based catalytic mat. with addition of small amounts of Cu, Co and Fe: E-2 3.46% Cu, 2.03% Fe, 1.35% Co; R-1 3.22% Cu, 1.96% Fe; R-2 3.17% Cu, 3.13% Co
Source: Adapted from Ref.¹⁰¹

catalyst reaches its optimum NO_x conversion rate (Fig. 7), particularly after aging (Fig. 8). This trimetallic-based system lends stability to the catalytic material, so that NO_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 C₃H₆ by Yogo *et al.*,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_x reduction capacity of zeolite-type catalysts. For instance, Deeba *et al.*¹⁰² reported interesting NO_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_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. CH₄ and C₃H₈) are used as reductant agents.^{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.^{105–108} An interesting work on the catalyst choice for the HC-SCR process was conducted by Nakatsuji *et al.*,¹⁰⁵ and remarkable results were shown for the Ag/Al₂O₃ catalyst. This catalyst can be active at 300 °C and exhibit good catalytic stability in the presence of SO_x, which is further improved by the addition of WO₃, MoO₃, 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_x conversion of 75%.

Several works have been published on platinum-group metals, mainly due to their relatively high surface stability.^{107, 108} Bamwenda *et al.*¹⁰⁹ studied platinum-group metals (Pt, Pd, Rh and Ir) deposited on different supports (TiO₂, ZnO, ZrO₂ and Al₂O₃) for the SCR of NO in the presence of C₃H₆. They found that the alumina supported catalysts showed both the highest activity for NO conversion and the highest selectivity toward N₂ formation. The catalytic activities followed the Pt/Al₂O₃ > Rh/Al₂O₃ > Pd/Al₂O₃ > Ir/Al₂O₃ order, whereas Rh/Al₂O₃ was found to have the highest selectivity toward N₂ formation.¹¹⁰

Other studies have been carried out for Ag supported on Al₂O₃^{105–108} or saponite.¹⁰⁸ Miyadera *et al.*¹⁰⁵ have shown that 2 wt.% Ag/Al₂O₃ can reduce NO with ethanol (a higher molar ratio of C₂H₅OH/NO_x than 1.25), even in the presence of water vapor, although several byproducts may appear (e.g. N₂O, NH₃, CH₃CN 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 (C₁–C₃ hydrocarbons) on the HC-SCR of NO in a Ga₂O₃–Al₂O₃ system has been studied by Miyahara *et al.*¹¹⁰: the most efficient NO abatement was achieved with C₂ hydrocarbons, whereas C₃ hydrocarbons were less selective for N₂ 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 Ga₂O₃–Al₂O₃ 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/TiO₂–ZrO₂) for the SCR of NO with C₃H₆ 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/TiO₂–ZrO₂ 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 C₃H₆ in the presence of O₂ and moisture. The catalytic behavior of Au-species depends on the metal oxide support. In fact, an activity scale has been drawn up: α-Fe₂O₃ ~ ZnO < MgO ~ TiO₂ < Al₂O₃. The highest conversion to N₂ (around 70%) at 427 °C has been achieved over a 0.1–0.2 wt.% Au/Al₂O₃ catalyst.^{111, 112} It is worth noting that the conversion of NO to N₂ over Au/Al₂O₃ was increased slightly by the presence of water. Thus, in order to improve the performances of the latter catalyst, Mn₂O₃ was then mixed with Au/Al₂O₃.¹¹³ This mechanical mixture exhibited interesting results for the HC-SCR of NO in the 250 and 500 °C temperature range. This catalyst has been considered one of the most effective for the NO emission control of lean-burn gasoline and Diesel engines.^{111–113}

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 adsorber 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 N₂ when a rich air-to-fuel mixture is injected.¹¹⁴

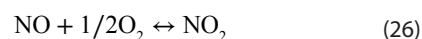
Since the rich mode of operation is not feasible for Diesel engines, periodic fuel injections are necessary. The amount of fuel and the periodicity of the injections, as well as the storage capacity of the materials, are the main parameters that need to be optimized to reduce the fuel penalty associated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

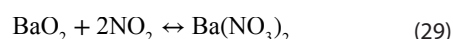
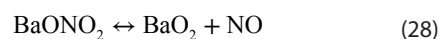
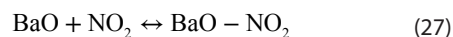
During operating conditions, the NO_x reduction takes place according to a two-stage mechanism, as shown in Fig. 9. The NO_x trap combines the effect of an oxidation catalyst (e.g. platinum), an adsorbent material (e.g. BaO), and a reduction catalyst (e.g. rhodium).

The exhaust is rich in NO (a thermodynamically stable species at high-temperatures), but traps are more effective toward NO₂ entrapment. Therefore, the step immediately before NO_x adsorption should be the NO oxidation to NO₂ 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}:



The NO₂ formed on the solid surface is trapped on an adsorbent (BaO) in the form of a nitrate (e.g. Ba(NO₃)₂), which is chemically stable at the operating conditions.

Thus, the following reaction steps can occur^{10, 60}:



The adsorption capacity of an NO_x 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 reductant conditions for NO abatement are thus achieved.

The first regeneration step consists of the decomposition of the Ba(NO₃)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



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 H₂ react with the

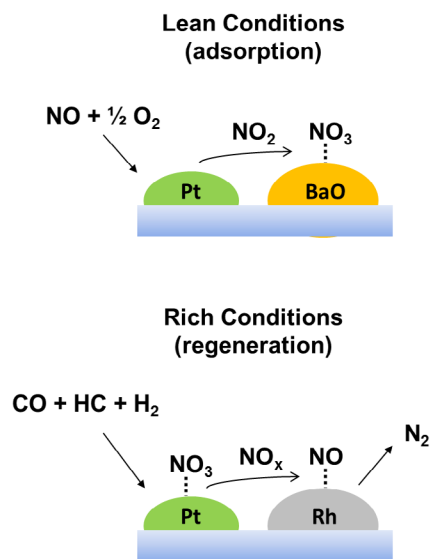
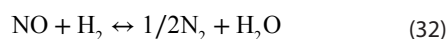
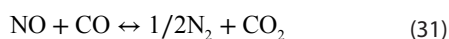


Figure 9 The basic concept of NO_x storage and reduction mechanisms

Source: Reprinted from Refs.^{10,66}

NO species to form N₂, CO₂, and H₂O (equations (24), (31) and (32)).⁶⁰



The operating temperature of these NO_x traps has a lower limit, which is determined by the Pt activity toward the NO oxidation, as well as the NO_x release and reduction in the regeneration step; on the other hand, the upper limit is related to the stability of the NO₃ species, which undergo thermal decomposition at high temperatures, even under lean conditions.¹¹⁹

It is worth noting that several complex phenomena may appear on the surface of NO_x traps, since they are multicomponent materials which have different functionalities. For instance, BaCO₃ and Ba(OH)₂ coexist with BaO on the catalyst surface.¹²⁰ Moreover, NO_x 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 NO_x species.¹²¹ Therefore, it is very difficult to investigate the NO_x storage/release mechanisms of these catalytic materials.

NO_x adsorbents are sensitive to sulfur species: sulfur is a poison for Pt-sites and, in the form of SO₃, it is competitive with NO₂ in the formation of barium salts (e.g. BaSO₄), thus causing a loss of activity toward the adsorption of NO₂ (= competitive adsorption). BaSO₄ is more stable than the corresponding nitrate, and hence its decomposition occurs at higher temperatures.¹¹⁹ Finally, the possibility of having parasitic reactions that lead to undesired products (e.g. NH₃, N₂O, H₂S) reduces the NO_x trap efficacy, and a careful control of the secondary emissions is also necessary.

Multifunctional catalysts

NO_x 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).^{121, 122} 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 NO_x conversion efficacy among these metal groups: the inclusion of K-, Na-, and Cs- based oxides in the adsorbent catalyst formulation increases the NO_x reduction to between 350 and 600 °C.¹²³ 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 NO conversion, due to the hydrocarbons, which makes the adsorbent catalyst more fuel demanding.¹²⁴ Finally, alkali-based materials exhibit low performances and give rise to leaching effects in the presence of water vapor.¹²⁵ It is therefore necessary to find a trade-off between the good NO_x reduction activity at high temperatures of alkali metal oxides and their excessive mobility, in order to include them in Ba-based systems.

NO_x 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.¹²³ Another washcoat component is TiO₂, whose acidity gives a lower sulfur affinity, although it also reduces the stability of nitrates.¹²⁶ 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 NO₂ and on the overall conversion performance of NO_x are summarized in Fig. 10.¹²⁷ 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 H₂, CO, or HC, to convert the stored nitrates. The activity of a complex multicomponent catalyst toward NO_x reduction is reported in the work by Takahashi *et al.*¹²⁸: the catalyst consisted of an Al₂O₃-based washcoat of CeO₂-ZrO₂ oxygen storage materials, with Ba and K oxides as the NO_x 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 NO_x concentration gradually increases with time, up to reach a constant level.

Shaded area A is related to the NO_x amount stored in the catalyst, while shaded area B is related to the number of regenerated NO_x storage sites on the catalyst. Takahashi *et al.*¹²⁸ then

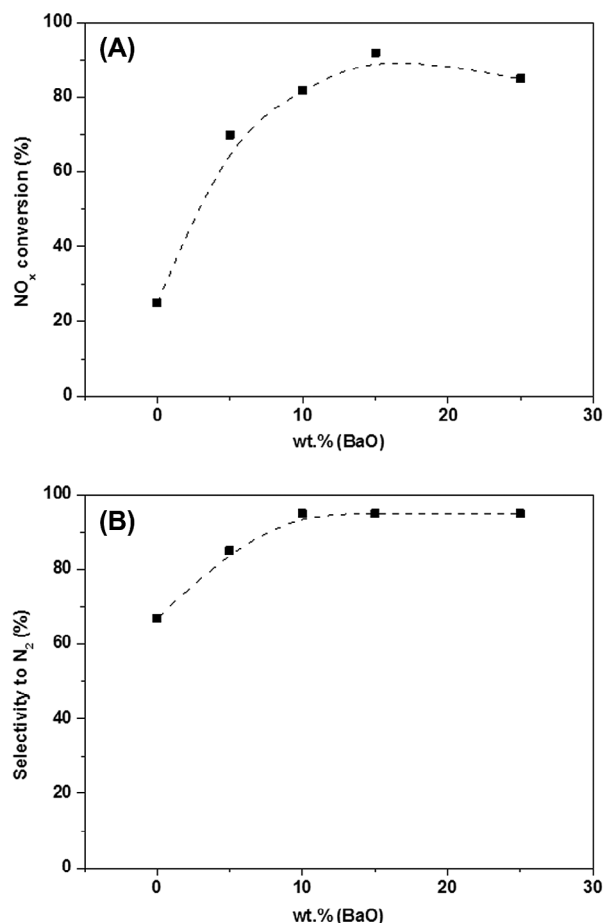


Figure 10 NO_x conversion (Section A) and selectivity to N₂ (Section B) on BaO loading. NO = 500 ppm, O₂ = 5% (with C₃H₆ = 0.7% during regeneration), temperature = 375 °C and GHSV = 60,000 h⁻¹

Source: Adapted from Ref.¹²⁷

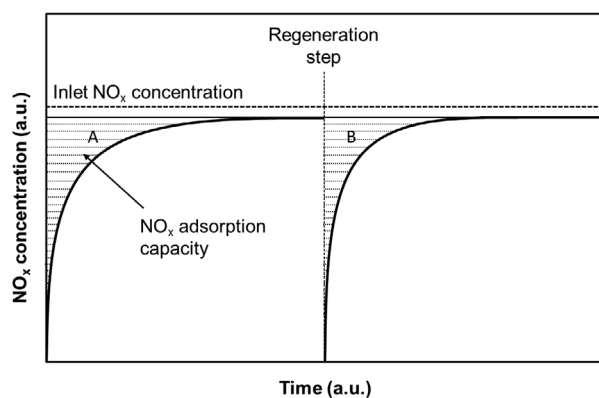


Figure 11 NO_x concentration curves, during lean and rich periods, in the inlet and outlet using Lean1 and gases at 250 °C

Source: Adapted from Ref.¹²⁸

established that the effectiveness of the reducing agents follows the following order: C₃H₆ < CO < H₂.

One extremely interesting attempt to improve the NO_x absorbers activity is the one from Toyota,¹²⁹ which investigated the effect of an oscillating air: fuel ratio for the regeneration

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_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_x abatement efficiency. A relevant example is the embodiment of an SCR catalytic functionality in a NO_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 in¹³⁰). The concept is based on the fact that, in the presence of H₂ during the rich pulses of the NO_x trap regeneration, NH₃ can be formed by direct reaction with the previously stored NO_x¹³¹; CO instead leads to NH₃ 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 CO₂ and H₂O in the exhausts.¹³¹ The suitable proportion of the SCR and NO_x trap catalysts in the overall formulation is determined by the amount of NH₃ generated in the NO_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 NH₃ produced in the NO_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 NH₃ generated in the NO_x trap layer is better utilized in an adjacent SCR layer.¹³⁰ The optimal configuration in terms of relative thickness of the layers depends on the operating temperatures and SCR site density.

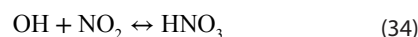
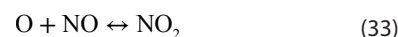
Plasma-assisted catalytic NO_x reduction

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

Non-thermal plasma (NTP) discharges in exhaust gas have been investigated as a potential technology to reduce NO_x and PM emissions in Diesel exhaust as well as NO_x and cold start hydrocarbons in lean gasoline exhaust.

NTP is generated, by means of an electrical excitation, to induce thermodynamically unstable NO_x species; the latter should decompose into N₂ and O₂.

In automotive applications, the reduction of NO_x is preferable. On the other hand, oxidative NO_x reactions dominate the subsequent kinetics, converting most flue gas NO to NO₂ and HNO₃¹³³⁻¹³⁵ through reactions with plasma-produced oxygen and hydroxyl (equations (33) and (34)).



Several other byproducts can be produced, including N₂O, N₂O₃, N₂O₄, HONO, and HONO₂, 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 *et al.* investigated NO_x abatement for Diesel

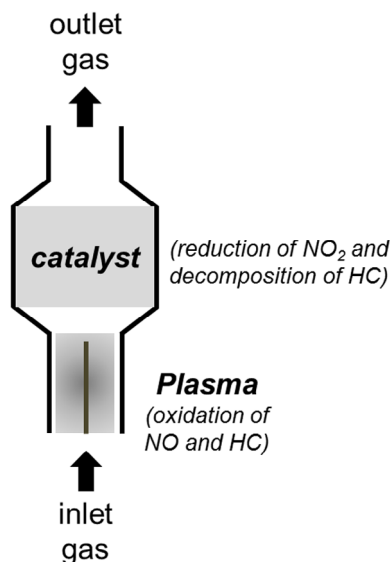


Figure 12 Scheme of the plasma-assisted catalytic reduction system developed at Lawrence Livermore National laboratory. Source: U.S. Patent N° 5711147. Issued January 27, 1998. Adapted from Ref.¹³⁶

exhaust, for which pulsed voltages (namely 24 kV and 600 Hz) were shown to be more effective than a direct current (about 80% NO_x conversion).¹³⁴ HNO₃ (and other acidic byproducts) can be removed easily at a stationary combustion facility in the form of solid nitrates using a downstream scrubber. However, neither chemical scrubbing nor the conversion of NO to HNO₃ constitutes a practical approach for mobile engine NO_x control, due to the requirements of onboard scrubbing chemicals, the periodic disposal of accumulated solid waste, and the requirement of an acid scrubber. Yamamoto *et al.*¹³⁵ have proposed a plasma reactor followed by a Na₂SO₃ solution scrubber to reduce volumes, even though this technology can only be used for Diesel engine trucks.

Combinations of plasma with solid catalysts, referred to as “plasma-assisted catalysts” or simply “plasma catalysts”, have been suggested for NO_x reduction.¹³⁵

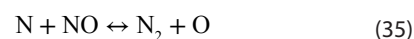
As a whole, plasma reactors are pulsed corona-type reactors and the catalyst is generally placed after the plasma device (Fig. 12).¹³⁹ Although plasma aftertreatment favors oxidation over reduction, a useful synergism can be observed when it is combined with a catalyst.¹³⁴ The reducing capability of some catalysts is enhanced considerably when NO_x is presented to catalytic surfaces as NO₂ (peroxy radicals favor the conversion of NO to NO₂) rather than NO.^{137–140} This means that the NTP technology may significantly improve catalyst selectivity and removal efficiency. Thus, lower temperatures can be used in NO_x reduction with plasma-catalyst technology than with NTP. An increase in temperature improves catalytic activity but the action of plasma is only retained from room temperature to 300 °C. Moreover, the presence of water vapor and oxygen promotes the NO removal rate, as a consequence of synergistic phenomena on the catalyst surface.¹³⁷

Several catalysts, including γ-Al₂O₃, TiO₂, MnO₂/TiO₂, Ag/TiO₂, V₂O₅-WO₃/TiO₂, HZSM-5, NaX, Cu-ZSM and Na-Y and Ba-Y, have been proposed to be active for this technology.^{135, 138, 139} The best performance for NO_x removal at low temperatures

(150–270 °C) has been achieved using Na- and Ba-doped zeolite Y. However, promising results (90% NO_x removal) have also been obtained with In/γ-Al₂O₃ catalysts in the presence of sulfur oxides.¹⁴⁰

Over the years, several strategies have been proposed to improve NO_x abatement via plasma-assisted catalytic technologies. Among these, the multiple-step treatment strategy, whereby two or more plasma-catalyst reactors are utilized in series, has been shown to increase the maximum NO_x conversion.¹⁴¹ Moreover, this technology should reduce the energy and/or hydrocarbon supplies for fixed conversion efficiency. Similarly, the HC-SCR process occurs via oxidation of NO, followed by the reduction of NO₂ with hydrocarbons (*vide supra*); hence, NTP can oxidize NO without depleting the number of hydrocarbons available for the reduction of NO₂ to N₂.¹⁴² This means that the function of SCR catalysts could be greatly simplified by focusing on the reduction of NO₂ by hydrocarbons.

A different approach has been studied by Bittenson *et al.*,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_x chemical reduction.



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 the electrode of the plasma reactor; in this case, the electrical power supply has a larger frequency: 40–60 kHz.

Simultaneous NO_x and soot removal systems

The stringent regulation limits on both NO_x and PM are forcing the automotive industry, one hand, to maximize engine control to reduce pollutant emissions, and on the other hand to pile up a number of costly catalytic converters; this results in rather high pressure drops, complex control features, inefficiency linked to considerable weight and space consumption and elevated costs. In this context, Diesel particulate traps appear to be necessary. Our research group has been involved in various European R&D programs (e.g. CATATRAP, DEXA-cluster, TOP-Expert, ATLANTIS) for several years, with the aim of developing novel multifunctional catalytic traps.¹⁴⁴ The simultaneous removal of soot and NO_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_x and soot from Diesel engine exhausts has clearly been pointed out in several kinetic studies (Fig. 13).^{14, 15, 145–149} Fino *et al.*¹⁴⁵ studied the kinetics of a soot-NO-O₂ 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 two NO molecules. Hence, the adsorbed NO dissociates into N (ads) and O (ads) with subsequent formation of either N₂ or N₂O. However, this mechanism does not account for the positive effect of molecular oxygen, which should conversely

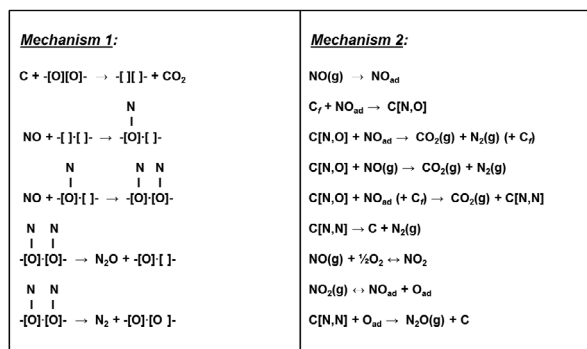


Figure 13 Reaction mechanisms proposed for the soot/NO_x/O₂ reacting system over perovskite-type catalysts

Source: Adapted from Ref.¹⁴²

lower the reaction rate by filling up the oxygen vacancies over the oxidation catalysts.^{145–147} 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_r) and the NO molecule adsorbed on the catalyst surface (NO_{ad}). Finally, N₂ can be formed through the reaction of C(N,O) with further NO_{ad} (LH-type kinetics) or directly with a gaseous NO molecule (ER-type kinetics). However, it is also possible for N₂ 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_r as a consequence of carbon combustion. The other beneficial effect is the easy formation of NO₂, 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 NO₂ (via the “fast SCR reaction”). On the other hand, the NO₂/NO ratio has to be kept close to one for effective SCR + SCF systems.

DeSoot-DeNO_x Catalysts

La-K-Cu-V-based perovskites¹⁴⁵ have shown their potential application as active catalysts for the simultaneous removal of NO_x and soot. The role of vanadium species in the perovskite lattice has been found to be prevalent in obtaining outstanding NO_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.¹⁴⁵ On the other hand,

nanostructured spinel-type oxide catalysts, that is, AB₂O₄ (where A = Co and Mn, B = Cr and Fe) have proved to be particularly active in the simultaneous removal of soot and NO_x in the 350–450 °C temperature range.^{146, 147} The best compromise between soot and NO abatement below 400 °C has been shown by the CoCr₂O₄ 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_{1-x}A_xFe_{1-y}B_yO₃ (where A = Na, K, Rb and B = Cu) have displayed high catalytic activity toward carbon combustion and NO conversion in the same temperature range.¹⁴⁴ 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_{0.9}K_{0.1}Cr_{0.9}O_{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-NO₂-NO cycles before it leaves the catalyst (the efficiency of NO_x 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 hydrotalcite can favor soot combustion, but can also lead to a 30% conversion of NO_x under “real” conditions. Lin *et al.*¹⁵⁴ have shown high catalytic activity of BaAl₂O₄ systems for the simultaneous removal of soot and NO_x under “loose” contact conditions.

It is worth noting that ceria-based catalysts have received a great deal of attention because CeO₂ alone, or in combination with other metals/metal oxides, may exhibit promising oxidation activity under either O₂ or in a NO_x/O₂ 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 CeO₂-based materials and their structural stability. The redox behavior and the availability of chemisorbed oxygen (α-species) are important features for/of these materials.^{156–158} Atribak *et al.*¹⁴⁹ have reported interesting results with Ce–Zr mixed oxides for soot combustion under NO_x/O₂. Among the different mixed oxides, Ce_{0.76}Zr_{0.24}O₂ provided the best performance.¹⁵⁹ The same authors observed that the most active mixed oxides are those which combine high surface areas

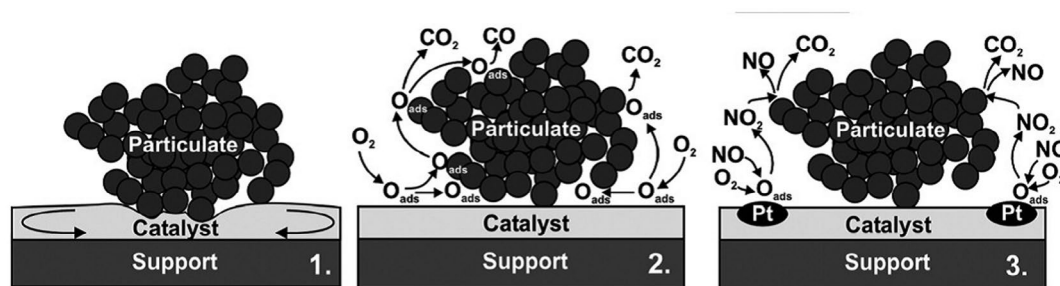


Figure 14 Simultaneous abatement of NO_x and soot over different solid catalysts: 1 = mobile catalyst; 2 = catalyst promoting oxygen spillover; 3 = catalyst coupling a NO → NO₂ functionality¹⁴⁸

with a homogeneous distribution of cerium and zirconium throughout the particles (Ce/Zr surface ratio about 3.2).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_x and soot removal depend on the interaction between the two solids and the gas mixture.^{160, 161} Nanostructured CeO₂-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).^{162–165} Moreover, the effects of cooperation between active sites (or between different phases) are favored, thus leading to a simultaneous NO_x and soot abatement.

Some issues pertaining to Diesel NO_x aftertreatment catalysts

One of the main current issues for NO_x aftertreatment catalysts is that no material seems to ensure a high NO_x abatement throughout the whole Diesel exhaust temperature range (i.e. 200–500 °C).^{2–4, 8, 14, 30} As reported above, many multicomponent catalysts have been designed over the years to increase their NO_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.^{166, 167} 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 O₂ concentrations; however, high values of these parameters are known to adversely affect NO_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.⁹⁵ Feeley et al.^{102, 168} have found that long-term exposure of Cu-ZSM-5 to SO₂ leads to its permanent deactivation. Conversely, Pt-based catalysts may exhibit good resistance to poisoning by SO₂. Nevertheless, these catalysts favor the oxidation of SO₂ 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_x catalysts, a further problem still has to be solved, that is, the formation of N₂O instead of N₂ with a subsequent negative environmental impact, due to the fact that N₂O is a greenhouse gas.¹⁶⁹

Sensitivity to water vapor is a very critical limitation for the automotive application of solid catalysts. In fact, since combustion exhaust streams are rich in water vapor (10–16%), catalysts should be able to operate in the presence of high levels of water vapor. Given the fact that NO_x levels are often <2% (typically at ca. 50 ppm level), it is very difficult to find a catalyst with active sites, which are necessary for NO sorption, that will not be flooded by water. Because of the high exhaust velocities (GHSV > 30,000 h⁻¹), it is impractical to try

to separate such large quantities of water from such a huge volume of gas. Therefore, the thermal and hydrothermal stability of catalysts is pivotal for any successful NO_x decomposition technology. The effect of water on the stability of Cu-ZSM-5 has been widely investigated (*vide supra*).^{47–50} Zeolite activity decreases to various extents in the presence of water, according to the amount of water and the reaction temperature. This effect is probably due to the fact that water, like NO_x, is a good Lewis base and competes for the same active sites on which NO_x reduction must occur.⁹⁵ Conversely, Corma et al.⁵⁴ observed that the deactivation of Cu-ZSM-5 occurs through the partial dealumination of the zeolite, the reversible migration of copper species, and the irreversible formation of catalytically inactive and stable Cu–Al clusters, which have some resemblance to CuAl₂O₄, but without the symmetry of Cu in the spinel structure. In order to improve the hydrothermal resistance of zeolites, 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.¹⁷⁰ Nevertheless, the low selectivity, and hence the relatively high amounts of N₂O 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_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.¹⁷¹ These are average values, but a more than 80% particulate matter emission reduction was recorded in tests with pure biodiesel¹⁷² with respect to fossil one. These emission reductions are reached at the price of a modest 10% emission increase in nitrogen oxides (NO_x) for pure biodiesel, which is close to zero for a 20% biodiesel content,¹⁷¹ therefore not entailing radically different catalytic formulations.

Moreover, as in the case of innovative biofuels like farnesane, which often require a re-calibration 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.¹⁷³

Conclusions

The progressive requirements for fuel-efficient diesel cars highlight the problem of the necessity of removing NO_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_x by means of ammonia/urea or hydrocarbons. The SCR of NO_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_x removal can be obtained with NH₃-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 NO_x 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% NO_x 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_x (NO_x traps) from lean exhaust, followed by release and catalytic reduction under rich conditions. This strategy has been shown to achieve ca. 70–90% NO_x reduction, and seems the most promising approach for NO_x abatement in diesel engines, since it does not require a reducing agent. NTP has been proposed as a promising technology to reduce NO_x and PM emissions in Diesel exhaust. At present, however, this approach appears more complicated than other advanced technologies for NO_x abatement.

The stringent regulation limits for both NO_x 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 NO_x 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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