Thesis for the degree of Doctor of Philosophy

Catalytic removal of NO$_x$ and soot from mobile sources

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‘You’ve got to find what you love. And that is as true for your work as it is for your lovers. Your work is going to fill a large part of your life, and the only way to be truly satisfied is to do what you believe is great work. And the only way to do great work is to love what you do. If you haven’t found it yet, keep looking. Don’t settle.’

Steve Jobs
Commercial vehicles and diesel passenger cars will be subjected in a near future to very stringent emission regulations regarding nitrogen oxides (NOx) and particulate. To handle these limits the use of exhaust after-treatment technologies is required. Different strategies have been proposed for lean-burn engines; one such strategy is the Diesel Particulate NOx Reduction (DPNR) system that accomplishes the simultaneous removal of NOx and particulate. In this thesis work the behavior of a model PtBa/Al2O3 and PtK/Al2O3 NSR catalyst in both NOx storage/reduction and soot oxidation is investigated.

It is found that the presence of soot reduces the NOx storage capacity of the catalyst, evaluated in presence of water and CO2 in the feed stream in the range 200–350 °C and with different values of the NO inlet concentration. Besides the presence of soot favors the decomposition and the reduction of the stored nitrates, while soot is being oxidized. A direct reaction between the stored nitrates and soot is suggested, that has been explained on the basis of the surface mobility of the adsorbed nitrates. This soot oxidation pathway involves surface species and parallels the NO2-soot oxidation that occurs in the presence of gas-phase NO2. This has also been confirmed by dedicated TPD and TPO experiments. However the presence of soot does not appreciably affect the behavior of the catalysts in the reduction by H2 or CO of the stored nitrates, being in all cases N2 the major reaction product along with minor amounts of ammonia.

Mechanistic aspects involved in the formation of N2 and of N2O during the reduction of gas-phase NO and of NOx stored over PtBa/Al2O3 catalyst are also investigated using unlabelled ammonia and labelled NO. It appears that N2 formation occurs primarily through the statistical coupling of N-atoms formed by dissociation of NOx and NH2-related surface intermediates, although an SCR-pathway (involving the coupling of NH2 and NO-derived ad-species) is also likely to occur. It appears as well that the formation of nitrous oxide involves either the coupling of two adsorbed NO molecules or the recombination of an adsorbed NO molecule with an adsorbed NH3 fragment.

Mechanistic aspects of NO oxidation reaction are also investigated with other catalytic systems of interest like Rh and Co-based catalysts. It is shown that NO oxidation on RhO2 and Co3O4 is limited by O2 activation at vacancies on oxygen-saturated surfaces, as also found on Pt and PdO. Oxygen binding energies set vacancy densities and turnover rates. One electron reductions accessible to RhO2 and Co3O4 facilitate O2 activation and allow faster 16O2–18O2 exchange and NO oxidation than expected from their oxygen binding strengths.
Keywords

Soot oxidation, Diesel particulate filter, 4-Ways catalysts, Lean deNOx, NOx trap promotion, LNT systems, Pt–Ba/Al₂O₃ catalyst, Pt–K/Al₂O₃ catalyst, Combined soot–NOx removal, DPNR, Lean NOx traps, NO₂ storage and reduction, Structure sensitivity
List of Publications

This thesis is based on the work contained in the following papers referred to by roman numerals (I-VIII) in the text:

I. *Study of DPNR catalysts for combined soot oxidation and NOx reduction*
   Lidia Castoldi, Nancy Artioli, Roberto Matarrese, Luca Lietti, Pio Forzatti

II. *Effect of soot on the storage-reduction performances of LNT PtBa/Al2O3 catalyst*
    Nancy Artioli, Roberto Matarrese, Lidia Castoldi, Luca Lietti, Pio Forzatti
    Catalysis Today 169 (2011) 36-44

III. *Interaction between soot and stored NOx during operation of LNT Pt-Ba/Al2O3 catalysts*
     doi:10.1016/j.cattod.2011.11.026

IV. *Diesel soot and NOx abatement on Pt-K/Al2O3 LNT catalyst: influence of temperature and ageing*
    R. Matarrese, N. Artioli, L. Castoldi, L. Lietti, E. Finocchio, P. Forzatti
    in preparation

V. *The NOx reduction by CO on Pt-K/Al2O3 Lean NOx Trap Catalyst*
   L. Castoldi, L. Lietti, R. Bonzi, N. Artioli, P. Forzatti, S. Morandi, G.Ghiotti

VI. *FT-IR study of the surface redox states on platinum-potassium-alumina catalysts*
    T. Montanari, R. Matarrese, N. Artioli, G. Busca
    Applied Catalysis B: Environmental 105 (2011) 15–23

VII. *Pathways for N2 and N2O formation during the reduction of NOx over Pt-Ba/Al2O3 LNT catalysts investigated by labelling isotopic experiments*
    L. Lietti, N. Artioli, L. Righini, L. Castoldi, P. Forzatti
    Industrial & Engineering Chemistry Research (2012)
    DOI: 10.1021/ie2021976

VIII. *Catalytic NO Oxidation Pathways and Redox Cycles on Dispersed Oxides of Rhodium and Cobalt*
    Brian M. Weiss, Nancy Artioli, Enrique Iglesia,
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Introduction

1. Introduction

1.1 Background

Diesel-equipped vehicles are considered as one of the primary sources of NO\textsubscript{x} and particulate (soot) emissions in industrialized countries. Accordingly regulations to limit their emission are becoming very strict. In Europe, the current Euro 5 rules limit NO\textsubscript{x} and soot emissions from light-weight diesel vehicles (up to 2500 kg) at 0.18 and 0.005 g/km, respectively, but a more drastic reduction is required for NO\textsubscript{x} emissions in the upcoming Euro 6 regulations (0.08 g/km).

The soot removal relies on the use of diesel particulate filters (DPFs): these devices, usually made by cordierite or SiC, remove a significant fraction of the particulate by filtration. The filters must be periodically regenerated to remove the entrapped soot, thus avoiding excessive pressure drops at the exhaust: moreover the filter may be catalyzed to promote soot combustion at lower temperatures (DOC, Diesel Oxidation Catalyst).

Concerning NO\textsubscript{x}, either Selective Catalytic Reduction (SCR) or Nitrogen Storage Reduction (NSR), also quoted as Lean NO\textsubscript{x} Trap (LNT), represent the top contenders for reducing NO\textsubscript{x} concentrations in the exhausts from diesel and lean burn gasoline engines. The SCR technique is based on the reaction between NO and NH\textsubscript{3}, which is produced by hydrolysis of an aqueous urea solution injected into the exhausts from an on-board tank:

\[ 4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \] (1)

Metal-substituted zeolites or vanadia-tungsta-titania catalysts are generally used as catalytic materials, although the former are generally preferred in view of their better high-temperature durability when the SCR catalyst is placed downstream the DPF.

On the other hand the NSR catalysts make no use of any external reductant and operate the NO\textsubscript{x} reduction under cyclic conditions by alternating long lean phases during which NO\textsubscript{x} emitted in the exhaust gases are adsorbed on the catalyst, with subsequent short rich periods (typically in the order of few seconds) in which the stored NO\textsubscript{x} are reduced by H\textsubscript{2}, CO and Hydrocarbons (HC) present in the flue gases to produce nitrogen. LNT catalysts are generally made by a high surface area support (such as γ-Al\textsubscript{2}O\textsubscript{3}), alkaline/alkaline-earth metal oxides (such as K\textsubscript{2}O and BaO) and precious metals like Pt, Rh, Pd; other components are also present in fully formulated catalysts (e.g. CeO\textsubscript{2}).
While the SCR technique is generally used in heavy vehicles (mini-van and trucks), NSR catalysts are generally preferred for small engines. Hybrid NSR + SCR configurations have also been proposed, since they guarantee higher NOx removal efficiencies. De-NOx devices are used together with De-soot devices, along with Diesel Oxidation Catalyst (DOC) as well to respect the complex emission standards. The optimal design of the aftertreatment exhaust system is still a matter of debate: the DOC is generally placed upstream the DPF and SCR/LNT converters, while different solutions have been proposed for the DPF and the DeNOx catalyst. In fact the DPF may be placed downstream the deNOx catalyst (to prevent hot gases generated upon regeneration of the DPF to reach the LNT/SCR catalysts), but in this case the DeNOx catalysts must manage the presence of soot in the exhausts. Integrated (or one-pot) solutions have also been proposed, like Catalyzed Diesel Particulate Filters (CDPFs) which act as DOC but also remove soot, or the DPNR (Diesel Particulate-NOx Reduction) technology which has been recently proposed by the Toyota group. The DPNR technique has the unique capacity to remove simultaneously soot and NOx and is based on the use of a catalyzed filter on which a NSR catalyst is deposited. In this way soot is removed by the filter while NOx are reduced according to the NSR technology. Soot oxidation occurs during the lean phase, possibly involving NO2 (formed upon NO oxidation) and/or adsorbed NOx species. In view of this, the catalytic NO oxidation to NO2 is an important issue. This reaction has been largely studied in the literature in a wide range of operative conditions and using various catalytic systems. Among them, Rh and Co represent a valid alternative to the Pt and Pd catalytic system. In the case of Co-based catalysts, the rate of NO oxidation has been correlated with the reducibility of CoOx clusters, suggesting that chemisorbed oxygen atoms O* binding and the availability of vacancies determines turnover rates on Co-based catalysts.

### 1.2 Objectives

Concerning the study of DPNR systems, the aim of the work is to provide new insights on the pathways involved in the NOx storage-reduction and soot oxidation over model PtBa/Al2O3 and PtK/Al2O3 LNT catalyst on the interactions among the related catalyst functions. For this purpose, a systematic study has been performed on the DPNR selected catalyst samples in which the reactivity in the NOx storage-reduction and in the soot oxidation has been investigated in a wide temperature range (150-350°C) and at different NO inlet concentrations with Isothermal step concentration (ISC) experiments. The interaction between soot and the stored NOx species has been further studied by Temperature Programmed Methods under inert flow (TPD) and in the presence of oxygen (TPO) in which the stability/reactivity of the stored NOx species has been analyzed both in the presence and in the absence of
Soot. The experiments have also been carried out over a Platinum-free catalyst in order to assess the role of Pt in the stability/reactivity of adsorbed nitrates as well.

Mechanistic aspects of the reduction of stored NOx and the pathways involved in the formation of N₂ and N₂O during regeneration of Ba based NSR catalyst have been also investigated. Experiments have been carried out with different reductants (H₂ and CO) and by means of isotopic labeling experiments as well. The results collected over the Pt-Ba/Al₂O₃ catalyst have been compared with those collected in the case of a Pt-K/Al₂O₃ catalyst in order to highlight possible similarities and differences.

Concerning the catalytic NO oxidation reaction, the elementary steps involved in the NO oxidation on Rh and Co catalysts and their kinetic relevance and site requirements were probed using isotopic tracers and the kinetic effects of NO, O₂, and NO₂ pressures on turnover rates have been investigated.
2. Diesel emissions and abatement technologies

Pollution has become a subject of central concern due to increasing mobility [1]: in the last sixty years, motor vehicles increased from 40 to 700 million and their number raised up to 920 million in 2010 because of the growing demand in developing countries [2].

In particular, vehicles powered by internal combustion engines are some of main responsible for the production Nitrogen Oxides (NO\textsubscript{x}), Carbon Oxides (CO\textsubscript{x}), Volatile Organic Compounds (VOCs) and Particulate Matter (PM) (Figure 2.1).
Diesel emissions and abatement technologies

Emissions control regulations have been introduced in all the industrialized countries in order to reduce the emissions from both gasoline and Diesel engines.

In particular Diesel vehicles are increasing more their worldwide penetration, starting from European countries (Figure 2.2) where Diesel motorisation in 2008 reached gasoline one [4].

Figure 2.1 - USA pollutants emission by sources [3]

Figure 2.2 - Share market: gasoline and Diesel
II. Diesel emissions and abatement technologies

To comprehend this market change it is useful to analyze some differences between the two kinds of engine, summarized in Table 2.1:

<table>
<thead>
<tr>
<th></th>
<th>Diesel</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vehicle weight</td>
<td>More</td>
<td>Less</td>
</tr>
<tr>
<td>Noise and vibration</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Starting</td>
<td>Quite instant</td>
<td>Instant</td>
</tr>
<tr>
<td>Air/fuel ratio</td>
<td>&gt;14.7 (Lean condition)</td>
<td>14.7 (Stoichiometric)</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>Less</td>
<td>More</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>15/24</td>
<td>9/12</td>
</tr>
<tr>
<td>Efficiency</td>
<td>35%</td>
<td>Less 30%</td>
</tr>
<tr>
<td>Turbocharging</td>
<td>Applied</td>
<td>Not used</td>
</tr>
</tbody>
</table>

Table 2.1 - Diesel vs gasoline features [5]

The lower fuel consumption is one of the main reasons of the increasing diffusion of Diesel engines equipped vehicles. This is due to a higher engine efficiency, that is also enhanced by turbocharging, which allows a better fuel combustion [5]. Furthermore the life of Diesel engine is generally about twice as long as gasoline one, also thanks to the better fuel lubrication properties [6]. Last but not least, lean-burn engines offer the prospect of reducing the emissions of CO₂ (Figure 2.3).

![Figure 2.3 - Gasoline vs Diesel: CO₂ emissions [7]](image)

However, Diesel engines produce higher emissions of NOₓ and PM (Figure 2.4) which have negative effects both on mankind and environment.
In particular most of the nitrogen oxides are irritant for eyes, skin, and respiratory tract [8]. Nitrogen dioxide (NO₂) is more acutely toxic (about 30 times more toxic) than nitric oxide (NO), except at lethal concentrations when nitric oxide may kill more rapidly. Acute effects in a healthy subject can be seen for very high NO₂ concentrations (>1990 μg/m³ [9]). From 400-500 μg/m³ some alterations of respiratory functions can be observed in asthmatic people. For a long period exposure it is recommended a maximum NO₂ concentration equal to 40 μg/m³ as yearly average in order to prevent collateral damages.

Furthermore NOₓ are responsible for the diminishing of photosynthetic activity, the soil acidification, the reduction of visibility and the so-called acid rain. They also contribute to the photochemical smog: acid nitric production, formation with VOCs of peroxyacetyl nitrate (PANs), aldehydes and ozone. Finally, nitrous oxide (N₂O) is considered one of the major greenhouse gases which, for some researchers [10], are responsible for the global warming (actually a phenomena not yet scientifically demonstrated).

Particulate matter, as well, leads to the above-mentioned negative effects on environment; in addition it causes the monuments fouling. On mankind, the main problem is connected to respiratory system: a constant and long exposure could be responsible for a lung cancer.

Therefore it is obvious why limits on the emissions of these pollutants become more and more stringent.
In the following sections legislative aspects about NO\textsubscript{x} and PM regulations will be presented. Furthermore, abatement technologies (applied or which research focuses on, to reach the required standards), with particular regard to Diesel engines, will be introduced.
2.1 Emission standards

All over the world, emissions legislation has become increasingly stringent and this encourages new research projects. Several sets of standards have already been defined in the past two decades for different types of vehicles. Tier 1 standards were published in 1991 in the U.S. and progressively phased-in between 1994 and 1997. Then, Tier 2 standards were adopted in 1999 with a phase-in implementation schedule from 2004 to 2009. Tier 1 standards were applied to light-duty vehicles, while Tier 2 regulation introduced more stringent numerical emission limits relative to the previous Tier 1 requirements, and a number of additional changes were made that are more stringent for larger vehicles. Similar emission limits were adopted for all vehicles regardless of the fuel consumption including gasoline, diesel, or alternative fuels. The sulfur levels in gasoline were required to be reduced by 30 ppm with an 80 ppm sulfur cap in 2006. Diesel fuel of maximum sulfur level of 15 ppm was made available for highway use beginning in 2006. Tier 4 standards designed for the period of 2008-2015 require that emissions of particulate matter and NO\textsubscript{x} be further reduced by about 90%. Sulfur was recommended to be reduced to 15 ppm (ultralow sulfur diesel) as of June 2010 for nonroad fuel and in June 2012 for locomotive and marine fuels. Such emission reductions can be achieved only through the use of control technologies—including advanced exhaust gas after-treatment systems, catalytic particulate filters, and NO\textsubscript{x} adsorbers.\textsuperscript{1}

As shown in Table 2.2, progress in European standard regulations also highlights more stringent emission limits especially for NO\textsubscript{x} emissions within the Euro 6 standard regulations.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\textbf{standard regulation}\textsuperscript{a} & \textbf{gasoline engine} & & & & \textbf{diesel engine} & & \\
& CO & HC & NO\textsubscript{x} & HC + NO\textsubscript{x} & CO & NO\textsubscript{x} & HC + NO\textsubscript{x} & particulates \\
\hline
\textbf{Euro 1 (1993)} & 2.72 & & 0.97 & & 2.72 & 0.97 & 0.14 & \\
\textbf{Euro 2 (1996)} & 2.20 & & 0.5 & & 1.00 & 0.90 & 0.10 & \\
\textbf{Euro 3 (2000)} & 2.30 & 0.20 & 0.15 & & 0.64 & 0.50 & 0.56 & 0.05 \\
\textbf{Euro 4 (2005)} & 1.00 & 0.10 & 0.08 & & 0.50 & 0.25 & 0.30 & 0.025 \\
\textbf{Euro 5 (2009)} & 1.00 & 0.10 & 0.06 & & 0.50 & 0.18 & 0.25 & 0.005 \\
\textbf{Euro 6 (2014)} & 1.00 & 0.10 & 0.06 & & 0.50 & 0.08 & 0.17 & 0.005 \\
\hline
\end{tabular}
\caption{EURO emission standard for light-duty vehicles}
\end{table}

\textsuperscript{a} Measured from New European Driving Cycle (g/km).

European legislation concerns only some kinds of pollutants: CO, HC (Hydrocarbons), PM and NO\textsubscript{x}. On the contrary CO\textsubscript{2} is not officially regulated, but EU and automotive manufactures came to a voluntary agreement few years ago [13].

Furthermore, starting from the EURO 3 stage, vehicles must be equipped with an On Board Diagnostic (OBD) system for emissions control [14]. Driver must be notified in case of a malfunction or deterioration of the emission system that would cause emissions to exceed mandatory thresholds.

Moreover since Euro 5, a particle number emission limit, in addition to the mass-based limits, has been introduced. This to prevent the emission of ultra fine particles, which are more dangerous for human health, because of their major ability to penetrate in respiratory system. To measure particle number a
II.

Diesel emissions and abatement technologies

A new method is adopted: PMP (*Particulate Matter Protocol*). One of the main concerns about a number of particle limit emission is the difficulty and the reliability of measure, but current system has been demonstrated to be repeatable and reproducible between laboratories [14].

Actually, every country has its own emission standards, but it is worth of note that European legislation is followed also by all but three Asian countries (the exception are Japan, South Korea and Taiwan). To put it in another way a population of 3 billion people follows the European standards. Precisely the delay in implementation of EU standards is three or four years. Hence this gives European legislators a special responsibility: the earlier we introduce standards in EU, the more perspective there is for cities in China, India and elsewhere to improve their appalling air quality [14]. Nevertheless European regulations are not the strictest ones: Japan and USA have traditionally harsher environment policies. There has been much talk in recent years about the need to harmonise global emission standards. In particular, the car industry has always been keen on this topic, in fact a car that just has to pass one emissions test could then be sold everywhere: Asia, Europe and USA [14]. Indeed some of the USA federal states (California, New York, Massachusetts, Maine, Vermont) have adopted more stringent standards.

The technological development is obviously close to issued laws; Figure 2.5 shows the strategies adopted by automobile industry in order to respect the required standards for both PM and NOx:

![Figure 2.5 - Measures to achieve emission levels for Diesel equipped vehicles [15]](image)

In the passage from EURO 1 to EURO 3, the optimization of engine and injection system were required, as well as the use of an oxidation catalyst (DOC) in order to abate particulate matter.

With EURO 3, NOx limits were introduced for Diesel engines and issued standards for both the pollutants were respected with a further optimization of engine, injection system, combustion and fuel. This, since EURO 4 has not ever been possible: for the engine out-emission there is a well-known trade-off between the two pollutants mentioned above. Over a period of time, thanks to the so-called *primary techniques* the trade-off curve moved to lower values of both NOx and PM. However this is not enough to join the limit emission of further legislation for both the pollutants, therefore *secondary techniques* are required.

In particular, the passage from EURO 4 to EURO 5 saw the DPF system as compulsory for particulate matter abatement and a deNOx after-treatment technology as necessary on heavier vehicles which are
II. Diesel emissions and abatement technologies

equipped with an always more complex abatement technology. Eventually, only applying deNO\textsubscript{x} system EURO 6, US and Japanese NO\textsubscript{x} limits will be respected.

In next paragraph, some of the main primary and secondary techniques (applied on vehicles or still under study) will be presented.

It is worth of note that, to obtain the required standards, several technologies have to be put together. Actually, the performances of commercial catalytic post-treatment systems are not optimized to fulfill the forthcoming U.S. standard legislation and those that will be implemented in Europe near 2014, particularly the low limit of NO\textsubscript{x} emissions from diesel engines.
2.2 Abatement technologies

In order to reduce both NO\textsubscript{x} and PM are necessary:

- *primary* techniques which limit pollutant formation;
- *secondary* techniques which work on flue gases, purifying them through chemical or mechanical treatments.

Primary techniques are not sufficient to reach the required standards because of the so-called trade-off: operative conditions influence in opposite way the pollutant formation. In Figure 4.28 the effect of air/fuel ratio, defined as:

\[ AFR = \frac{\text{mass of air used by the engine}}{\text{mass of fuel burned by the engine}} \]  
\[ \lambda = \frac{AFR_{\text{effective}}}{AFR_{\text{stoichiometric}}} \]  

Lambda (\( \lambda \) = stoichiometric combustion ratio) is an alternative way to represent AFR:

The vertical line in Figure 2.6 separates the *rich-mixtures* (AFR < 14.7) and *lean-mixtures* (AFR > 14.7) for gasoline engines. Typically Diesel engines work in lean conditions where it is evident the opposite behavior in HC/CO (soot precursors) and NO\textsubscript{x} production.
II. Diesel emissions and abatement technologies

2.2.1 Primary techniques

Developments in fuel composition, injection systems, combustion process and engine technology allow the trade-off curve to move to lower values of both \( \text{NO}_x \) and PM.

2.2.1.1 Fuel

An improvement in fuels composition was imposed since EURO III [17]. One of the parameters strictly ruled by legislation is the sulphur content (Table 2.3).

<table>
<thead>
<tr>
<th></th>
<th>EURO III</th>
<th>EURO IV</th>
<th>EURO V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur ppm</td>
<td>350</td>
<td>50</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2.3 - Sulphur content ruled by legislation [18]

It precludes the use of the most effective PM and \( \text{NO}_x \) control technologies and it affects directly the PM emissions: for every 100 ppm reduction in sulphur, there is a particulate abatement of 0.16% for light-duty vehicles and of 0.87% for heavy-duty vehicles [18].

Cetane number is the reference index for Diesel fuels: the higher it is the better fuel qualities are. The minimum value is fixed to 51 and it depends on fuel composition; for instance a large amount of aromatics lowers it to 40-45 and this produces more difficulties in cold starting and increases combustion noise, HC and \( \text{NO}_x \) production. Furthermore the aromatic content is correlated with particulate emissions [18].

Density and viscosity are the physical properties which most affect the mass of fuel injected into the combustion chamber and, thus, the AFR [18] and the consequent pollutants formation.

At present, researchers are interested in the formulation of alternative fuels:

- **Bio - Diesel**, in particular the RME (Rape Methyl Ether) which affects pollutants emissions as listed in Table 2.4

<table>
<thead>
<tr>
<th>Emission [g/kWh]</th>
<th>Diesel fuel</th>
<th>RME</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_x )</td>
<td>17.9</td>
<td>19.6</td>
</tr>
<tr>
<td>PM</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>CO</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td>HC</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 2.4 - Emissions of RME vs Diesel Fuel [4]

The major \( \text{NO}_x \) production is connected to higher oxygen content in Bio - Diesel.

- **Synthetic Diesel** obtained by Fischer - Tropsch process. It is evident (Figure 2.7) the reduction of all the main pollutants.
II. Diesel emissions and abatement technologies

Figure 2.7 - Reduction of emissions with a synthetic fuel [4]

2.2.1.2 Injection system and strategies

Fuel atomization, thus the ignition and combustion process, depends on injection system. It is possible to distinguish:

- **Indirect injection**: fuel is injected into a small prechamber which is connected to the cylinder by a narrow opening. The initial combustion takes place in this prechamber. This has the effect of slowing the rate of combustion, which tends to reduce audible noise [21];

- **Direct injection** fuel is injected directly into the cylinder; the piston incorporates a depression which is where initial combustion takes place [21].

Direct injection system is used for both gasoline and Diesel engines, on the contrary, indirect injection is typical for Diesel. However, it is not so applied to modern cars because of its lower efficiency compared to direct systems: the reduced material volume of the direct injection Diesel engines decreases heat losses, therefore cold starting is easier and with a less production of pollutants. A particular kind of direct injection is the TDI (Turbocharged Diesel Injection), commercialized by Volkswagen Group, which is a gas compressor used for forced-induction of an internal combustion engine. Like a supercharger, the purpose of a turbocharger is to increase the density of air entering the engine to create more power. However, a turbocharger differs in that the compressor is powered by a turbine driven by the engine's own exhaust gases [22]. Another very famous system is Multijet, introduced by FIAT in 2002. It is a common rail system, characterized by five injectors that allow a slower combustion and permit a better control of the engine during the cold start [23].

Furthermore there are several injection strategies:

- air staging which consists of air fed at different stages;
II. Diesel emissions and abatement technologies

- fuel staging which consists of air and fuel fed at different stages;
- early injection [13] which consists of a mixing between fuel and gas before the ignition. This avoid the condition for soot formation;
- late injection [13] which consists of a simultaneously mixing and burning of the charge using a swirl;
- EGR which works by recirculating a portion of the engine’s exhaust gas back to the combustion chamber. Recirculated exhaust gas consists of inert gas (CO₂ and H₂O) which dilutes the incoming air reducing a possible oxygen excess and lowering the adiabatic flame and peak combustion temperature, responsible for the formation of thermal NOₓ. In modern Diesel engines, the EGR gas is cooled by a heat exchanger which allows the introduction of a great mass of recirculated gas (Figure 2.8).

![Figure 2.8 - EGR diagram](image)

Diesel engines operate with an excess of air and they benefit from EGR rate as high as 50% in controlling NOₓ emissions, but an increase in particulate matter production is present due to the reduction of the specific heat ratio of the combustion gases in the power stroke. Even if the combination of good mixing and high EGR helps to reduce soot and NOₓ [13] a particulate matter abatement technology is required, typically DPF (*Diesel Particulate Filter*).
II. Diesel emissions and abatement technologies

2.2.2 Secondary techniques

With primary techniques the trade-off curve was lowered (Figure 2.9) but, to cope with the emissions standard, secondary techniques are necessary: in particular a DPF system to abate particulate matter and a deNOx catalyst to reduce nitrogen oxides emissions.

![Particles and NOx Trade-off](image)

**Figure 2.9 - Trade-off curve [25]**

2.2.2.1 Particulate matter

In order to respect the PM and HC/CO limit emissions imposed by EURO IV the introduction of **DOC (Diesel Oxidation Catalyst)** was critical. It is a flow-through device that consists of a stainless steel canister containing a honeycomb-like structure or substrate (Figure 2.10).

![DOC system](image)

**Figure 2.10 - DOC system [26]**

The substrate has a large surface area coated with a catalyst layer containing a small, well dispersed amount of precious metals such as platinum or palladium [27].

The DOC is also called 2-way oxidation catalyst because, as the exhaust gases pass through the catalyst, CO and unburned compounds are oxidized according to the following reactions:
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\[
4 \text{HC} + 5 \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 4\text{CO}_2
\]  \hspace{1cm} (1.3)

\[
2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2
\]  \hspace{1cm} (1.4)

Diesel oxidation catalyst removes up to 90% of carbon monoxide and hydrocarbons. It can also reduce Diesel particulate matter by up to 30%, though typically it is in the region of 8-10% [26].

Actually the used catalysts lead to the oxidation of NO to NO\(_2\), which is more dangerous for human health but which is very useful to improve the performances of downstream devices:

- DPF regeneration (CRT\(^*\) – Continuously Regeneration Trap);
- NH\(_3\) - SCR nitrogen oxides reduction at low temperature.

Nowadays, in order to submit PM limit emissions, almost all the Diesel vehicles are equipped with a DPF. (Diesel Particulate Filter). It is a wall-flow ceramic monolith, derived from the flow-through supports used for catalytic converters. The adjacent channels are alternatively plugged at each end in order to force the Diesel aerosol through the porous substrate wall, which acts as a mechanical filter. The particulates are not able to flow through the wall and is deposited in the channel walls (Figure 2.11).

![Figure 2.11 - DPF filter structure [28]](image)

The main advantage of the wall-flow particulate filter is the high surface area per unit volume which, combined with the high collection efficiency (over 95%), makes this technique very attractive. The filter walls have a porous structure that is carefully controlled during the manufacturing process: typical values of material porosity are 45 - 50% and medium pore size is 10 - 20 µm [28].

Two kinds of filter materials are commonly used: cordierite and silicon carbide. The first one is a synthetic ceramic developed for flow-through catalyst substrates and then adapted to filter; silicon carbide has been recently introduced as filter material, because of its better durability in high thermal stress applications, but, due to its weight and high cost, the market is still dominated by cordierite [13].
Actually other materials are studied, for example aluminium titanate whose properties are impressive compare to SiC materials: low thermal expansion and high strength; in fact no cracks in the filter material were observed even after a long run of severe regeneration cycles. Further, a tight control of pore size reduces the typical backpressure on filter with soot presence [29].

The particulate collection mechanism is governed by:

- Depth filtration (particles with diameter size lower than the filter porosity are deposited inside the porous material);
- Cake filtration (particles are deposited on the channel as show in Figure 2.12).

![Figure 2.12 - SEM-image of a DPF section showing the soot accumulation on a channel (left) and distinguishing the soot from the ash layer (middle and right) [28]](image)

Obviously when filter collects the particulate matter from the exhaust gas an increase in filter backpressure is present. This provokes higher fuel consumption and reduces available torque [30]. Moreover the capacity of the filter is not infinite and it has to be regenerated. The regeneration process can be classified as active or passive.
Active methods

The active methods consist of burning off the collected particulate. Under the conditions met in Diesel exhaust systems regarding flow and oxygen concentration, the required reaction rates for complete regeneration are attained at temperatures above 550 °C, which are scarcely reached at urban driving conditions. Thus several regeneration techniques have been suggested over the last 20 years, the most simple and effective based on catalysts: coated filter [31] or fuel doping [32].

The soot combustion temperature is lowered by doping fuel with catalytic additives (Fuel Borne Catalyst), typically organometallic compounds: the organic part is oxidized in the engine combustion chamber, while the metallic part is well dispersed in soot. A lot of metals have been proposed: cerium [33] and iron [34] for their low cost and low toxicity. Actually copper [35] and molybdenum [36] have a higher activity but they have a negative influence on men health.

Although the oxidation rate of soot is significantly increased, additional heating is necessary due to the low exhaust gas temperatures under all operating conditions. PSA Peugeot-Citroen was the first car manufacturer that commercialized system represented in Figure 2.13 - Schematic representation of an active regeneration system [37]

Figure 2.13 - Schematic representation of an active regeneration system [37]

The system consists of a wall-flow SiC filter, an oxidation catalyst in front of the filter, a dosing filter for fuel additive and a number of sensors associated with a specific engine software which allows the regeneration process and guaranties system diagnosis. During the regeneration mode, occurring every 400-500 km, three injections are performed:

- a pilot fuel injection to control the initiation of the heat release;
- a second injection to insure stable and late combustion;
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- a third injection (post injection) to allow the necessary exhaust gas temperature.

Actually the increase of the exhaust gas temperature is obtained by the oxidation of HC of the third injection thanks to the catalyst placed in front of the filter. This contribute is much more significant at low engine load and speeds.

These filters have to mainly face the ash accumulation which makes necessary to clean or to substitute the filter itself. Furthermore the additive tank has to be refilled periodically [28].

The alternatives to this kind of filters are the washcoated ones (Catalyzed Ceramic Traps), commercially introduced in 1985 on Mercedes cars sold in California [28]. The main component of the filter is the wall-flow monolith (Figure 2.14), whose walls are coated with an active catalyst: oxides of base metals, noble metals as well as a mixture of both.

![Figure 2.14 - Washcoated Filter](image)

The main disadvantage of this system is the pure contact between the catalytic coating and the soot particles: only particulate in direct contact with the catalyst can be oxidized. Moreover sulphur oxides, in exhaust gas, thanks to water can be transformed in sulphates which increase the particulate matter emissions.

Some catalytic coating may overcome the above limitation: liquid phase catalysts such as molten salts. These catalysts are based on eutectic mixtures of metal oxides that are liquid at relative low temperatures. Due to the liquid state, the soot particles may be wetting by the catalyst providing a better contact [38].

Other kinds of filter exist, for example the sintered metals or the bobbin filters.

The first consist of metal plates that can be deformed like metal sheets (Figure 2.15) in order to be finalised to cell-like structures. Their advantages are the very good heat conduction (easier active regeneration) and the low susceptibility at thermal stresses.
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On the other hand, bobbin filters consist of a number of perforated cylindrical metal tubes with ceramic fibres threads woven in a diamond pattern (Figure 2.16). Their advantages are the high filtration efficiency and the low pressure drops.
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Passive methods

As said before, the filter regeneration can be also passive, since additional heat is not required. One of the main applied system is CRT\textsuperscript{®} (Continuously Regeneration Trap), patented by Johnson Matthey [40]. As presented in Figure 2.17 it consists of a Platinum catalyst and a particulate filter.

![CRT\textsuperscript{®} filter system](image)

The device is made up of two chambers where the oxidation step is separated from the soot collection/combustion process. The first chamber contains a substrate coated with a highly active Platinum catalyst which allows the oxidation of a portion of NO to NO\textsubscript{2}, which is the key to the soot burning collected by CRT filter. In fact, in presence of NO\textsubscript{2}, soot is oxidized at lower temperatures than with oxygen: compatible with the typical exhaust gas temperatures. The filter can be uncoated or coated with Pt to enhance the soot combustion. In order to have a high system efficiency, fuel has to have a low sulphur content (30 ppm is recommended) and NO\textsubscript{2}/PM ratio has to be at least 25 [30].

This device had a lot of success, but, in view of more stringent legislation about nitrogen oxides, its performances are not so promising.

Another system capable to reduce Diesel particulate matter at low oxidation temperature is the Plasma regeneration device. The soot is oxidized in air ionised by an electric arc [41]. Some reactive species, such as OH, O radicals or NO\textsubscript{2} facilitate the combustion. To achieve the required regeneration two configurations have been proposed:

- Two stage reactor patented by Johnson Matthey. It is made up of a plasma, which generates the oxidant species, and of a downstream DPF [42]; however, in order to reduce both particulate and nitrogen oxides a deNO\textsubscript{x} catalyst is required;

- One stage reactor patented by AEA Technology. It utilizes a bed of ceramic pellets placed between two electrodes. A system of channels in the inner electrode directs the exhaust gas through the pellet bed (Figure 2.18);
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![Diagram of a single stage plasma reactor](image)

**Figure 2.18 - Single stage plasma reactor [43]**

In this reactor, the presence of carbonaceous particles affects the chemical reactions, in particular a less production of NO₂ is observed.

2.2.2.2 **Nitrogen oxides**

In order to abate NOₓ several secondary techniques are available, all connected to a catalyst activity. One of the emerging is NH₃-SCR (Ammonia-Selective Catalytic Reduction) both for light-duty and heavy-duty applications [13]. Alternatives are mainly HC-SCR (Hydrocarbon-Selective Catalytic Reduction) and LNT (Lean NOx Trap).

**Selective Catalytic Reduction of NOx with Ammonia (Urea)**

The SCR process was first applied in 1970s in Japanese stationary plants for the reduction of NOₓ emissions by using ammonia as reducing agent. In Europe it was introduced 1985 and today is very diffuse: from power and co-generation plants, to glass, steel and cement factories. This process is up today regarded as the most effective method for NOₓ reduction [45]. It is presently considered to be also the best technology for the removal of nitrogen oxides of Diesel engines equipped vehicles. In fact it is the only one that grants an optimum compromise between low emissions and fuel consumption.

The SCR process, for stationary plants, is well represented by the so called Standard - SCR which follows a 1:1 stoichiometry for ammonia and NO according to reaction 1.6:

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]  
(Standard SCR) \hspace{1cm} (1.6)

It occurs when more than 90 % of nitrogen oxides consist of NO (usually flue gases have this composition, for that the reaction is named as standard). It takes place fast in the temperature range 250 - 450 °C.
However, to describe SCR process applied on mobile systems, two more reactions are necessary. They occur in presence of NO₂ that, on vehicles, comes from the oxidation of NO by DOC. When reactive system is characterized by an equimolar amount of NO and NO₂ the *Fast-SCR* occurs.

\[ 2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \]  \hspace{1cm} \text{(Fast SCR)} \hspace{1cm} (1.7)

It is called *fast*, because of its higher reactivity compared to *Standard overall* at low temperatures.

When reactive system consists of pure NO₂ the *NO₂ - SCR* occurs. Above 250 °C the process stoichiometry is as follows:

\[ 8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \]  \hspace{1cm} \text{(NO₂ SCR)} \hspace{1cm} (1.8)

Nowadays research is focusing on development of selective catalysts, experimenting different suitable materials. SCR techniques for stationary application are very well established but improvements are necessary to allow a wide diffusion of this technology on mobile systems, in particular Diesel engine equipped vehicles. By reactions 1.6 - 1.8 it is evident that the reducing agent is ammonia, but it has problem of toxicity, handling (it is gaseous at environment conditions) and flammability, so it cannot be used directly on mobile systems. The solution is to produce ammonia *in situ*, for example using an aqueous urea solution (it is liquid and no toxic). The commercial name of this solution, patented by BASF, is Adblue®. It is a solution with a concentration of 32.5%w/w, so at the mixture eutectic point. Actually, alternative products are studied because of the Adblue® limitations:

- high freezing point (-11 °C);
- deposition of solid matter caused by a delayed evaporation;
- low ammonia content (0.2 kgNH₃/kg) [46].

Urea is usually atomized into the hot exhaust gas. The first steps are the evaporation of water from droplets and the urea melting. Subsequently, urea is thermally decomposed into equimolar amounts of ammonia and isocyanic acid that is in turn hydrolyzed.

Anyway the ammonia slip has to be reduced, to this purpose an accurate control system could be installed: monitoring several parameters such has NOₓ flow rate and temperature the ammonia injection is modified. Another solution, coupled with the former, could be a further oxidation step, in order to abate residual ammonia. The system described is more adapt for big Diesel engines. The greatest problem for its application on small vehicles is represented by the volume.

As said before, if *Fast-SCR* occurs, overall at low temperatures, an improvement in abatement performances is observed. It proceeds with an equimolar consumption of both the nitrogen oxides involved according to 1.7. Actually, this reaction has a complicated chemistry, which has been extensively studied on V₂O₅-WO₃/TiO₂ [48, 49, 50, 51, 52] and it is still under study for new commercial zeolites catalysts: a mechanistic pathway similar to that proposed for V₂O₅-WO₃/TiO₂ well explains data on BaNa-Y zeolite [53] and on transition metal zeolite [54] with particular regard to Fe-Zeolite [55]. Zeolites offer a number of advantages over vanadia/titania catalysts: they are active over a wider
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Temperature range, they are more resistant to thermal excursions, and the spent catalyst can present less of a disposal problem.

Automobile manufacturers aim to replace traditional $V_2O_5$-WO$_3$/TiO$_2$ with catalysts having a wider working temperature window: mainly to solve the high-temperature anatase-rutile TiO$_2$ deactivation, the SO$_2$ enhanced oxidation to SO$_3$ and the loss of vanadium above 650 °C. Moreover V compounds are toxic, with an increasing toxicity with the valence: pentavalent compounds, like $V_2O_5$, are the most dangerous, in fact it was reported to be carcinogenic for rats by inhalation [60], although the interpretation of the results has recently been disputed. Further it has not been classified as to carcinogen by the U.S. EPA (1991).

Several kinds of zeolite were proposed as nitrogen oxides reduction catalysts, overall for mobile applications, even if some stationary plants already use them [13].

Selective catalytic reduction with hydrocarbons (HC-SCR)

The selective catalytic reduction for NO$_x$ using hydrocarbons is a technique similar to NH$_3$ but using unburned or injected HC as the reducing agent instead of ammonia. Since the concept of HC-SCR was first developed a vast amount of research has been undertaken and published, however a commercialisation of the system still lies in the future.

Even though a lot of effort has been paid to understand the reaction mechanism for reduction of NOx by hydrocarbons under lean conditions the reaction steps remain unclear. In the literature several reaction pathways have been proposed and they seem to be dependent on factors like the type catalyst, reducing agent, reaction conditions, presence of water and sulphur oxides in exhaust gases. Essentially three types of active catalyst have been identified, i.e zeolites, metal oxides and nobles metal. The major unsolved problems of this technique could be summarized as follows:

- Catalysts require some form of HC enrichment; HC levels in diesel exhaust, especially in modern engines, is too low for any significant NOx reduction using diesel exhaust itself (passive DeNOx).
- Even with HC enrichment, the maximum conversion efficiency at realistic HC/NOx ratios is low, on the order of 30 - 50%.
- Temperature window of known catalysts is narrow and not always corresponds to the exhaust gas temperature range at which most NOx is emitted from the engine.
- Catalyst durability needs to be improved in terms of both resistance to poisons and, in some cases, hydro-thermal durability.
- Catalysts need to be more selective towards reducing NOx to nitrogen, as opposed to nitrous oxide.

Solutions to these problems can be classified into two groups: (1) optimization of catalyst formulation and (2) optimization of the emission control system. Better catalysts could provide such benefits as
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Improved efficiencies, wider temperature window, or, last but not least, better durability. Even in the absence of new, breakthrough catalyst formulations, significant improvement can be achieved by system optimization. Reported ideas include using two catalysts, possibly of different formulations, optimized catalyst locations (close-coupled, underfloor), optimized HC enrichment strategies (including exhaust flow by-passes), exhaust gas cooling, and more.

Lean NO\textsubscript{x} Trap

Lean NO\textsubscript{x} Trap (also known as NRS NO\textsubscript{x} storage reduction) system is generally regarded as one of the leading technologies for the control of NO\textsubscript{x} emission under lean-burn conditions. It is, nowadays, studied in depth because seen as promising for passenger cars: it is cheaper than NH\textsubscript{3}-SCR for engines less than about 2.0 to 2.5 litres capacity as shown in Figure 2.19 [13].

![Figure 2.19 - LNT /SCR cost comparison](image)

A typical LNT catalyst consists of at least one precious metal (such as Pt, Pd or/and Rh), NO\textsubscript{x} storage material (alkaline or alkaline-earth), and a high-surface-area support (i.e. Y-Al\textsubscript{2}O\textsubscript{3}). In this approach no additional reducing agent is required. These systems cycle through two stages of operation: under lean-conditions (for about 1 min) NO is oxidized to NO\textsubscript{2} over precious metal and then is stored in a form of nitrate/nitrite at the surface of Ba-containing material. After changing periodically to short cycles of fuel-rich conditions (less the 1 s) the stored NO\textsubscript{x} are reduced to N\textsubscript{2} by unburnt HC over noble metal catalyst, resulting in the regeneration of the catalyst. The activity of NO\textsubscript{x} adsorbers covers a fairly wide catalyst temperature window, extending from about 200°C to 450-500°C. In diesel NO\textsubscript{x} adsorber systems, the maximum performance typically occurs in the 350-380°C range. The lower end of the temperature window is determined by the catalyst activity in regards to the oxidation of NO to NO\textsubscript{2}, as well as NO\textsubscript{x} release and reduction. The upper temperature is related to the thermodynamic stability of nitrates, which undergo thermal decomposition at higher exhaust temperatures, even under lean
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conditions. The NOx adsorber temperature window is in fairly good correlation with diesel engine loads and exhaust temperatures at which most of diesel NOx generation occurs. It is this favourable position of the temperature window and the high NOx conversion efficiency, which makes NOx adsorbers an attractive diesel NOx control technology. However several issues still have to be answered before the LNT technology can be confirmed as an option for commercial vehicles.

The main drawback hindering the widely commercial use of the NSR catalyst for mobile lean NOx reduction is its sensitivity to sulphur poisoning. Fuel and lubricant oil are the major sources for the sulphur in the exhaust gas. Reduced sulphur species including hydrogen sulphide (H2S) and carbonyl sulphide (COS) may be also present in the gas during the rich excursions. In the presence of an oxidation catalyst, these compounds form stable sulphates with the NOx storage materials. The adsorption of sulphur is preferential over the adsorption of NOx. Stable sulphates, such as Al2(SO4)3, are also formed with washcoat materials. As a result, the catalyst performance gradually declines and fewer sites are available for NOx adsorption.

The sulfur is removed by passing a rich, hot stream (700°C) for a total of about 10 minutes every 3000 to 6000 miles (5000 to 10,000 km). Although earlier LNTs lost perhaps 50% of their capacity over 15 to 20 desulfation cycles, newer versions now lose only about 25% of the fresh NOx capacity. Further, in the past it was difficult to control desulphation temperature to within 700 to 800°C. Newer control strategies now allow this degree of control, and perhaps even better.

Given this, LNTs are effective to about 60 to 70% NOx efficiency in ‘realworld’ light-duty systems.

Finally, there has been much recent interest in combining LNTs with SCR. In this case, a downstream SCR catalyst stores ammonia that is generated in the LNT during rich operation. The ammonia can react with slipped rich NOx or lean NOx, increasing system efficiency, or decreasing the platinum group metals (pgms) loading, and hence cost at constant efficiency. A recent variant of this method employs a NOx adsorber/SCR double layer configuration. The system exhibits excellent low-temperature NOx conversion in the 200°C range, but poor high temperature conversion over 350°C. Another feature is that desulphation occurs at 500ºC, as compared with 700 to 750°C for conventional LNT systems [8].
2.2.2.3 Combined technologies

In order to comply with the more stringent limit emissions for Diesel equipped vehicles, concerning both PM and NO\textsubscript{x}, it is necessary to design complex after-treatment systems obtained by combining some of the above described technologies. Actually the aim is not only to reduce emissions but also costs, volume and mass. Indeed vehicles, due to the presence of several after-treatment devices are heavier and this causes indirectly an increase in fuel consumption and in CO\textsubscript{2} production.

The amount of pollutant emissions strongly depends on vehicle size and the after-treatment systems, as well, are connected to the vehicle volume and capacity (Figure 2.20).

![Figure 2.20 - Light duty Diesel MiNO\textsubscript{x} applications [75]](image)

Typically, the bigger the vehicle is, the more complicated is the after-treatment system. It is worth of note that, at the present, the smallest Diesel cars need only a PM abatement technology, but with the increase of dimensions it is necessary the combination with a deNO\textsubscript{x} system.

The choice of the nitrogen oxides after-treatment system is closely dependent on vehicle size and weight (Figure 2.21):

![Figure 2.21 - DeNO\textsubscript{x} system required depending on vehicle weight [25]](image)

It is worth of note that the heavier is the vehicle the higher is NO\textsubscript{x} production and a SCR system is required to fulfil limit emissions.

Actually, to put a classic SCR system on a medium size vehicle is a problem connected to the presence of the big urea storage tank. A possible solution is an in situ NH\textsubscript{3} production, for instance, by a LNT system. This was proposed by Daimler in the BlueTEC\textsuperscript{®} technology.
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BlueTEC® technology

BlueTEC® is a modular exhaust treatment package that can be aligned with different vehicle and engine types to ensure the most stringent emission limits both of NO\textsubscript{x} and PM.

The first element of this technology consists of engine and combustion optimization measures designed to achieve the lowest possible raw emissions during cylinder combustion.

The second BlueTEC® component is the oxidizing catalytic converter which reduces carbon monoxide and unburned hydrocarbons emissions.

Component number three is the maintenance-free particulate filter. This filter, which reduces particulate emissions by up to 98 percent and its emission levels are on a par with the limits specified in EURO V standards. Actually this device, in BlueTEC® I technology, is interposed between LNT and SCR catalytic converters (Figure 2.22).

Thus NO\textsubscript{x} reduction takes place in two stages: first by the LNT and second by the SCR catalyst, supported by ammonia from the LNT. The system shows a discontinuous behavior: during the rich phase LNT is regenerated and the ammonia produced is stored by SCR catalyst; during the lean phase LNT and SCR abate NO\textsubscript{x}. Furthermore the SCR deNO\textsubscript{x} activity makes up for the loss in LNT performance over time due to fuel sulfur poisoning.

It is evident that the above after-treatment systems take up a lot of space and research focuses on more compact systems. For example, to reduce the occupied volume, LNT and SCR could be put together in a single device, like proposed by Honda. In 2006, they announced the launch of a new Diesel car equipped with a NO\textsubscript{x} reduction catalyst, combining NO\textsubscript{x} adsorber catalyst (NAC) and a SCR catalyst in a two-layer structure: one adsorbs NO\textsubscript{x} and generates ammonia during the regeneration, the other adsorbs the ammonia and uses it for a SCR reaction to further reduce NO\textsubscript{x} [82].
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**SCRT<sup>®</sup> technology**

Other companies like Einox and Johnson-Matthey propose a configuration that combines CRT<sup>®</sup> (*Continuously Regenerating Trap*) technology with SCR to reduce nitrogen oxides (NO<sub>x</sub>). The combination of these technologies in SCRT<sup>®</sup> provides a system which reduces all legislated Diesel engine emissions in Figure 2.23.

![Figure 2.23 - Emission reduction capability [83]](image)

As already said, the SCRT<sup>®</sup> system combines two major components, the CRT<sup>®</sup> and the SCR, integrated into a single compact unit, as shown in Figure 2.24.

![Figure 2.24 - Eminox SCRT<sup>®</sup> after-treatment system layout [83]](image)

At the CRT<sup>®</sup> outlet flow, gas consists of CO<sub>2</sub>, H<sub>2</sub>O, NO e NO<sub>2</sub>. In fact, in upstream section platinum catalyst allows the reactions (1.3)-(1.4) and the following:

\[
\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2
\]  

(1.24)

Some of the NO<sub>2</sub> continuously oxidizes particulate matter collected in DPF according to:


C + 2NO₂ → CO₂ + 2NO \hspace{1cm} (1.25)

The exhaust gas goes through SCR section, which consists of two chambers, one to mix the urea with the exhaust gas and the second, containing a coated monolith developed to realize the deNOₓ activity.

It is very important to dose exactly the amount of required urea, otherwise all the nitrogen oxides will not be consumed and ammonia could be emitted from the tail pipe. In order to avoid the first problem a nitrogen oxide and temperature sensors provide to an ECU (Electronic Control Unit) the necessary information to be able to dose the urea accurately. On the other hand, to abate possible unconverted ammonia, a slip catalyst (an oxidation catalyst) is placed downstream.

Even if SCRT® is considered as a compact system, actually it consists of three or four catalyst bricks (oxidation catalyst, particulate filter, SCR monolith and ammonia slip catalyst). Thus, the occupied-space problem is not completely solved. Moreover, the gas flowing through the SCR section has a larger amount of NO, than NO₂; that means a lower efficiency of deNOₓ activity, overall during low speed and engine load. The solution to this problem could be a different after-treatment configuration: putting SCR section upstream of DPF.

At present, the proposed layouts are mainly two: DOC + SCR + DPF and DOC + DPF + SCR. It is worth of note that in both the configurations DOC is in first position, upstream of the other devices. In fact, in this way, it allows greater system durability at high temperatures, contributing to convert, thanks to oxidation reactions, CO and unburned hydrocarbons to CO₂ and H₂O. As the reactions occurring in DOC are exothermic, they generate the necessary heat for the thermal DPF regeneration. Moreover this device supplies an extra amount of NO₂, useful to passively regenerate the DPF and to enhance the NOₓ conversion in the SCR section (mostly at low temperatures thanks to the Fast-SCR).
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**DPNR® technology**

If LNT process is sufficient in order to fulfil limit emissions, it may be coupled with a particulate matter abatement system in a single device: the DPNR. It was proposed by Toyota and commercialized in large scale, for the first time, on Avensis in year 2002. This system is a combination of a highly porous wall-flow ceramic particulate filter coated with a NOx absorber catalyst (Figure 2.25) which contains both precious metals (Pt, Rh), in order to oxidize NO to NO2 and reduce NOx, and a storage component containing alkaline or earth alkaline metals.

![Figure 2.25 - DPNR catalyst](image)

This device works in an alternative way (lean/rich conditions) as show in

This device works under cyclic conditions, alternating a lean phase during which the NOx produced by the engine are adsorbed on the alkaline or earth-alkaline metal oxide component (with nitrate species formation), with a short rich phase, during which the stored nitrate species are reduced to nitrogen. This cyclic process is reported in Figure 2.26.

![Figure 2.26 - DPNR process scheme](image)

This catalytic system allows continuous soot oxidation at exhaust temperature as low as 250°C, achieved by a pre-turbo fuel injection upstream the DPNR catalyst. One of the problem of this system is the sulfur poisoning. To prevent it, when the sulfur accumulated in DPNR catalyst reaches a certain level, the...
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catalyst’s bed temperature is increased in order to release the sulfur. Nowadays Toyota is developing a sulfur trap catalyst, placed upstream of the DPNR: the trap reduces sulfur accumulation on the catalyst and it also reduces the thermal deterioration caused by the earlier method of sulfur discharge [78]. Furthermore, to reduce the thermal deterioration of the catalyst, Toyota is now looking at a new ceria-based catalyst which is effective for suppression of Pt sintering.

The described system is one of the first examples of a compact devices, but it can be applied only on small vehicles because its efficiency, at present, does not meet the limit emissions for heavier vehicles, in particular concerning NO\textsubscript{x} emissions. Furthermore this system, at the present state of the art, will not be able to fulfil future legislation limits also for light-duty vehicles.
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3. Research approach and scientific methods

The behavior of PtBa/Al₂O₃ and PtK/Al₂O₃ NSR catalyst in both the NOₓ storage/reduction and soot oxidation is investigated in this thesis work. For this purpose model catalysts have been prepared and characterized in line with the procedure outlined in section 3.1. In section 3.2 thus the configurations of the experimental setup and methods have been briefly described.

3.1 Preparation and characterization of the catalysts

The model PtBa/Al₂O₃ (1/20/100 w/w) catalyst used in this study has been prepared by incipient wetness impregnation with dinitro-di-ammine platinum (Strem Chemicals, 5%) and then with barium acetate of an Al₂O₃ support, obtained by calcination at 700 °C of a commercial alumina (Versal 250 from UOP). After each impregnation steps, the powders was dried overnight in air at 80 °C and calcined at 500 °C for 5 h. The selected impregnation order (first Pt and then Ba) has been adopted in order to ensure a good dispersion and stability of the noble metal on the alumina support, in line with the recipes of Toyota patents [1]. The Pt-free sample (Ba/Al₂O₃, 20/100 w/w) was also prepared by impregnation of alumina with an aqueous solution of barium acetate (Sigma Aldrich, 99%), followed by drying overnight in air at 80 °C and calcination at 500 °C for 5 h. Surface area and pore size distribution of the prepared catalyst samples were determined by N₂ adsorption–desorption with the BET method using a Micromeritics TriStar 3000 instrument. The specific surface area of the ternary PtBa/Al₂O₃ sample is near 160 m²g⁻¹; a lower surface area value was determined for the Ba/Al₂O₃ sample (105 m²g⁻¹). The surface area contraction is accompanied by a slight reduction of the pore volume, from 0.80 cm³/g for the PtBa/Al₂O₃ catalyst down to 0.63 cm³/g for the binary Ba/Al₂O₃ sample. The Pt dispersion of the PtBa/Al₂O₃ sample was also estimated by hydrogen chemisorption at 0°C (TPD/R/O 1100 Thermo Fischer Instrument). The measured Pt dispersion value was near 60%.

The Ba/Al₂O₃ and PtBa/Al₂O₃ catalysts were characterized by XRD analysis (Brüker D8 Advanced Instrument equipped with graphite monochromator on the diffracted beam). The XRD patterns showed both the monoclinic (JCPDS 78-2057) and orthorhombic (Whiterite, JCPDS 5-378) polymorphic forms of BaCO₃, in addition to microcrystalline γ-Al₂O₃ (JCPDS 10-425).

The K/Al₂O₃ and Pt-K/Al₂O₃ catalysts were also prepared by the incipient wetness impregnation method, using aqueous solutions of CH₃COOK (Sigma Aldrich, 99%) and Pt(NH₃)₄(NO₃)₂ (Strem
III.

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Chemicals, 5% Pt in ammonium hydroxide) to impregnate the γ-alumina support calcined at 700°C (Versal 250 from UOP, surface area of 207 m²/g and pore volume of 0.96 cm³/g). In the case of the Pt-K/Al₂O₃ catalyst the impregnation was carried out in sequential manner: the alumina support was first impregnated with the Pt dinitrodiammine solution, and then with the K acetate solution. After each impregnation step the catalysts were dried at 80°C overnight and then calcined at 500°C for 5 h. The final loading was 5.4/100 w/w for the K/Al₂O₃ catalyst and 1/5.4/100 w/w for the Pt-K/Al₂O₃ catalyst. The following surface areas and pore volumes were measured by N₂ adsorption-desorption at 77K: 179 m²/g and 0.84 cm³/g for the K/Al₂O₃ sample; 176 m²/g and 0.9 cm³/g for the Pt-K/Al₂O₃ sample. The Pt dispersion, as determined by H₂ chemisorption at 0°C, was ~ 65%. Mean Pt particle size measured by HRTEM was 1.5 nm [⁴], in good agreement with the mean Pt particle sizes (dₚ) calculated from the empirical relationship often used for monometallic catalysts, dₚ(nm) = 1.1/(H/Pt), where H/Pt is the Pt dispersion measured from H₂ chemisorption.

Printex-U (Degussa), whose properties are well addressed in literature [⁵], was used as model soot. It presents a surface area of 95 m²/g and a carbon content higher than 90%. The ash content is negligible, as common for synthetic soot. Catalyst-soot mixtures were prepared by gently mixing in a vial the catalyst powder (74-105 µm) with the soot, thus realizing a loose contact which is representative of the soot/catalyst contact mode occurring in the DPNR system where soot is entrapped in the filter pores [⁶]. A soot loading (w₅oo/w₅cₐt) near 11% has been typically employed.

The Rh and Co catalysts used to study the elementary steps and site requirements of NO oxidation have been prepared by using as supports γ-Al₂O₃ (Sasol, SBa-200, 180 m² g⁻¹) and SiO₂ (Davisil, Grade 646, 300 m² g⁻¹) respectively. Both supports were heated to 750°C at 0.07 °C s⁻¹ in flowing dry air (Praxair, Extra Dry, 1 cm³ s⁻¹ g⁻¹) and held for 4 h. Rh(NO₃)₃•H₂O (Sigma Aldrich) or Co(NO₃)₃•(H₂O)₆ (Sigma-Aldrich) were added to de-ionized distilled water (Barnstead, Nanopure) and the solution was added dropwise to γ-Al₂O₃ or SiO₂ to the incipient wetness point (0.45 g solution (g Al₂O₃)⁻¹, 0.9 g solution (g SiO₂)⁻¹) to prepare samples with 0.8% and 2.4% wt. Rh and 10% wt. Co. Impregnated supports were heated in ambient air at 120°C for 4 h and then in flowing dry air (Praxair, extra dry, 1 cm³ s⁻¹ g⁻¹) for 4 h by heating at 0.07 °C s⁻¹ to a temperature between 400-875°C. Rh- or Co-containing samples were then heated to 600°C or 400°C K, respectively, at 0.07°C s⁻¹ and held in 9% H₂/He (Praxair, 99.999% purity, 1 cm³ s⁻¹ g⁻¹) for 5 h. Materials were treated with 0.5% O₂/He (Praxair, 99.999% purity, 1 cm³ s⁻¹ g⁻¹) at 22°C for 1 h before exposure to ambient air.
3.2 Experimental setup and method

3.2.1 TPD, TPO, TPSR and Transient experiments

All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7 mm i.d) heated by a tubular furnace controlled by a PID regulator (Eurotherm 2408). The temperature of the catalyst was measured and controlled by a K-type thermocouple (outer diameter 0.5 mm) directly immersed in the catalyst bed. Cooling down of the reactor was realised with compressed air. The flow rates of the gases were measured and controlled by mass-flow controllers (Brooks 5850 TR), and the gases were mixed in a single stream before entering the reactor. The helium line pass through a saturator allowing co-feeding of water. The reactor outlet was connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum) for the on-line analysis of the outlet gases. The following mass-to-charge ratios (m/e) have been used to follow the reaction products: \( \text{H}_2 \) (m/e=2), \( \text{N}_2 \) (m/e=28), \( \text{NN} \) (m/e=29), \( \text{N}_2 \) (m/e=30), \( \text{NO} \) (m/e=31), \( \text{N}_2\text{O} \) (m/e=44), \( ^{15}\text{NNO} \) (m/e=45), \( ^{15}\text{N}_2\text{O} \) (m/e=46), \( \text{H}_2\text{O} \) (m/e=18), \( \text{NH}_3 \) (m/e=15), \( \text{NO}_2 \) (m/e=46), \( ^{15}\text{NO}_2 \) (m/e=47), and \( ^{15}\text{NH}_3 \) (m/e=16). The mass-spectrometer data were quantitatively analysed using the fragmentation patterns and the response factors determined experimentally from calibration gases. Relevant interferences in the mass-to-charge signals were taken into account in determining the products composition. A gas chromatograph (micro GC Agilent 300A) equipped with a Poraplot Q and a 5 Å molecular sieve capillary column was used for the online analysis of \( \text{CO}_2 \), \( \text{N}_2\text{O} \), and \( \text{H}_2\text{O} \); and of \( \text{O}_2 \), \( \text{N}_2 \), and \( \text{CO} \) respectively. Furthermore, a UV analyzer (Limis 11HW, ABB) was also used in continuous to detect simultaneously \( \text{NH}_3 \), \( \text{NO} \), and \( \text{NO}_2 \).

Transient Response Method (TRM) experiments

The \( \text{NO}_x \) storage and reduction activity of the catalytic system has been studied in the presence and in the absence of soot by performing lean-rich cycles at constant temperature. In a typical run, a stream of He + 3% \( \text{O}_2 \) (100 cm\(^3\)/min) was fed to the reactor and the catalyst temperature was set at the desired value. After stabilisation of the concentration signals a rectangular step feed of \( ^{15}\text{NO} \) or \( \text{NO}(250-1000\text{ppm}) \) was admitted at constant temperature, by means of a pneumatically actuated four-way valve by keeping constant the overall flow rate. The \( \text{NO}_x \) storage proceeded up to nearly steady-state, then the inlet NO concentration was stepwise decreased to zero. After a few minutes the \( \text{O}_2 \) concentration was also decreased in a stepwise manner to zero. The catalyst reduction was accomplished by imposing stepwise changes in the \( \text{H}_2 \) concentration (4000 ppm) at the reactor inlet with a second four-way valve. In each step the total gas flow was always maintained constant with He as balance. A stream of Ar was also present in the feed gases as inert tracer: accordingly the lag
time of the system could be carefully evaluated, but it has always been found negligible. Note that the lean and rich phases have been separated with a He purge in between in order to analyze separately the catalytic performances of the investigated catalyst during the lean and rich phases, and to avoid any spurious effects due to temperature variations upon lean/rich switches. 1% v/v H₂O and 0.1% v/v CO₂ are always present in the feed; even if the CO₂ and H₂O concentrations are lower than in real applications, their effects are still representative [1].

TPD, TPO and TPSR experiments
In order to analyse the interaction between soot and the stored NOₓ, TPD, TPO and TPSR experiments were also performed over PtBa/Al₂O₃ and Ba/Al₂O₃ catalysts. Accordingly NOₓ have been stored onto the catalytic surface in the absence of soot at 350°C with NO or ¹⁵NO(1000 ppm v/v) in He + O₂ (3% v/v) + H₂O (1% v/v) + CO₂ (0.1% v/v); then the catalyst has been cooled at room temperature in He, extracted from the reactor and mixed with soot (11 % w/w). TPD and TPO experiments have been carried by heating the so-prepared catalyst-soot mixture at a rate of 10°C/min in He + H₂O (1% v/v) + CO₂ (0.1% v/v) in the absence and in the presence of 3% v/v O₂, respectively, from room temperature to 500°C.

In the case of TPSR experiments, a rectangular step feed of NH₃ (1000 ppm in He) or H₂ (4000ppm in He ) has been admitted to the reactor at r.t. and the catalyst temperature has been linearly increased to 400°C (heating rate 10 °C/min, hold 1 hour), while monitoring the concentration of the products exiting the reactor. The results collected with the catalyst/soot mixture have been compared with those obtained in analogous experiments performed in the absence of soot.

3.2.2 FT-IR experiments
Absorption/transmission IR spectra were run on a Perkin-Elmer FT-IR System 2000 spectrophotometer equipped with a Hg-Cd-Te cryo-detector, working in the range of wavenumbers 7200-580 cm⁻¹ at a resolution of 2 cm⁻¹. For IR analysis powder samples were compressed in self-supporting discs (10 mg cm⁻²) and placed in a commercial heated stainless steel cell (Aabspec) allowing thermal treatments in situ under vacuum or controlled atmosphere and the simultaneous registration of spectra at temperatures up to 600°C.

Before the NOₓ storage, the K/Al₂O₃ and Pt-K/Al₂O₃ samples were conditioned by i) outgassing at 500°C for 30 min, ii) one or two cycles consisting of NO₂ adsorption at 350°C and reduction with H₂ at 350°C (for Pt-K/Al₂O₃ catalyst) or out-gassing at 500°C (for K/Al₂O₃ sample), necessary to eliminate
the carbonates present on calcined powder \(^1\), \(\text{iii})\) oxidation at 500°C for 30 min and cooling in oxygen down to the temperature requested. NO\(_3\) storage was carried out at 350°C by admitting, on the Pt-K/Al\(_2\)O\(_3\) disc, freshly prepared NO/O\(_2\) mixtures (\(p_{\text{NO}} = 5\) mbar, \(p_{\text{O}_2} = 20\) mbar) or, on the K-Al\(_2\)O\(_3\) disc, NO\(_2\) (\(p_{\text{NO}_2} = 5\) mbar) up to catalyst saturation (ca. 20 min), and outgassing at the same temperature. The spectra of the stored NO\(_3\) were collected at 350°C or after cooling down the discs at the chosen temperature. The reduction was accomplished in CO (\(p_{\text{CO}} = 10\) mbar) and was performed both in isothermal conditions and at increasing temperature. The reduction in isothermal conditions was accomplished at 280°C and 350°C: at each temperature the spectra were run at increasing exposure times. For the reduction experiments at increasing temperature, the samples were cooled down at 100°C under vacuum, then heated in CO in the range 100-400°C. NO (Praxair, purity \( \geq 99.0\% \)) was freshly distilled before use. Conversely, NO\(_2\) (Praxair, purity \( \geq 99.5\% \)), O\(_2\) (Praxair, purity \( \geq 99.999\% \)) and CO (Praxair, purity \( \geq 99.9\% \)) were directly used.

### 3.2.3 NO Oxidation Rate Measurements

NO oxidation rates were measured on 0.12-0.18 mm Rh/Al\(_2\)O\(_3\) and Co/SiO\(_2\) aggregates. Samples were held on a porous quartz frit within a tubular reactor (10 mm). Reactants (15% O\(_2\)/He, 2% NO/He, 1% NO\(_2\)/He, and 5% CO\(_2\)/He) and He carrier (Praxair, 99.999% purity) were metered using electronic controllers (Porter Instruments) to achieve a broad range of reactant pressures (1-12 kPa O\(_2\), 0.04-0.25 kPa NO, 0.02-0.25 kPa NO\(_2\), 0-2 kPa CO\(_2\)). A resistively-heated furnace with a controller (Watlow, 96 series) and a K-type thermocouple were used to maintain constant temperatures (275-400°C). Inlet and outlet concentrations were measured using an infrared analyzer (MKS 2030; 2 cm\(^3\) cell; 2 cm pathlength; 65°C). NO oxidation rates are reported as turnover rates (TOR, mol NO converted (mol Rh\(_s\) or Co\(_s\))\(^1\) s\(^{-1}\)) at NO conversions below 15%.

### 3.2.4 Isotopic Oxygen Exchange Measurements

\(^{16}\text{O}_2\)\(^{18}\text{O}_2\) exchange rates were measured on Co and Rh catalyst using a gradientless batch reactor (498 cm\(^3\) volume), in which reactants were circulated by a graphite gear pump (Micropump; 2 cm\(^3\) s\(^{-1}\)). Gases (99.999% chemical purity) were obtained from Praxair (90% O\(_2\)/Ar, He) and Ikon Isotopes (\(^{18}\text{O}_2\), 96% isotopic \(^{18}\text{O}\) purity). Catalysts were heated to 300-380°C at 0.07 °C s\(^{-1}\) and held for 1 h in flowing 2 kPa \(^{16}\text{O}_2\)/Ar/He (30 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) before the reactor was evacuated and filled with an
equimolar $^{16}$O$_2$-$^{18}$O$_2$ mixture and He as balance. Isotopomer concentrations were measured by periodic pulses injected into a mass spectrometer (MKS Mini-Lab).

References

4. Results and discussion

4.1 Study of DPNR catalysts for combined soot oxidation and NOx reduction

4.1.1 Introduction

The main pollutants emitted by diesel engine exhausts are nitrogen oxides and soot particles. For this reason, the simultaneous abatement of NOx and particulates from diesel exhaust gas represents an outstanding issue. The current three-way technology used near stoichiometric conditions is unable to meet upcoming regulations in Europe, United States and Japan. The existing technical solutions involving an exhaust gas recirculation to get an optimal NOx/particulates compromise by controlling the recirculated gas rate will likely be unable to fulfill the next Euro 6 standard regulation. The implementation of an optimal strategy is not an easy task because a reduction of NOx induces an increase in particulate emission and reversibly subsequent reduction of particulate matter will induce an increase in NOx emission. Consequently such a situation implies to reconsider the actual end-of-pipe technologies commercially available combining diesel particulate filter (DPF) and DeNOx catalysts \(^1\).

Commercial NOx abatement technologies are actually available. They are essentially developed for heavy-duty vehicles such as the urea selective catalytic reduction (SCR). For light vehicles a competition between SCR and NOx storage and reduction after-treatment systems exist. In this complex technological context, the development of integrated De-NOx and De-soot after-treatment technologies have also been proposed. One example is the Diesel Clean Advanced Technology (D-CAT) emission control system recently proposed by the Toyota group. Its Avensis model is equipped with the D-CAT package which includes the DPNR (Diesel PM and NOx Reduction) system, a combination of a diesel particulate filter with a NOx adsorber-catalyst \(^2\). The DPNR converter features a newly developed, highly porous ceramic filter coated with a catalyst exclusively developed by Toyota for its NOx storage reduction catalytic converter (NSR catalysts), initially designed for use with Toyota’s lean-burn (high-oxygen) gasoline engines \(^3\).

NSR systems or Lean NOx traps (LNTs) \(^4,5,6\) are based on the use of a catalyst containing precious metals such as Pt, Pd and Rh for the reduction and oxidation reactions, and alkali or alkaline-earth
metal components such as Ba or K that store NOx as nitrite and nitrate species \[^{1,8}\]. Overall, NOx are reduced to N2 over NSR catalyst by alternating lean and rich periods, i.e. a lean period of 30-90 s during which the NOx emitted in the exhaust gases are stored on the catalyst surface, and a short 3-5 s rich period during which the stored NOx are reduced to N2 by H2, CO and unburned hydrocarbons. Several studies deal with the reactivity and characteristics of Ba containing catalysts (see for example Refs. \(^9,10,11,12\)), but reports on the specific behaviour of K-based catalysts are scarce in the literature, particularly on the reduction step. The reactivity of different reducing agents (e.g. H2, CO, C3H6 and C3H8) has been investigated in the case of Ba-containing catalysts; these studies indicate that hydrogen is the most effective reductant for lean NOx traps \[^{13,14,15,16,17}\].

In recent papers of various research groups, including ours, mechanistic aspects of the reduction of NOx stored over Ba-based NSR catalytic systems have been reported when H2 is used as a reductant \[^{18,19,20}\]. It has been shown that the reduction by H2 under near isothermal conditions of NOx stored onto Pt-Ba/Al2O3 (and onto Pt-K/Al2O3 as well) is not initiated by the thermal decomposition of nitrates/nitrites ad-species with release of NOx in the gas phase, but involves a Pt catalyzed surface pathway which is active at low temperature and leads to nitrogen \[^{21,22}\]. It has also been proposed that under near isothermal conditions N2 is formed exclusively via a consecutive reaction scheme which involves the fast reaction of H2 with stored NOx to give ammonia followed by the slower reaction of ammonia with residual stored NOx to give N2 \[^{23}\]. However, it has been also pointed out that the reaction of ammonia with residual stored NOx to give N2 is slower over Pt-Ba/Al2O3 than over Pt-K/Al2O3.

Soot oxidation over NSR catalyst has been also investigated; various surface compounds such as nitrates and active oxygen generated during storage and reduction steps are proposed as active soot oxidation species and, thereby, decreasing the oxidation temperature. NO2 produced over noble metals of NSR catalysts can be trapped as nitrates and can also react with soot generating NO again \[^{24}\]. Under lean conditions NSR system can be expected to function as catalyzed soot filter (CSF). DPNR or NSR catalysts in this respect will have obvious advantages as it can reduce emission of both the pollutants and acts as ‘4-way’ catalyst.

Only a few studies over ‘4-way’ catalytic materials that can store NOx, such as CeO2, Ba and K-containing catalysts, for soot oxidation are reported \[^{25}\]. In our previous works \[^{26,27}\], it has been shown that soot oxidation occurs during the lean phase only, while NO is being oxidized to NO2 and nitrites/nitrates are being stored on the catalyst surface. NO2 is an efficient and well recognized oxidizing agent for soot, but surface nitrates may have a role as well according to that proposed by Makkee et al. \[^{28}\].
It has been reported that K-promoted catalysts have good activity in the soot possibly due to the high mobility of some K compounds. However, the high mobility causes K to present a technological problem associated with its interaction with the monolith support, and loose due to volatilization and/or stripping by condensed water. For this reason, the stability of the Pt-K/Al₂O₃ catalyst during lean-rich cycles it is an important aspect that needs to be taken to account.

4.1.2 NOₓ storage and soot oxidation on Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ catalysts

In this thesis work the reactivity of model Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ catalysts in the simultaneous removal of NOₓ and soot has been investigated under a variety of experimental conditions (NO concentration, temperature, and particulate loading), performing lean-rich cycles in the presence of water and CO₂.

The results obtained during the lean-rich cycles performed at 350°C over Pt-Ba/Al₂O₃ catalyst have been reported in Figure 4.27 in the absence (A, B) and in the presence of soot (C, D) (see Paper I).

**Figure 4.27**– Storage-reduction cycle performed at 350°C over PtBa/Al₂O₃ (A and B) and Pt–Ba/Al₂O₃–soot mixture (C and D). Trace a is the CO₂ production due to soot oxidation.
In the absence of soot (Figure 4.27A), upon the NO step addition (at t = 0 s) the NO outlet concentration increases with time, approaching the asymptotic values corresponding to the NO inlet concentration after about 2000 s. Also NO₂ is observed due to the occurrence of the oxidation of NO by O₂ according to the stoichiometry of reaction (1):

\[
\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2
\]  

(1)

During the NO pulse, CO₂ evolution is also observed. This is due to the formation of nitrate species upon NOₓ adsorption [29,30], that replace carbonates with release of CO₂ according to the stoichiometry of reaction (2),

\[
\text{BaCO}_3 + 2 \text{NO} + 3/2 \text{O}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2
\]  

(2)

In fact upon subtracting half of the adsorbed NO concentration value (i.e. ½ (NO_{IN} – NO_{out})) to the actual CO₂ concentration curve, a flat CO₂ trace is obtained (trace a of Figure 4.27A).

Finally, upon NO shutoff, a tail is observed in the NO and NO₂ concentrations due to the desorption of weakly adsorbed NOₓ species, whose release is favored by the decrease in the NOₓ partial pressure.

In presence of soot (Figure 4.27C), the evolution of NO and NO₂ are qualitatively similar to those observed for the soot-free catalyst.

An increase in the CO₂ outlet concentration is also observed. It results from two contributes: one is related to the decomposition of carbonates on the catalytic surface due to nitrates formation (in line with reactions (2)-(3)), and the other is due to soot combustion.

\[
\text{BaCO}_3 + 3 \text{NO}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{NO} + \text{CO}_2
\]  

(3)

As in the absence of soot, upon NO shutoff, a release of NO and NO₂ takes place due to the desorption/decomposition of the NOₓ species previously stored. Upon switching off the O₂ feed, additional NOₓ are also desorbed. Both desorption contributions appear to be remarkable if compared to those observed in the case of the soot-free catalyst: this indicates that soot has a destabilizing effect on the nitrate species adsorbed onto the catalytic surface. The reasons for the destabilizing effect of soot on the stored nitrates are not yet fully understood; one can speculate that nitrates species, which are considered mobile on the catalytic surface [30], may directly interact with soot particles leading to its oxidation.
IV.

Results and discussion

The results obtained during the lean NOx adsorption over the Pt-Ba/Al2O3-soot mixture (Figure 4.27C) showed that the presence of soot decreased the NOx storage capacity of the catalyst; in particular the presence of roughly 10% w/w of soot decreased by nearly 30% the amounts of stored NOx with respect to the soot-free catalyst. Moreover soot leads to an appreciable decrement of the rate of NOx adsorption: these effects are seen also at different temperatures (200-350°C, see Paper II) and when different values of the NO inlet concentration (250-1000ppm, see Paper II) are used in the experiments, as clearly reported in Errore. Non è stato specificato un nome segnalibro. Figure 4.2 and Figure 4.29 that show the amount of stored NOx in function of time in the absence (dotted lines) and in the presence of soot (solid lines) at the different temperature (Figure 4.28) and NO inlet concentration (Figure 4.29).

![Diagram](image)

**Figure 4.28** Amounts of adsorbed NOx versus time over PtBa/Al2O3 (dotted lines) and over PtBa/Al2O3/soot mixture (solid lines) at different temperatures
IV. Results and discussion

Figure 4.29 Amounts of adsorbed NOx versus time over PtBa/Al$_2$O$_3$ (dotted lines) and over PtBa/Al$_2$O$_3$/soot mixture (solid lines) at different NO inlet concentrations.

During NO$_x$ storage (Figure 4.27 A, C), soot oxidation occurs also thanks to the presence of NO$_2$ formed upon NO oxidation over Pt sites. In fact the NO$_2$ concentration at the reactor outlet in the presence of soot is significantly lower than that observed in the absence of soot, thus pointing out the involvement of NO$_2$ in soot oxidation. The decrease of the NO$_2$ concentration may explain also the observed decline in the NO$_x$ storage properties of the catalyst. In fact, in line with the occurrence of a “nitrate” pathway for the storage of NO$_x$ (i.e., NO oxidation to NO$_2$ followed by NO$_2$ adsorption in the form of nitrates via a disproportion reaction), Ba and soot compete for reaction with NO$_2$, as suggested by Sullivan et al. [31], leading to the observed decrease in the NO$_x$ storage properties.

The reactivity and the thermal decomposition of nitrates has been investigated by TPD (Figure 4.30)/TPO experiments in the presence and in the absence of soot (see Paper I-III).
Figure 4.30. TPD run after NOx adsorption at 350 °C (1000ppm NO+O₂ (3%, v/v) in He+H₂O(1%, v/v) + CO₂ (0.1%, v/v)) over (A) PtBa/Al₂O₃ catalyst; (B) PtBa/Al₂O₃/soot mixture

It has been observed that the adsorbed NOₓ oxidize soot at temperature well below those corresponding to their thermal decomposition originating NO₂ in the gas phase. It has been found that the presence of soot favors the decomposition and the reduction of the stored nitrates, while soot is oxidized. In fact the presence of soot shifts the decomposition/reaction of the stored nitrates at lower temperatures, and the stoichiometry of the released products reflects the occurrence of a partial reduction of the initially stored NOₓ, as well as the oxidation of soot. Hence a direct reaction between the stored nitrates and soot has been suggested, that has been explained on the basis of the surface mobility of the adsorbed nitrates, soot particles being the driving force for the process acting as reduced centers. This soot oxidation pathway involves surface species and parallels the NO₂-soot oxidation that occurs in the presence of gas-phase NO₂ . These surface reactions do not require the presence of the noble metal (Pt) that they occur also in the case of the Ba/Al₂O₃ catalyst sample as well. As expected, it is favored by the contact between the nitrates and soot. In fact when nitrates are stored onto the soot, the nitrate/soot reaction is monitored at lower temperatures (see Paper III for the details).

De-NOₓ and De-soot activity has been also investigated over a model Pt-K/Al₂O₃ by performing lean-rich cycles at constant temperature. These results were compared to the one obtained with Pt-Ba
/Al₂O₃ catalyst in order to underline analogies and differences and assess the role of the storage component in both NOₓ abatement and soot combustion (Papers IV-V).

The Pt-K/Al₂O₃ (Pt 1%; K 5.4% wt/wt) catalyst used for this study has been characterized in comparison with 1% Pt/Al₂O₃ catalyst (Paper VI). IR spectra of adsorbed CO at −140 °C and at room temperature allowed the detection of oxidized Pt centers and of their very strong oxidizing ability. TPD and IR spectra of adsorbed CO₂ allowed to characterize the basicity of the samples. The data indicate that the presence of K in Pt-K/Al₂O₃ catalyst seems to increase the reducibility of Pt, whose highly oxidizing species are not observed after outgassing at 350 °C. Additionally, the basicity of K/Al₂O₃ increases the electron density on reduced Pt, as evidenced by the slightly lower CO stretching frequency of Pt carbonyls.

Pt species are located near the basic oxide species of the K/Al₂O₃ ‘support’ and their behavior is influenced by the presence of adsorbed carbonate species.
IV. Results and discussion

Figure 4.31 NO (100ppm)/O2(3%) adsorption over Pt-K/Al₂O₃ (A) and Pt-K/Al₂O₃/soot (B) in presence of water 1% and CO₂ 0.1% at 350°C

Figure 4.5 shows the results of a typical NOₓ adsorption at 350°C in the absence and in the presence of soot, respectively (Figure 4.31.A and B). In the absence of soot (Figure 4.31.A) upon NO step addition at t = 0 s the NOₓ outlet concentration presents a delay of about 200 s, while the evolution of NO₂ is seen starting from 250 s. The outlet concentrations of both NO and NO₂ increase with time and eventually reach a steady state level indicating that saturation of the catalyst surface with NOₓ is attained. CO₂ evolution is also observed during the lean phase, due to the formation of nitrates that replace surface carbonates.

When the NOₓ storage is carried out in the presence of soot (Figure 4.31B), significant differences are apparent. The NOₓ dead time is reduced (to ca. 90 s) and the amounts of NOₓ stored up to steady-state are lower than those measured in the absence of soot (0.38 vs 0.58 mmol/g_cat) indicating a reduction in the storage capacity of the catalyst. Besides, a much higher production of CO₂ is observed, indicating the occurrence of the soot oxidation. The NO₂ concentration is significantly lower than in the absence of soot because of to the participation of NO₂ in soot oxidation. Notably, upon NO and O₂ shutoff, a release of NOₓ takes place due to the desorption/decomposition of the NOₓ previously stored indicating a destabilizing effect of soot on the stored NOₓ.

ISC experiments have been performed in similar condition varying the reaction temperature in the range 250-350°C. It is observed that the NOₓ storage behavior of the catalyst is affected by the temperature: the NOₓ breakthrough and the amounts of NOₓ stored up to steady state increase with temperature. Also the NO₂ concentration measured at the reactor outlet at the end of the NOₓ dose
(i.e. at steady-state) increases with temperature. In fact under our experimental conditions NO$_2$ formation is far from chemical equilibrium and the observed increase with temperature of the NO$_2$ concentration is hence expected being the reaction kinetically controlled. Accordingly, the NO/NO$_2$ molar ratio calculated at the end of the storage phase decreases with temperature.

Temperature also affects the rate of NO$_x$ adsorption that increases with T, as observed in the case of Pt-Ba/Al$_2$O$_3$ catalysts as well. A direct comparison between the amounts of NO$_x$ stored at steady-state on the Pt-K/Al$_2$O$_3$ and Pt-Ba/Al$_2$O$_3$ catalyst samples is shown in Figure 4.32 (Paper IV).

![Figure 4.32 Amounts of stored NO$_x$ versus time over Pt-K/Al$_2$O$_3$ and Pt-Ba/Al$_2$O$_3$ catalysts (A) in the absence of soot and (B) in the presence of soot](image)

It appears that the amounts of NO$_x$ stored on Pt-K/Al$_2$O$_3$ are higher than those on Ba-based catalyst, although at 350°C the storage capacity of the two catalysts is very similar, both in presence (solid lines) and in the absence of soot (dotted lines). Finally, the amounts of NO$_x$ desorbed upon NO shutoff are higher over Pt-K/Al$_2$O$_3$ than over Pt-Ba/Al$_2$O$_3$. These results show that the presence of soot affects the NO$_x$ storage capacity and the stability of the adsorbed species of both samples.

In order to investigate more in details the effect of the soot loading on the catalyst behaviour, and the stability of the Pt-K/Al$_2$O$_3$ upon repeated soot oxidation cycles, several lean-rich cycles have been carried out over the same sample. For this purpose a sequence of NO$_x$ adsorption and reduction cycles (6-7 cycles) has been performed in the presence of soot over a fresh Pt-K/Al$_2$O$_3$ at 350°C until the complete consumption of soot (run 1); after that, the clean catalyst has been mixed...
again with soot and has been again cycled under the same experimental conditions until complete soot oxidation (Run 2). This procedure has been repeated three times.

The data point out that ageing the LNT Pt-K/Al₂O₃ catalyst by repeated soot oxidation cycles, the NOₓ storage capacity decreases; indeed, the amount of NOₓ stored on aged Pt-K/Al₂O₃ catalyst (i.e. clean catalyst) is lower than that on the fresh catalyst.

The NO/NO₂ molar ratio strictly depends on the soot present; the amount of soot decreases the ratio decreases since NO₂ is not involved in the soot combustion. Notably, the same NO/NO₂ molar ratio is calculated on the fresh and aged catalyst, indicating the ageing process does not involve Pt sites.

The observed decrease in soot oxidation activity over aged K-containing catalyst can be attributed to the volatile nature of K-active species, like nitrates (melting point 334°C) [32, 33]. The mobility of such compounds is expected to be high, leading to good contact with soot and bringing an additional activity. The degradation of catalyst should be due to the sublimation of K during soot combustion [34]. The loss of K have as consequence a lower amount of storage sites; accordingly, the storage capacity of system decreases and a lower amount of K-nitrates are available to oxidize soot.

4.1.3 NOₓ reduction on Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ catalysts

The reduction of the stored NOₓ on Pt-Ba/Al₂O₃ has been reported in Figure 4.27 in the absence (B) and in presence of soot (D). This process is not significantly affected by the presence of soot, although some minor changes in the N₂ selectivity (a slight increase in the presence of soot) have been observed.

In both cases, upon H₂ admission, the H₂ outlet concentration profile shows a dead time during which it is completely consumed to give at first N₂ and NH₃ later on, according to the overall stoichiometry of reactions (4) and (5):

\[
\text{Ba(NO}_3\text{)}_2 + 5 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{N}_2 + 5 \text{H}_2\text{O} \quad (4)
\]

\[
\text{Ba(NO}_3\text{)}_2 + 8 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NH}_3 + 5 \text{H}_2\text{O} \quad (5)
\]

In line with the stoichiometry of reaction (4), upon admission of 4000 ppm H₂ the N₂ outlet
concentration immediately increases to the level of 800 ppm; then NH$_3$ formation is observed in correspondence of the decrease of the N$_2$ trace, at the end of the reduction. Slightly after the NH$_3$ breakthrough the H$_2$ concentration trace increases up to the inlet concentration value.

According to previous studies of our group [35,36] the reduction of stored nitrates by H$_2$ occurs via a two-step molecular pathway which involves a first step leading to the formation of NH$_3$, followed by the slower reaction of ammonia with residual nitrates to form N$_2$:

$$3 \text{Ba(NO}_3\text{)}_2 + 10 \text{NH}_3 + \text{CO}_2 \rightarrow 3 \text{BaCO}_3 + 8 \text{N}_2 + 15 \text{H}_2\text{O}$$  \hspace{1cm} (6)

The sum of reactions (4) and (5) accounts for the overall stoichiometry of reduction of nitrates with hydrogen to give N$_2$ (reaction 6). Notably, the temporal evolution of reduction products, with nitrogen being detected at the reactor outlet first and ammonia later, is in line with the integral behaviour of the catalytic bed [35,21]. In fact upon regeneration a hydrogen front travels along the catalyst bed. NH$_3$ is formed at the H$_2$ front upon reaction of H$_2$ with the stored NO$_x$; the formed NH$_3$ then reacts with NO$_x$ stored downstream the H$_2$ front, leading to the formation of N$_2$. When the front reaches the end of the catalytic bed, there are no NO$_x$ stored downstream and this leads to the evolution of ammonia, which follows that of N$_2$.

During the reduction phase, a CO$_2$ uptake has also been observed due to the formation of carbonates onto the Ba sites on which NO$_x$ were previously stored; finally, after NO$_x$ reduction, the formation of small amounts of CO is also observed due to the occurrence of the inverse water gas shift (RWGS) reaction (8):

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$$  \hspace{1cm} (7)

Calculation showed that the reaction is limited by thermodynamic constraints; the relevance of this reaction appears to be limited by the presence of water in the feed [35].

Finally mechanistic aspects involved in the formation of N$_2$ and N$_2$O during the reduction of NO$_x$ stored over the model PtBa/Al$_2$O$_3$ NSR catalyst have been investigated by means of isotopic labeling experiments. A combined use of MS, UV-Vis and GC analysis has been adopted allowing the complete quantitative analysis of the reaction products. The reduction of the stored labelled nitrites species (Figure4.34Figure 3.33) with $^{14}$NH$_3$ leads to the selective formation of N$_2$ since only very small amounts of nitrous oxide have been observed in the reduction of nitrites only.
Figure 3.33 - TPSR run with NH$_3$ (1000ppm) after $^{15}$NO$_x$ adsorption at 150°C (1000 ppm $^{15}$NO + O$_2$ 3% v/v in He) over Pt-Ba/Al$_2$O$_3$ catalyst

The observed N$_2$ isotopic distribution includes all possible N$_2$ isotopes, i.e. $^{15}$N$_2$, $^{14}$N$_2$ and the mixed $^{15}$N$^{14}$N species. Based on the pathway suggested for NO and NH$_3$ reaction on Pt-based catalysts, it has been found that the observed product distribution can be explained on the basis of the statistical coupling of $^{15}$N- and $^{14}$N-adatoms originated upon NH$_3$ and NO$_x$ decomposition on Pt. However, the simultaneous occurrence of a SCR-like pathway, involving the formation and decomposition of a NH$_x$-NO intermediate originating from ammonia and NO$_x$, and leading to the selective formation of the mixed $^{15}$N$^{14}$N species is also likely. In fact, at the early stages of the reduction of stored labeled nitrites with unlabeled ammonia, the reduction process is selective towards the formation of the mixed $^{15}$N$^{14}$N isotope, suggesting the occurrence of a SCR-like pathway.

Similar results have been obtained upon reduction of the stored labelled nitrates by $^{14}$NH$_3$ (Figure 4.36). The formation of all nitrogen isotopes is seen although in this case the abundance of the double labeled $^{14}$N$_2$ isotope is similar to that of the $^{15}$N$^{14}$N species. Hence also in the case of the stored nitrates, the route for nitrogen formation involves the statistical coupling of the $^{14}$N- and $^{15}$N-containing reactants, along the pathways already suggested above for nitrites reduction.
Isotopic labeling experiments also provide indications on the pathways involved in the formation of N\textsubscript{2}O. This species is formed in very limited amounts during the reduction by ammonia of stored NO\textsubscript{x} species (nitrites and nitrates); much higher quantities have been observed during the reduction of gaseous \textsuperscript{15}NO with NH\textsubscript{3}. Since no formation of unlabeled nitrous oxide has been observed, the participation of \textsuperscript{15}NO is necessary for the formation of nitrous oxide. In line with literature proposals, it has been suggested that nitrous oxide formation involves (on the Pt sites) either the coupling of two adsorbed NO molecules or the recombination of an adsorbed NO molecule with an adsorbed NH\textsubscript{x} fragment. Accordingly, N\textsubscript{2}O formation is greatly enhanced in the presence of gas- phase NO. Temperature also drives the selectivity to nitrous oxide. This product is favored at low temperature and is likely related to the oxidation state of Pt: at high temperatures Pt is kept in a reduced state by ammonia, and this would favor NO dissociation on the Pt sites thus preventing N\textsubscript{2}O formation. Besides, N\textsubscript{2}O could be reduced to N\textsubscript{2}. The presence of oxygen in the feed stream favors N\textsubscript{2}O formation, since it increases the concentration of molecularly adsorbed NO species and inhibits N\textsubscript{2}O reduction. The route involving the coupling of NO-ad-species is however inhibited by the presence of oxygen, and hence nitrous oxide formation involves adsorbed NO and NH\textsubscript{x} fragments.
Furthermore the reduction of NO\textsubscript{x} stored at 350 °C onto the Pt-K/Al\textsubscript{2}O\textsubscript{3} LNT catalyst has been deeply investigated under dry conditions by using CO as reductant that allows the formation of stable intermediates useful to identify the reaction pathways.

The results collected during CO TPSR over K/Al\textsubscript{2}O\textsubscript{3} and over Pt-K/Al\textsubscript{2}O\textsubscript{3} highlight that, in the presence of Pt, the reduction of nitrate species by CO is faster considering that the onset temperature of the reaction is lower (∼210 vs 340 °C), and the conversion of CO is higher. Besides, it appears that the reduction does not require as a first step the thermal release of NO\textsubscript{x} in the gas phase because the reaction is seen at temperatures well below that of the thermal decomposition of adsorbed NO\textsubscript{x}.

The results collected during the CO-ISCP experiment over Pt-K/Al\textsubscript{2}O\textsubscript{3} (Figure 3.35) are in line with the results of CO-TPSR experiments.

**Figure 3.35** ISC experiments at 300 °C over the Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst (storage phase, NO 1000 ppm + O\textsubscript{2} 3% v/v in He; reduction phase, CO 2000 ppm in He).
It is shown that the admission of 3% v/v O$_2$ causes the evolution of a small amount of N$_2$, produced by the oxidation of surface N-containing species that remain adsorbed at the catalyst surface after the previous reduction with CO. Upon the NO step addition (at $t = 0$ s), NO and NO$_2$ show a dead time and then their concentration rapidly increases with time, approaching the asymptotic concentrations corresponding to the NO$_x$ feed concentration (NO + NO$_2$) after about 2000 s. Accordingly, significant amounts of NO$_x$ were stored. Formation of NO$_2$ in the gas phase indicates that Pt is active in the NO oxidation reaction; as indicated in a dedicated FT-IR analysis, nitrates are the major adsorbed species present after adsorption in NO/O$_2$ at 300 °C.

Upon admission of CO, $\sim$360 ppm N$_2$ and $\sim$1730 ppm CO$_2$ are immediately produced, together with negligible amounts of NO (30 ppm). CO is completely consumed for about 200 s; afterward, CO is detected at the reactor outlet: its concentration increases and approaches the inlet value. After CO breakthrough, the N$_2$ and CO$_2$ concentrations (and NO production) decrease. When the nitrogen concentration is close to zero (i.e., when stored NO$_x$ are almost depleted), H$_2$ production is observed. When the CO feed is stopped (after 1700 s from the CO admission), a small amount of nitrogen is produced, along with CO$_2$.

The reduction by CO under nearly isothermal conditions of nitrates stored onto the Pt-K/Al$_2$O$_3$ catalyst at high temperature (300 °C) occurs according to a Ptcatalyzed surface pathway, has already demonstrated at low-temperature for the reduction by H$_2$ of NO$_x$ stored over the same catalyst used in this study, leading mostly to nitrogen. Hydrogen is more effective than CO because the onset temperature of the reduction is lower (120 vs 210 °C). The same conclusions apply to a Pt-Ba/Al$_2$O$_3$ catalyst, as reported before [15,37] and this suggests that the reduction of stored NO$_x$ with H$_2$ and with CO over LNT catalysts might present analogies that are worth being investigated.
The results of CO-TPSR (Figure 4.36) and CO-ISC experiments over Pt-K/Al₂O₃ and of the complementary FTIR study indicate that the reduction by CO of nitrates stored onto the Pt-K/Al₂O₃ catalyst under dry conditions occurs according to the stoichiometry of the following overall reactions:

\[ 2\text{KNO}_3 + 5\text{CO} \rightarrow \text{K}_2\text{CO}_3 + \text{N}_2 + 4\text{CO}_2 \]  
\[ 2\text{KNO}_3 + 8\text{CO} \rightarrow 2\text{KNCO} + 6\text{CO}_2 \]  

Reactions 8 and 9 account for the consumption of CO and of nitrates, and for the formation of CO₂.

In particular, reaction 9 accounts for the consumption of nitrates with the formation of isocyanates (revealed by FT-IR) and CO₂; reaction 8 accounts for the formation of N₂, CO₂, and carbonates at the catalyst surface, as revealed by FT-IR. The formation of isocyanates and carbonates at the surface explains the fact that the N balance and the C balance in the gas phase is far from 100% at the end of the CO-TPSR experiment. In particular, reaction 8 does not occur in the low-temperature range (210-250 °C) where N₂ is not detected. FT-IR spectra reveal also that bidentate nitrates stored onto the catalyst surface are reduced at first and ionic ones start to be reduced later on, i.e. the ionic nitrates result more resistant to the CO reduction.

Similar results have been obtained when H₂ was used as a reductant instead of CO; [38, 39] also, in that case, FT-IR measurements put in evidence a different reactivity between ionic and bidentate nitrates toward H₂. These features agree well with TPSR data where two contributions of reductant
(H₂ and/or CO) consumption are apparent. The data are consistent with the reaction pathway already proposed for N₂ formation in the case of Pt-Ba/Al₂O₃ [37,40]: large amounts of NCO species are left at the catalyst surface after reduction of CO under dry conditions; these species can be oxidized to give N₂ during the subsequent lean phase either by oxygen or by NO + O₂, NO₂, surface nitrites, and/or surface nitrates. N₂ is formed primarily according to an in-series two-step process, where NCO species are formed first and then are converted to nitrogen upon reaction with NOₓ stored species. In analogy with the reaction pathway for the reduction by CO of nitrates stored over Pt-Ba/Al₂O₃ under dry conditions, the reduction by CO of nitrates stored onto the Pt-K/Al₂O₃ catalyst occurs according to the stoichiometry of the following overall reactions (9) and (10):

\[ 6\text{KNO}_3 + 10\text{KNCO} \rightarrow 8\text{N}_2 + 8\text{K}_2\text{CO}_3 + 2\text{CO}_2 \]  

Hence, NCO species are considered intermediates in the formation of N₂, whose formation occurs exclusively according to the stoichiometry of the reactions (9) and (10) the sum giving the overall reaction(8). Besides, analogies could be found for both the catalytic systems also with the reduction of stored nitrates by H₂, where the in-series two-step molecular pathway previously reported, has been proposed for N₂ formation \^[Errone. Il segnalibro non è definito. 38, 40\] The following overall reactions are involved:

\[ 2\text{KNO}_3 + 8\text{H}_2 \rightarrow 2\text{NH}_3 + \text{KOH} + 4\text{H}_2\text{O} \]  

\[ 6\text{KNO}_3 + 10\text{NH}_3 \rightarrow 8\text{N}_2 + 6\text{KOH} + 12\text{H}_2\text{O} \]  

In the case of reduction by CO, NCO ad-species play as intermediates in the reduction instead of NH₃. The reduction by CO of NOₓ stored over Ba- and K containing catalysts shows slightly distinct features. Over Pt-Ba/Al₂O₃, only ionic nitrates were observed, giving during the CO reduction two FT-IR bands at 2222 and 2164 cm⁻¹ related to NCO species, whereas both bidentate and ionic nitrates are present on Pt-K/Al₂O₃ and mainly the band at 2225 cm⁻¹ is detected.

The CO-TPSR experiment over Pt-Ba/Al₂O₃ has shown [37, 40] that the reaction of surface nitrates to give nitrogen is slower than that responsible for the initial reduction of nitrates to give NCO species. The formation of nitrogen in this case via the reduction of nitrates by CO is explained as the sum of the reduction of nitrates by CO to give surface NCO species and the subsequent oxidation of these species by surface nitrates to give nitrogen. Also, in the case of Pt-K/Al₂O₃, the reaction of surface nitrates to give nitrogen seems to be slower than that responsible for NCO species formation. In fact, the formation of nitrogen is observed only above 250 °C, while evidence for the formation of N-
containing species from 210 °C is provided by the consumption of CO and by the simultaneous evolution in the gas phase of CO\(_2\) with no N-containing species. Accordingly, FT-IR measurement shows that isocyanates are formed and their storage on the surface is higher at the low temperatures. However, in this case, the reaction between surface nitrates and surface NCO species to give nitrogen is faster and more efficient than over the Ba-containing system. The reason for the higher NO\(_x\) reduction efficiency to N\(_2\) pointed out by the Pt-K/Al\(_2\)O\(_3\) catalyst may be related to the higher mobility of the adsorbed surface species. It has been speculated that the reduction of the stored NO\(_x\) implies the surface mobility of these species toward Pt, where they are reduced by the reductant [\(^{36}\)]. In the case of CO as a reductant, isocyanate species are formed as intermediates. In the suggested pathway of the reduction of stored NO\(_x\) by CO, the rate-determining step is the slow reaction between nitrates and isocyanates, which involves two surface species. It is known that K-nitrates have a melting point lower than that of Ba-nitrates (334 vs 592 °C). Along this line, K-nitrates might have a higher surface mobility that facilitates their spillover from the K component onto the Pt particles and, as a consequence, their reaction with K-NCO species. As a result, the CO reduction is more efficient over the Pt-K/Al\(_2\)O\(_3\) catalyst than over the Pt-Ba/Al\(_2\)O\(_3\) catalyst.
4.2 NO Oxidation on dispersed oxides of Rhodium and Cobalt

4.2.1 Introduction

Nitrogen oxides must be removed from combustion exhaust to meet environmental regulations, which is challenging for streams that contain O\textsubscript{2} and low concentrations of CO and hydrocarbons. Catalyst sites are titrated by strongly-bound chemisorbed oxygen atoms (O*) during NO decomposition in the absence of reductants. As a result, open sites on O*-saturated surfaces, required for NO dissociation, are scarce \[41\]. Such conditions cause low NO conversions to N\textsubscript{2} and favor instead NO oxidation to NO\textsubscript{2}. NO\textsubscript{2}, however, adsors on metal oxides \[42\] and reduces to N\textsubscript{2} when soot or hydrocarbons are present in exhaust streams \[43, 44\]. These reactions provide an alternate abatement strategy for NO removal from lean-burn effluent streams, but require effective catalysts for NO oxidation to NO\textsubscript{2}.

4.2.2 Main Results

Kinetic experiments were carried out to study the effect of NO, O\textsubscript{2}, and NO\textsubscript{2} pressures on turnover rates and isotopic tracers were implied to measure the \textsuperscript{16}O\textsubscript{2}-\textsuperscript{18}O\textsubscript{2} exchange rates.

It was observed that on both catalysts, NO oxidation rates were first-order in NO and O\textsubscript{2} and inversely proportional to NO\textsubscript{2} pressure, as also observed on Pt and PdO. (Fig. 9)
These data suggest O$_2$ activation on isolated vacancies (*) on surfaces of Rh and Co oxides saturated with oxygen (O*) is the sole kinetically-relevant step. Quasi-equilibrated NO-NO$_2$ interconversion steps establish oxygen chemical potentials (and O* and * coverages) on these oxides during catalysis. These chemical potentials determine the oxidation state of Rh and Co clusters and are rigorously described by the prevalent O$_2$ virtual pressures (equals the value of the O$_2$ pressure that gives the same equilibrium O* coverage as a particular NO-NO$_2$ mixture), which are estimated using the formalism of nonequilibrium thermodynamics. RhO$_2$ and Co$_3$O$_4$ are the prevalent phases present during NO oxidation catalysts at relevant conditions. Turnover rates increased with increasing cluster size because vacancies, required for kinetically-relevant O$_2$ activation steps, are more abundant on large clusters, which delocalize electron density more effectively than small oxide clusters. NO oxidation turnover rates on RhO$_2$ and Co$_3$O$_4$ are higher than expected from the oxygen binding energy on Rh and Co metal surfaces or from the reduction potentials of Rh$^{3+}$ and Co$^{3+}$. NO oxidation rates fall in line with those measured on Pt and PdO when one-electron reductions processes, accessible for Rh$^{5+}$ and Co$^{3+}$ but not for Pt$^{2+}$ and Pd$^{2+}$, are used to describe the reactivity of RhO$_2$ and Co$_3$O$_4$. Such one-electron redox cycles also cause $^{16}$O$_2$-$^{18}$O exchange rates to be much larger than
IV. Results and discussion

NO oxidation rates, in contrast with their similar values on Pt and PdO, though O₂ activation on vacancies limits both NO oxidation and O₂.

These data and their interpretation in terms of elementary steps, the role of vacancies in kinetically-relevant O₂ activation steps, and the consequent higher reactivity of larger clusters provide a common framework to describe NO oxidation and the active species on catalysts of practical interest.

IV. Results and discussion


IV. Results and discussion


5. Concluding discussion

The reactivity of model DPNR catalysts such as Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ of have been addressed both in the soot oxidation and NOₓ reduction in the presence of water and CO₂. The results obtained during the lean NOₓ adsorption over the Pt-Ba/Al₂O₃-soot mixture showed that the presence of soot decreased the NOₓ storage capacity of the catalyst. Moreover soot leads to an appreciable decrement of the rate of NOₓ adsorption: these effects are seen also at different temperatures (200-350°C) and with different values of the NO inlet concentration (250-1000ppm). During NOₓ storage, soot oxidation also occurs, thanks to the presence of NO₂ formed upon NO oxidation over Pt sites. In fact the NO₂ concentration at the reactor outlet in the presence of soot is significantly lower than that observed without soot, thus pointing out the involvement of NO₂ in soot oxidation. The decrease of the NO₂ concentration may explain also the observed decline in the NOₓ storage properties of the catalyst. In fact, in line with the occurrence of a “nitrate” pathway for the storage of NOₓ (i.e., NO oxidation to NO₂ followed by NO₂ adsorption in the form of nitrates via a disproportion reaction), Ba and soot compete for reaction with NO₂, leading to the observed decrease in the NOₓ storage properties. On the other hand, the reduction of the stored NOₓ is not significantly affected by the presence of soot, although some minor changes in the N₂ selectivity (a slight increase in the presence of soot) have been observed.

Worth to note that the adsorbed NOₓ oxidize soot at temperature well below those corresponding to their thermal decomposition originating NO₂ in the gas phase. This has been shown by TPD /TPO experiments in which the reactivity / thermal decomposition of nitrates has been investigated in the presence and in the absence of soot. It has been found that the presence of soot favors the decomposition and the reduction of the stored nitrates, while soot is oxidized. In fact the presence of soot shifts the decomposition/reaction of the stored nitrates at lower temperatures, and the stoichiometry of the released products reflects the occurrence of a partial reduction of the initially stored NOₓ as well as the oxidation of soot. This reaction possibly involves the surface mobility of the stored nitrates, soot particles being the driving force for the process and acting as reduced centers.

Furthermore mechanistic aspects involved in the formation of N₂ and N₂O during the reduction of NOₓ stored over the model PtBa/Al₂O₃ NSR catalyst have been investigated by means of isotopic labeling experiments. The reduction of the stored labelled nitrites species with ¹⁴NH₃ leads to the selective formation of N₂ and very small amounts of nitrous oxide.
The observed $N_2$ isotopic distribution includes all possible $N_2$ isotopes, i.e. $^{15}N_2$, $^{14}N_2$ and the mixed $^{15}N^{14}N$ species. Based on the pathway suggested for NO and NH$_3$ reaction on Pt-based catalysts, it has been found that the observed product distribution can be explained on the basis of the statistical coupling of $^{15}N$- and $^{14}N$-adatoms originated upon NH$_3$ and NO$_x$ decomposition on Pt. However the simultaneous occurrence of a SCR-like pathway, involving the formation and decomposition of a NH$_x$-NO intermediate originating from ammonia and NO$_x$, and leading to the selective formation of the mixed $^{15}N^{14}N$ species is also likely.

Isotopic labeling experiments also provide indications on the pathways involved in the formation of N$_2$O. This species is formed in very limited amounts during the reduction by ammonia of stored NOx species (nitrites and nitrates); much higher quantities have been observed during the reduction of gaseous $^{15}NO$ with NH$_3$. Since no formation of unlabeled nitrous oxide has been observed, the participation of $^{15}NO$ is necessary for the formation of nitrous oxide. In line with literature proposals, it has been suggested that nitrous oxide formation involves (on the Pt sites) either the coupling of two adsorbed NO molecules or the recombination of an adsorbed NO molecule with an adsorbed NH$_x$ fragment. Accordingly, N$_2$O formation is greatly enhanced in the presence of gas-phase NO.

De-NO$_x$ and De-soot activity has been investigated also over a model Pt-K/Al$_2$O$_3$. It has been shown that the pathways for the adsorption and the reduction of NO$_x$ are similar for the Pt-Ba/Al$_2$O$_3$ and Pt-K/Al$_2$O$_3$ catalytic system. The presence of soot affects the NO$_x$ storage capacity and the stability of the adsorbed species of both samples.

The aspects related to the reduction of stored NO$_x$ at 350°C onto Pt-K/Al$_2$O$_3$ catalyst have been deeply investigated using also CO as reductant. It was shown that the reduction by CO of stored nitrates occurs through a Pt catalyzed surface pathway, which does not involve the thermal decomposition of stored NO$_x$ with release of NO$_x$ in the gas phase and leads mainly to nitrogen and CO$_2$. The reaction scheme already proposed in the case of Pt-Ba/Al$_2$O$_3$ catalyst operates also in the case of Pt-K/Al$_2$O$_3$ system and implies the formation of surface isocyanate species at first and in the second step the reaction of these superficial species with residual nitrates to give nitrogen. Over Pt-K/Al$_2$O$_3$ system this last surface reaction is more efficient than over the Ba-containing catalyst, so at the end of the reduction the amount of isocyanates species present on the surface is lower for Pt-K/Al$_2$O$_3$ then Pt-Ba/Al$_2$O$_3$ catalyst. A different mobility of the surface species involved in these reactions is invoked, having K-containing species higher mobility than Ba ones.

Another important part of this thesis work was focused on the study of the elementary steps involved in NO oxidation on Rh and Co catalysts. Kinetic experiments were carried out to study the
effect of NO, O₂, and NO₂ pressures on turnover rates. It was observed that turnover rates increased linearly with NO and O₂ pressures and were inversely proportional to NO₂ pressure, as also observed on Pt and Pd catalysts. NO oxidation rates are limited by O₂ activation on isolated vacancies (\(\ast\)) on surfaces of Rh and Co oxides saturated with oxygen (O\(\ast\)). RhO₂ and Co₃O₄ as the stable active phases during NO oxidation throughout the temperature and concentration ranges relevant to catalysis. Turnover rates increase with increasing cluster size, because the formation of kinetically-relevant vacancy sites becomes more facile on larger clusters, with more coordinatively saturated surfaces. NO oxidation turnover rates on RhO₂ and Co₃O₄ are higher than expected from oxygen binding energies on the respective metals or from the two-electron reduction potentials of Rh⁴⁺ or Co³⁺, but fall in line with the reactivity of Pt and PdO when one-electron reductions (accessible for Rh and Co, but not for Pt or Pd) are used to predict turnover rates.
Acknowledgments
Paper I

Study of DPNR catalysts for combined soot oxidation and NOx reduction

Lidia Castoldi, Nancy Artioli, Roberto Matarrese, Luca Lietti, Pio Forzatti
Abstract

The behavior of a model PtBa/Al₂O₃ model NSR catalyst in both the NOₓ storage/reduction and soot oxidation is investigated in this work. It is found that the presence of soot negatively influences the NOₓ storage capacity of the catalyst, evaluated at 623 K in presence of water and CO₂ in the feed stream: in fact the amounts of NOₓ stored in presence of soot decrease by nearly 30% in the presence of roughly 10% w/w of soot. The presence of soot has a destabilizing effect on the NOₓ adsorbed species, which decompose to a large extent in the absence of gas-phase NO and oxygen. This has also been confirmed by dedicated TPD and TPO experiments. However the presence of soot does not appreciably affect the behavior of the PtBa/Al₂O₃ catalyst in the reduction by H₂ of the stored nitrates, being in all cases N₂ the major reaction product along with minor amounts of ammonia.

During the storage of NOₓ, soot oxidation takes place. Notably, the stored NOₓ participate in the soot oxidation upon release of NO₂ and O₂ which actively oxidize soot. However a direct participation of the adsorbed NOₓ species in the oxidation of soot cannot be excluded.

Keywords: Soot oxidation, diesel particulate filter, 4-ways catalysts, Lean deNOₓ, NOₓ trap promotion, LNT systems, Pt–Ba/Al₂O₃ catalyst, combined soot-NOₓ removal, DPNR
1. Introduction

Current and upcoming environmental legislations in the most developed countries are imposing severe limits in NOx, hydrocarbon, CO and particulate (soot) emissions from diesel engines. While the control of soot emissions is currently accomplished by the use of the so-called Diesel Particulate Filters (DPF), suitable technologies for NOx abatement in lean-burn engines are still under development \[1\]. Among these, Lean NOx Traps (LNTs), also known as NOx storage-reduction (NSR) systems, have been proposed. The NSR technique utilizes an unsteady state operation by switching between fuel-lean and fuel-rich conditions \[2,3\]. Standard NSR catalysts consist of precious metals and alkaline/alkaline-earth metal oxides, typically platinum and barium, respectively, dispersed on metal oxide supports such as alumina. During fuel-lean periods, NOx are stored on the alkaline/alkaline-earth metal oxide; the stored NOx are then reduced to N\(_2\) during a short fuel-rich period \[3\].

To accomplish soot and NOx removal, both de-soot and a deNOx aftertreatment techniques must be used. In the late ’90, Toyota has developed a new technology able to remove simultaneously NOx and soot \[4,5\]. This system, called Diesel Particulate-NOx Reduction (DPNR), consists of is a porous ceramic filter coated with a catalytic layer consisting of a NSR catalyst. Like the NSR technology, this system accomplishes the reduction of soot and NOx under cyclic conditions: soot abatement occurs under lean conditions thanks to the presence of NOx and the excess oxygen in the exhaust gas, but it is claimed to occur during the rich phase as well.

In previous works of our group the potentiality of a model PtBa/Al\(_2\)O\(_3\) catalyst in the simultaneous removal of soot and NOx has been investigated. It has been found that the PtBa/Al\(_2\)O\(_3\) samples is able to oxidize soot in the presence of oxygen at temperatures above 623–673 K; the presence of NO in the gas phase significantly enhances the soot combustion activity \[6,7\], due to NO oxidation to NO\(_2\) on Pt followed by the reaction of NO\(_2\) with soot:

\[
2\text{NO}_2 + \text{C} \rightarrow 2\text{NO} + \text{CO}_2
\]  

(1)

In reaction (1), CO\(_2\) formation is envisaged but CO formation may occur as well. It is indeed well known that NO\(_2\) is a better oxidant than O\(_2\) \[8 and references herein reported\]; its reaction with the carbonaceous material leads to both CO and CO\(_2\) formation \[9\].

Based on a comparative study of a PtBa/Al\(_2\)O\(_3\) catalyst with a Pt/Al\(_2\)O\(_3\) sample, a role of the stored NOx species in the oxidation of soot has been suggested \[9\]. In a recent paper by Kustov and Makkee \[10\] the soot oxidation on a number of alkali-earth based catalytic systems pre-saturated with NOx,
like Ba(NO$_3$)$_2$/Al$_2$O$_3$, has been investigated. The authors show that stored nitrates contribute to the soot oxidation by lowering the temperature of soot oxidation. Along similar lines, Suzuki et al. [14] noted an increased combustion activity of soot when a NO$_x$ trap material is incorporated in the catalyst. On the other hand, Sullivan et al. [15] reported that the presence of a NO$_x$ trapping component like BaO does not promote per-se the particulate combustion. However the NO$_x$ trapping material promotes soot combustion due to the periodic localized increases in the NO$_2$ gas phase concentration during trap regeneration. On these bases, aim of this work was to provide new insights on the role in the soot combustion of NO$_x$ stored onto the catalytic surface of a model PtBa/Al$_2$O$_3$ DPNR catalyst. Besides, we wanted to analyze the effects of the presence of soot on the behaviour of the LNT catalyst in terms of NO$_x$ storage/reduction. For this purpose, NO$_x$ storage/reduction experiments have been performed over a model PtBa/Al$_2$O$_3$ catalyst by alternating lean/rich cycles both in presence and in absence of soot. The interaction between soot and the stored NO$_x$ species has also investigated by Temperature Programmed Methods under inert flow (TPD) or in oxygen (TPO) during which the stability/reactivity of the stored NO$_x$ species has been analyzed both in the presence and in the absence of soot.

2. Experimental

The model catalyst studied, PtBa/Al$_2$O$_3$ (Pt loading near 0.8% w/w and Ba loading near 17% w/w), was prepared by the wetness impregnation technique from solutions of dinitrodiammine platinum (Strem Chemicals) and barium acetate (Strem Chemicals, as reported elsewhere [6-13]). The catalyst presents a surface area near 160 m$^2$/g$_{cat}$ and pore volume of 0.8 cm$^3$/g$_{cat}$ (as determined by N$_2$ adsorption-desorption with a Micromeritics TriStar 3000 Instrument). The Pt dispersion is close to 15% (H$_2$ chemisorption at 273 K, measured with a TPD/R/O 1100 Thermo Fischer Instrument). Further detail of catalyst preparation and characterization are reported in Refs.[14,15,16].

Printex-U (Degussa) was used as model soot [17,18]. Catalyst-soot mixtures were prepared by gently mixing in a vial the catalyst powder with the soot for 24 h, thus realizing a loose contact. A catalyst/soot ratio of 9/1 w/w was typically utilized in reactivity tests.

All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7 mm i.d) connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum) and to a micro GC (Agilent 3000A) for the on-line analysis of the outlet gases [19]. The outlet NO, NO$_2$, NH$_3$ concentrations were also detected by a UV analyzer (Limas 11HW, ABB). 66 mg of the soot-catalyst (74-105 µm) mixture was used in each run, and the total gas flow was always set at 100 cm$^3$/min (at 273 K and 1 atm).
Before catalytic tests, the catalyst/soot mixture has been heated at to 773 K in He to remove any adsorbed species on the catalytic surface. The NO\textsubscript{x} storage and reduction activity of the catalytic system has been studied in the presence and in the absence of soot by performing lean-rich cycles at constant temperature (Isothermal Step Concentration experiments, ISC). During the NO\textsubscript{x} adsorption (lean phase, see Tab. 1), a pulse of NO (1000 ppm) has been admitted to the reactor in flowing He + 3\% (v/v) O\textsubscript{2} until catalyst saturation. Then after a He purge at the same temperature, catalyst regeneration (rich phase, see Tab. 1) has been carried out with H\textsubscript{2} (4000 ppm in He).

<table>
<thead>
<tr>
<th>Gas composition (%v/v)</th>
<th>Lean rich cycle</th>
<th>TPD</th>
<th>TPO</th>
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<tr>
<td></td>
<td>Lean phase</td>
<td>Rich phase</td>
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<tr>
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<td>0</td>
</tr>
<tr>
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<td>0</td>
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<tr>
<td>H\textsubscript{2}</td>
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<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>1</td>
<td>1</td>
<td>0.01</td>
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<tr>
<td>He</td>
<td>balance</td>
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Tab. 1. Experimental conditions of lean-rich cycles, TPD and TPO experiments. All the experiments have been carried out with a flow rate of 100cc/min (@ 0°C and 1 atm).

The catalyst samples have been conditioned by performing a few adsorption/regeneration cycles: conditioning lasted until a reproducible behaviour has been obtained, and this typically required 2-3 cycles. 1\% v/v H\textsubscript{2}O and 0.1\% v/v CO\textsubscript{2} were always present in the feed flow during both the storage and the reduction phase (table 1). The CO\textsubscript{2} concentration is lower than real applications, but it is anyway representative of carbon dioxide effect on the catalytic system performance \cite{16}. Besides such low value allows to appreciate even small changes in the CO\textsubscript{2} concentration during the experiments.

The selectivity to N\textsubscript{2} of the reduction process has also been estimated. Since the N\textsubscript{2} selectivity changes during the rich phase due to the variation in the product distribution with time, a time-weighted average N\textsubscript{2} selectivity (S\textsubscript{N2}) along the entire rich step has been estimated:

$$S_{N_2} = \frac{2n_{N_2}}{2n_{N_2} + n_{NO} + n_{NH_3}}$$  \hspace{1cm} (a)

In eq. (a) n\textsubscript{N2}, n\textsubscript{NO} and n\textsubscript{NH3} are the total molar amounts of N\textsubscript{2}, NO, and NH\textsubscript{3}, respectively, evolved during the entire reduction phase. These amounts are obtained by the integrals on time of the concentrations of the products evolved during the entire reduction phase. N\textsubscript{2}O has not been considered in eq. (a) since formation of this species has been found to be negligible.

The thermal stability of the stored NO\textsubscript{x} was analyzed by thermal decomposition in inert flow (Temperature Programmed Desorption, TPD). After NO\textsubscript{x} adsorption at 623 K the sample was cooled
in He at 523 K and then heated (10 K/min) in He + H₂O (1% v/v) and CO₂ (0.1% v/v) from 523 K up to 773 K (hold 30 min) (see Tab.1). These experiments have been carried out in the presence and in the absence of soot to analyze the effect of soot on the thermal stability of the adsorbed nitrates.

Finally, the behaviour of the catalysts in the soot combustion reaction was investigated by means of temperature-programmed oxidation (TPO). Like TPD experiments, after NO₃ adsorption at 623 K the catalyst was cooled in He down to 523 K and then heated (10 K/min) in He + O₂ (3%, v/v) + H₂O (1%) + CO₂ (0.1% v/v) from 523 K up to 773 K (see Tab.1). These experiments have been carried out in the presence and in the absence of stored NO₃.

Soot is progressively consuming during each test; accordingly several catalyst/soot batches have been used. All the experiments refer to a soot loading near 7-8% of the catalyst weight.

3. Results and discussion

**NO₃ adsorption phase** - The results obtained in the case of a rectangular step feed of NO (1000 ppm) in the presence of O₂ (3% v/v), CO₂ (0.1% v/v) and H₂O (1% v/v) at 623 K carried out on the PtBa/Al₂O₃ catalysts in the absence and in the presence of soot (soot loading near 8% of the catalyst weight) are shown in Figure 1A and Figure 1C, respectively. The outlet NO, NO₂ and NOₓ (NO+NO₂) concentration curves are displayed in the Figure as a function of time, along with that of the NO inlet concentration (dotted lines). In the absence of soot (Fig. 1A), upon the NO step addition (at t = 0 s) the NO outlet concentration increases with time, approaching the asymptotic values corresponding to the NO inlet concentration after about 2000 s. Also NO₂ (140 ppm at steady-state) is observed due to the occurrence of the oxidation of NO by O₂ according to the stoichiometry of reaction (2):

\[
\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2 \quad (2)
\]

The amount of NOₓ that has been stored on the catalyst surface at the end of the NO pulse is near 0.58 mmol/g kat. During the NO pulse, CO₂ evolution is also observed. This is due to the formation of nitrate species upon NO₃ adsorption [16,19], that replace carbonates with release of CO₂ according to the stoichiometry of reaction (3),

\[
\text{BaCO}_3 + 2 \text{NO} + 3/2 \text{O}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2 \quad (3)
\]

In fact upon subtracting half of the adsorbed NO concentration value (i.e. \( \frac{1}{2} (\text{NO}_{\text{in}} - \text{NO}_{\text{out}}) \)) to the actual CO₂ concentration curve, a flat CO₂ trace is obtained (trace a of Figure 1A).

Finally, upon NO shutoff near t = 3500 s, a tail is observed in the NO and NO₂ concentrations due to
the desorption of weakly adsorbed NO$_x$ species (0.11 mmol NO$_x$/g$_{cat}$ desorbed), whose release is favored by the decrease in the NO$_x$ partial pressure. The net amount of NO$_x$ stored before regeneration is hence near 0.47 mmol NO$_x$/g$_{cat}$.

In presence of soot (Fig. 1C), the evolution of NO and NO$_2$ are qualitatively similar to those observed for the soot-free catalyst. Upon NO admission, the outlet NO concentration increases with time reaching a steady-state level after 2000 sec. The formation of NO$_2$ is also observed, but in lower amount (60 ppm) if compared to the soot-free catalyst. The amount of adsorbed NO$_x$ at the end of the pulse is in this case near to 0.41mmol NO$_x$/g$_{cat}$, indicating a reduction in the storage capacity of the catalyst in presence of soot as also reported by Sullivan et al. [12].

Fig. 1 – Storage-reduction cycle performed at 623K over PtBa/Al$_2$O$_3$ (A and B)and Pt–Ba/Al$_2$O$_3$-soot mixture (C and D). Trace a is the CO$_2$ production due to soot oxidation.
A comparison of the amounts of NOx stored vs. adsorption time for different soot loadings (curve a: soot-free catalyst; curve b: soot loading 2.9% w/w; curve c: soot loading 8% w/w) is shown in Figure 2.

![Figure 2](image)

Fig. 2 - Adsorbed NOx versus time over PtBa/Al₂O₃ for different soot loadings: a) without soot, b) 2.9% w/w soot and c) 8%w/w soot

It clearly appears that the amount of soot present in the catalyst/soot mixture affects the NOx storage behavior of the LNT system. In particular, the decrease of the soot loading (from curve c to curve a) leads to an increase of the NOx storage capacity, in line with the results reported by Sullivan et al. [12]. These authors pointed out that the presence of soot is detrimental to the performance of a NOx trap since soot itself offers another reaction route for the utilisation of NO₂ rather than the desired formation of Ba(NO₃)₂ according to the stoichiometry:

\[
\text{BaCO}_3 + 3 \text{NO}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{NO} + \text{CO}_2
\] (4)

As a matter of facts, upon comparing Figure 1A and 1C, it is noted that the presence of soot affects the NO/NO₂ ratio. Indeed the NO/NO₂ value rises from a value near 6 for the soot-free catalyst sample to roughly 15 in presence of soot. The higher NO/NO₂ ratio measured in the presence of soot is due to the participation of NO₂ in soot oxidation, according to reaction (1).

In Figure 1C, upon NO admission, CO₂ evolution is also observed above its background of 1000 ppm. The increase in the CO₂ outlet concentration results from two contributes: one is related to the decomposition of carbonates on the catalytic surface due to nitrates formation (in line with reactions (3)-(4)), and the other is due to soot combustion. In order to evaluate the net CO₂ production due to the soot combustion, the contribution of the decomposition of the surface carbonates (reaction (3)) has been subtracted from the CO₂ outlet concentration trace; the obtained
CO$_2$ net production curve is shown in Figure 1C (trace a). During the lean phase roughly 4% of the soot initially present has been oxidized with a rate of approximately $1.08 \times 10^5$ mmol CO$_2$/s. Worth to note that at the investigated temperature soot combustion occurs only in the presence of NO. Besides, CO formation is not observed, possibly because the formed CO is further oxidized to CO$_2$ by O$_2$ on Pt sites.

Upon NO shutoff, a release of NO and NO$_2$ takes place due to the desorption/decomposition of the NO$_x$ species previously stored. Upon switching off the O$_2$ feed, additional NO$_x$ are also desorbed. Both desorption contributions appear to be remarkable if compared to those observed in the case of the soot-free catalyst: this indicates that soot has a destabilizing effect on the nitrate species adsorbed onto the catalytic surface. The reasons for the destabilizing effect of soot on the stored nitrates are not yet fully understood; one can speculate that nitrates species, which are considered mobile on the catalytic surface [20], may directly interact with soot particles leading to its oxidation.

The changes in the amounts of adsorbed NO$_x$ upon NO shut off are reported in Fig. 3 as a function of time for different soot loadings (curve a: soot-free catalyst; curve b: soot loading 2.9% w/w; curve c: soot loading 8% w/w). It appears that the higher the soot loading, the greater is the decrease of the amount of stored NO$_x$. After 2000 sec, the total amounts of NO$_x$ desorbed in the presence and in the absence of soot are near 0.12 mmol/g$_{cat}$ and 0.07 mmol/g$_{cat}$, respectively; these values correspond to 29 % and 12.4 % of the NO$_x$ adsorbed species present onto the catalytic surface at saturation. This clearly points out the lower stability of nitrates in presence of soot.

![Fig. 3 - Desorbed NOx versus time after NOx storage over PtBa/Al$_2$O$_3$ for different soot loadings: a) without soot, b) 2.9% w/w soot and c) 8%w/w soot](image)

**NO$_x$ reduction phase** - The reduction of the stored NO$_x$ has been carried out at 623 K by admission of
Study of DPNR catalysts for combined soot oxidation and NOx reduction

H₂ (rich phase, table 1). The results are shown in Figure 1B in terms of H₂, CO₂ and N₂, NH₃ outlet concentrations as a function of time in the case of the soot-free catalyst.

Upon H₂ admission (t = 0 s), the H₂ outlet concentration profile shows a dead time during which it is completely consumed to give at first N₂ and NH₃ later on, according to the overall stoichiometry of reactions (5) and (6):

\[ \text{Ba(NO}_3\text{)}_2 + 5 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{N}_2 + 5 \text{H}_2\text{O} \quad (5) \]
\[ \text{Ba(NO}_3\text{)}_2 + 8 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NH}_3 + 5 \text{H}_2\text{O} \quad (6) \]

In line with the stoichiometry of reaction (5), upon admission of 4000 ppm H₂ the N₂ outlet concentration immediately increases to the level of 800 ppm; then NH₃ formation is observed in correspondence of the decrease of the N₂ trace, at the end of the reduction. Slightly after the NH₃ breakthrough the H₂ concentration trace increases up to the inlet concentration value. The integral amounts of the reduction products (0.21 mmol/g_cat of N₂ and 0.07 mmol/g_cat of NH₃) well correspond to H₂ consumption (1.46 mmol/g_cat), according to the stoichiometry of reactions (5) and (6). N₂O is not observed among the reduction products, as indicated by GC analyses (detection limit near 10 ppm).

According to previous studies of our group [16,21] the reduction of stored nitrates by H₂ occurs via a two-step molecular pathway which involves a first step leading to the formation of NH₃, followed by the slower reaction of ammonia with residual nitrates to form N₂:

\[ 3 \text{Ba(NO}_3\text{)}_2 + 10 \text{NH}_3 + \text{CO}_2 \rightarrow 3 \text{BaCO}_3 + 8 \text{N}_2 + 15 \text{H}_2\text{O} \quad (7) \]

The sum of reactions (6) and (7) accounts for the overall stoichiometry of reduction of nitrates with hydrogen to give N₂ (reaction 5). Notably, the temporal evolution of reduction products, with nitrogen being detected at the reactor outlet first and ammonia later, is in line with the integral behaviour of the catalytic bed [16,21]. In fact upon regeneration a hydrogen front travels along the catalyst bed. NH₃ is formed at the H₂ front upon reaction of H₂ with the stored NO₃; the formed NH₃ then reacts with NOₓ stored downstream the H₂ front, leading to the formation of N₂. When the front reaches the end of the catalytic bed, there are no NOₓ stored downstream and this leads to the evolution of ammonia, which follows that of N₂.

During the reduction phase, a CO₂ uptake has also been observed due to the formation of carbonates onto the Ba sites on which NOₓ were previously stored; finally, after NOₓ reduction, the formation of small amounts of CO is also observed due to the occurrence of the inverse water gas
shift (RWGS) reaction (8):

\[
\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \tag{8}
\]

Calculation showed that the reaction is limited by thermodynamic constraints; the relevance of this reaction appears to be limited by the presence of water in the feed \[16\].

The reduction of the NO\textsubscript{x} adsorbed species in the presence of soot (Figure 1D) does not show significant differences with respect to the soot-free catalyst (compare Figure 1B and 1D). Also in this case H\textsubscript{2} is immediately and completely consumed and at the beginning of the reduction phase and only N\textsubscript{2} is observed among the products. After 150 sec the concentration of nitrogen decreases to zero, that of H\textsubscript{2} progressively increases and NH\textsubscript{3} is observed at the reactor exit. In the presence of soot the amount of both N\textsubscript{2} and NH\textsubscript{3} which have been produced is lower if compared to the absence of soot, i.e. 0.11 mmol/g\textsubscript{cat} of N\textsubscript{2} and 0.02 mmol/g\textsubscript{cat} of NH\textsubscript{3}. This is related to the reduced NO\textsubscript{x} storage capacity of the catalyst in presence of soot, as shown in Figure 2 (curve c). However, the N\textsubscript{2} selectivity calculated in the presence of soot is very similar to that measured in its absence, i.e. 86% vs. 92%.

**TPD experiments** - In order to analyze the stability of adsorbed NO\textsubscript{x} species in the absence and in the presence of soot, TPD experiments have been carried out (Table 1). Figure 4A and 4B shows the results obtained in terms of NO, NO\textsubscript{2}, and O\textsubscript{2} concentration traces versus time on Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} in the absence and in the presence of soot, respectively.

In the case of the soot-free Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst (Fig. 4A), no desorption peaks were observed below the adsorption temperature (623 K). This is in line with previous results \[16,22,23\] showing that the adsorption temperature rules the thermal stability of the adsorbed NO\textsubscript{x} species. Decomposition of nitrates occurs above the temperature of absorption and results in the initial evolution of NO\textsubscript{2}, followed by NO and O\textsubscript{2}. NO, O\textsubscript{2}, and NO\textsubscript{2} are likely produced through the following global reactions:

\[
\text{Ba(NO}_3)_2 \rightarrow \text{BaO} + 2 \text{NO} + 3/2 \text{O}_2 \tag{9}
\]

\[
\text{Ba(NO}_3)_2 \rightarrow \text{BaO} + 2 \text{NO}_2 + \text{O}_2 \tag{10}
\]
The process was not complete at temperatures as high as 773 K, corresponding to the maximum heating temperature; the catalyst was then kept at this temperature until desorption of nitrates was nearly complete (N-balance closes within 5.5%). After the TPD experiment a reducing treatment has been carried out with a stream of H₂ (4000 ppm in He+H₂O+CO₂) at 623 K to reduce the residual nitrates. During this treatment the formation of very small amounts of NH₃ (4.91×10⁻³ mmol/g-cat) have been detected.

In correspondence with the nitrate decomposition, a decrease of the CO₂ signal is observed, from the inlet value (1000 ppm) to a minimum of 840 ppm. This is due to the adsorption of CO₂ on Ba forming BaCO₃ upon decomposition of Ba nitrates. Note that the amount of CO₂ adsorbed is lower than that expected from nitrates decomposition (according to reaction (3)), possibly due to the formation of Ba oxide and/or hydroxide, along with BaCO₃.

TPD runs have also been performed in the presence of soot and results are shown in Fig.4B. The decomposition onset of the stored NOₓ is observed about at the same temperature of adsorption (623 K) for the reasons already discussed. The amounts of desorbed species is lower than that calculated in the absence of soot (0.11 mmol/g-cat vs 0.48 mmol/g-cat), as consequence of the minor amounts of NOₓ adsorbed onto the catalytic surface in the presence of soot, as already discussed. It is worth noticing that the distribution of desorbed products is different in the presence and in the
absence of soot (compare Figure 4A and 4B). Indeed in the presence of soot, NO represents the major decomposition product (Figure 4B), and no detectable amounts of NO₂ or O₂ are observed. This suggests that in the presence of soot NO₂ and O₂ produced from the nitrates decomposition are readily consumed in the soot combustion. In line with the occurrence of soot oxidation, the CO₂ concentration trace shows an increase, as opposite to what observed in the absence of soot (Figure 4A). This indicates that soot can be effectively oxidized at temperatures above the nitrate decomposition [10].

Finally, in Figure 4B it appears that the nitrates decomposition is concluded at lower temperature (near 773 K) than in the absence of soot. This indicates that the presence of soot favors the decomposition of the NOₓ adsorbed species, in line with isothermal experiments reported above (see Figure 3).

**TPO experiments** - TPO experiments have been carried out i) in the presence of adsorbed NOₓ species only, ii) in the presence of soot and iii) in the presence of both soot and adsorbed NOₓ species (Figure 5A-C, respectively). In the presence of adsorbed NOₓ species only (Figure 5A) the decomposition of the stored NOₓ was appreciable only above 623 K, with evolution of NO₂ and NO. Comparing these data with the results of TPD experiments discussed above (Figure 4A), it appears that the products distribution is similar, with NO₂ and NO evolution above 623 K (O₂ evolution could not be detected in this case due to the high oxygen concentration in the feed stream). At the end of the heating ramp (773 K), the nitrate decomposition process was not complete; for this reason the temperature was kept at this value for several minutes. Like the TPD experiment, in correspondence of the NOₓ desorption peak a decrease in the CO₂ concentration trace is observed, due to carbonates formation onto the catalytic surface. After the TPO experiment, the residual nitrates (roughly 18 % of the initially stored NOₓ) were removed by a reducing treatment with H₂ at 623 K.

In the presence of both nitrates and soot (Figure 5B), the nitrates decomposition occurs at slightly lower temperatures than in the absence of soot. As already discussed in the case of the TPD run (Figure 4B), no NO₂ is detected in this case at the reactor outlet due to its involvement in the soot oxidation. A significant CO₂ evolution is observed in this case, along with O₂ consumption. At 773 K the decomposition of nitrates is already complete and the subsequent reduction doesn’t show any production of reduction products: these results are in agreement with those reported above in the case of the TPD experiment.

Finally, Figure 5C shows the results of a TPO experiment carried out in the case of the soot-catalyst mixture, in the absence of pre-adsorbed nitrates. A minor CO₂ evolution is observed, produced by
soot oxidation, along with a corresponding $O_2$ consumption. A comparison with the experiment carried out in the presence of surface nitrates (Figure 5B) clearly points out that the presence of surface NO$_x$ favors the soot oxidation, as pointed out by the greater amounts of evolved CO$_2$ in this case, A 1.93 vs 1.36 mmol/g$_{cat}$.

According to Kustov and Makkee [10] soot is oxidized in the presence of nitrates through two routes: oxidation with NO$_2$ and oxidation with oxygen. Oxidation with NO$_2$ occurs upon nitrate decomposition; according to the authors, this mechanism may decrease the onset temperature for soot oxidation by some 100 K with respect to oxygen. The increase in the CO$_2$ concentration which is observed at the beginning of the TPO run carried out in the presence of adsorbed NO$_x$ (compare
Figure 5B and C) may result from soot oxidation by NO$_2$ evolved upon decomposition of the stored nitrates. In fact only NO evolution is observed in this case upon nitrate decomposition, as opposite to what observed in the absence of soot (see Figure 5A). This clearly indicates that NO$_2$ which evolves upon decomposition of the stored nitrates, is involved in soot oxidation likely according to the stoichiometry of reaction (1). Notably, the increase in the CO$_2$ formation is much higher than that expected from the stoichiometry of reaction (1). This is due to the so-called “NO recycle”, i.e. to the oxidation of NO produced according to reaction (1) to NO$_2$, catalyzed by Pt $^{[24]}$. Besides, it has also been reported that the presence of NO$_2$ enhances soot oxidation by oxygen $^{[25,26]}$. A specific role of the adsorbed NO$_x$ species in the soot combustion cannot be ruled out, as also previously reported $^{[6]}$. These mechanisms contribute to the significant increase in the soot oxidation which is observed when the soot combustion is carried out in the presence of adsorbed nitrates.

4. Conclusions

In this study the behavior of a model PtBa/Al$_2$O$_3$ model NSR catalyst in both the NO$_x$ storage/reduction and soot oxidation has been addressed. It has been found that the presence of roughly 10% w/w of soot decreases by nearly 30% the NO$_x$ storage capacity of the catalyst (0.58 mmol/g$_{cat}$ vs. 0.41 mmol/g$_{cat}$). The presence of soot has also a destabilizing effect on the NO$_x$ adsorbed species, likely due to the reaction between soot particles and the nitrate species which are mobile on the surface.

The behavior of the PtBa/Al$_2$O$_3$ catalyst sample in the reduction by H$_2$ of the stored nitrates has also been investigated, in the presence and in the absence of soot. It has been found that the presence of soot does not appreciably affect the features of the reduction of the stored NO$_x$, being in both cases N$_2$ the major reaction product along with minor amounts of NH$_3$.

During the lean-rich cycles, and in particular during the storage of NO$_x$, soot oxidation takes place, pointed out by CO$_2$ evolution. Soot oxidation takes place only upon NO admission, and is almost negligible in the presence of O$_2$ only. As pointed out by TPD experiments, the stored NO$_x$ participate in the soot oxidation upon release of NO$_2$ and O$_2$ which actively oxidize soot, although a direct participation of the stored NO$_x$ in the oxidation of soot cannot be excluded. The participation of the adsorbed NO$_x$ species in the soot oxidation has also been clearly pointed out by TPO experiments showing that the oxidation of soot is greatly enhanced by the presence of adsorbed NO$_x$ species: indeed larger amounts of CO$_2$ are produced upon soot oxidation when the reaction is carried out in the presence of stored NO$_x$. 

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References

Effect of soot on the storage-reduction performances of LNT PtBa/Al$_2$O$_3$ catalyst

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**Abstract**

The effect of soot on the storage-reduction performances of a PtBa/Al₂O₃ catalyst is investigated in this work. It is found that the presence of soot reduces the NOₓ storage capacity of the catalyst, evaluated in presence of water and CO₂ in the feed stream in the range 200-350°C and with different values of the NO inlet concentration. Besides the presence of soot favors the decomposition and the reduction of the stored nitrates, while soot is being oxidized. A direct reaction between the stored nitrates and soot is suggested, that has been explained on the basis of the surface mobility of the adsorbed nitrates. This soot oxidation pathway involves surface species and parallels the NO₂-soot oxidation that occurs in the presence of gas-phase NO₂.

Finally, the presence of soot does not influence appreciably the behavior of the PtBa/Al₂O₃ catalyst in the reduction by H₂ of the stored nitrates: in all cases N₂ is the main reaction product and ammonia is observed in minor amounts.

**Keywords**

Soot oxidation, DPNR catalysts, simultaneous NOₓ and soot removal, Diesel Particulate NOₓ Reduction, NSR catalysts
1. Introduction

Diesel-equipped vehicles are considered as one of the primary sources of NO\textsubscript{x} and particulate (soot) emissions in industrialized countries. Accordingly regulations to limit their emission are becoming very strict. In Europe, the current Euro 5 rules limit NO\textsubscript{x} and soot emissions from light-weight diesel vehicles (up to 2500 kg) at 0.18 and 0.005 g/km, respectively, but a more drastic reduction is required for NO\textsubscript{x} emissions in the upcoming Euro 6 regulations (0.08 g/km). This will require the use of exhaust after-treatment technologies able to reduce the NO\textsubscript{x} emissions in addition to the soot removal technologies already set by the Euro 5 standards (the so-called Diesel Particulate Filter, DPF) [1].

The soot removal devices, usually made by a cordierite or SiC filter, provide excellent filtration efficiency but must be periodically regenerated to remove the entrapped soot in order to avoid increased pressure drop. The active regeneration is usually performed by increasing the filter temperature (at 650°C or more) by fuel injection so that the particulate is burnt by oxygen present in the exhaust. This procedure implies an extra fuel consumption; moreover, excessive heating can damage the filter.

Alternative solutions have been proposed to regenerate the filter at lower temperature. An example is the CRT (Continuously Regenerating Trap) technology, proposed by Johnson Matthey [2,3], which is constituted by a catalytic system (the pre-oxidizer) that oxidizes CO and unburned hydrocarbons (UHCs), followed by a non-catalytic wall-flow filter for the particulate. The pre-oxidizer also converts NO to NO\textsubscript{2}, which then oxidizes at low temperature the particulate matter trapped and is back-reduced to NO:

\[
\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \quad (1)
\]

\[
2 \text{NO}_2 + \text{C} \rightarrow 2 \text{NO} + \text{CO}_2 \quad (2)
\]

Thanks to the high combustion activity of NO\textsubscript{2} towards soot, the wall-flow trap regeneration process is continuously performed at low temperature, without additional fuel addition. However it must be pointed out that the efficiency of this system depends on the activity in the NO to NO\textsubscript{2} oxidation, and on the NO\textsubscript{x} concentration as well. In fact, the NO\textsubscript{x} content of the exhaust may be not high enough to ensure the complete filter regeneration.

Integrated De-NO\textsubscript{x} and De-soot after-treatment technologies have also been proposed. One example is the DPNR (Diesel Particulate-NO\textsubscript{x} Reduction) concept, recently developed by the Toyota group [4,5]. This system consists of both a new catalytic filter and a new diesel combustion technology. The new catalytic converter for DPNR is a porous ceramic wall-flow filter coated with a NO\textsubscript{x} Storage
Reduction (NSR) catalyst layer. The catalytic material is constituted by a high surface area support (e.g. γ-alumina), a noble metal (Pt), and alkaline or earth-alkaline metal oxides which present a high NOx-storage capacity. These catalytic systems work under cyclic conditions, alternating long lean periods with short regeneration periods under rich condition. During the lean phase the NOx produced by the engine are oxidized and adsorbed on the alkaline or earth-alkaline metal oxide component (with nitrite-nitrate species formation); during the rich phase the nitrate-nitrite species are reduced to molecular nitrogen by CO, H2 and UHCs. The NOx storage-reduction mechanism in the DPNR system is similar to that already proposed by Toyota for NSR systems [6,7,8,9]. Soot oxidation occurs under lean conditions thanks to the presence of NOx and the excess of oxygen in the exhaust gas; soot removal is also claimed to occur during the rich phase as well. Whereas the behaviour of NSR catalysts is well investigated [10,11,12,13,14,15], studies on DPNR systems are still scarce [16,17]. In particular, in previous works the performances of a model PtBa/γ-Al2O3 catalyst in the simultaneous NOx and soot removal has been investigated [18,19]. It has been found that under cycling conditions, i.e. alternating lean-rich phases according to the typical DPNR operation, the Pt-Ba/Al2O3 sample is able to simultaneously remove soot and NOx. It has also been shown that NOx species stored onto the trapping component of the catalyst participate in the combustion of soot via the release of NOx upon nitrate decomposition and/or by directly reacting with soot according to a surface reaction [18,20]. Along similar lines, Kustov et al. showed that the stored nitrates may decrease the temperature of soot oxidation when nitrate decomposition occurs in a proper temperature range, due to the release of NO2 in the gas phase [16]. The same authors also suggested that the presence of an oxidation function (provided e.g. by Pt) is essential [21]. Along similar lines Sullivan et al. [22] reported that the presence of a NOx trapping component like BaO in Pt/SiO2 system does not promote per-se the particulate combustion, but favours soot combustion due to the increases in the NO2 gas phase concentration upon nitrate decomposition. Accordingly there is a general consensus on the fact that the NOx storage function of the NSR catalysts affects the combustion of soot.

Besides, soot may have a role on the NOx storage capacity of the catalysts as well. In a recent work we have shown that the presence of soot negatively influences the NOx storage capacity of the catalyst under representative conditions (i.e. in the presence of water and CO2 in the feed stream) [23]. The presence of soot also decreases the stability of the NOx adsorbed species, thus suggesting an interaction between soot and the stored NOx.

Aim of the present work is to provide new insights on the pathways involved in the NOx storage-reduction and soot oxidation over a model PtBa/Al2O3 catalyst, and on the interactions among the
related catalyst functions. For this purpose, a systematic study has been performed on the DPNR behaviour of the selected catalyst sample in which the reactivity in the NO\textsubscript{x} storage-reduction and in the soot oxidation has been investigated in a wide temperature range (200-350°C) and at different NO inlet concentrations (250-1000 ppm). Experiments have been performed under nearly isothermal conditions, i.e. in the absence of significant temperature effects upon lean/rich switches. This has been accomplished by using a low reductant concentration (4000 ppm) and by separating the lean and the rich phases by an inert purge in between.

2. Experimental

The PtBa/Al\textsubscript{2}O\textsubscript{3} (1/20/100 w/w) sample used in this study has been prepared by incipient wetness impregnation of a γ-Al\textsubscript{2}O\textsubscript{3} calcined at 700°C (Versal 250 from UOP) with a solution of Pt(NH\textsubscript{3})\textsubscript{2}(NO\textsubscript{2})\textsubscript{2} (Strem Chemicals, 5% Pt in ammonium hydroxide) followed by drying at 80°C and calcination at 500°C for 5 h. The obtained Pt/Al\textsubscript{2}O\textsubscript{3} sample was then impregnated with an aqueous solution of Ba(CH\textsubscript{3}COO)\textsubscript{2} (Strem Chemical, 99%), dried at 80°C and further calcined at 500 °C for 5 h to prepare the ternary Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalyst. The selected impregnation order (first Pt and then Ba) has been adopted in order to ensure a good dispersion and stability of the noble metal on the alumina support, in line with the recipes of Toyota patents [\textsuperscript{24}]. The obtained catalytic powder was grinded and sieved at 70-100 μm before use.

The catalyst was characterized by XRD analysis (Brüker D8 Advanced Instrument equipped with graphite monochromator on the diffracted beam), surface area and pore size distribution by N\textsubscript{2} adsorption-desorption at 77K (Micromeritics TriStar 3000 instrument) and Pt dispersion by hydrogen pulse chemisorption at 0°C (TPD/R/O 1100 Thermo Fischer Instrument).

The PtBa/Al\textsubscript{2}O\textsubscript{3} sample presents a surface area near 160 m\textsuperscript{2}/g\textsubscript{cat} and pore volume of 0.8 cm\textsuperscript{3}/g\textsubscript{cat}, while the Pt dispersion is close to 60%. In the XRD patterns of the freshly calcined PtBa/Al\textsubscript{2}O\textsubscript{3} catalyst both the monoclinic (JCPDS 78-2057) and orthorhombic (Whiterite, JCPDS 5-378) polymorphic forms of BaCO\textsubscript{3} were detected in addition to micro-crystalline γ-Al\textsubscript{2}O\textsubscript{3} (JCPDS 10-425); no other crystalline phases were observed. Further details of catalyst preparation and characterization are reported elsewhere [\textsuperscript{12,15,20,25,26}].

Printex-U (Degussa) was used as model soot [\textsuperscript{27,28}]. Catalyst-soot mixtures (soot loading near 10 % w/w) were prepared by gently mixing in a vial the catalyst powder with soot, thus realizing a loose contact.
All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7 mm i.d) connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum), to a micro GC (Agilent 3000A) and to a UV analyzer (Limas 11HW, ABB) for the on-line analysis of the outlet gases (NO, NO₂, N₂, O₂, CO, CO₂, N₂O and NH₃).

66 mg of the soot-catalyst mixture composed by 60 mg of catalyst and 6 mg of soot was used in each run, and the total gas flow was always set at 100 cm³/min (at 0°C and 1 atm). When the pure catalyst was used, the sample weight was 60 mg.

Before the catalytic tests, the catalyst/soot mixture has been heated at 400°C in He in order to desorb/decompose any species weakly adsorbed on the soot/catalytic surface. The NOₓ storage and reduction activity of the catalytic system has been studied in the presence and in the absence of soot by performing lean-rich cycles at constant temperature (Isothermal Step Concentration experiments, ISC) in the range 200-350°C. In a typical run, a stream of He + 3% O₂ (100 cm³/min) was fed to the reactor and the catalyst temperature was set at the desired value. After stabilisation of the concentration signals a rectangular step feed of NO (1000 ppm) was admitted at constant temperature, by means of a pneumatically actuated four-way valve by keeping constant the overall flow rate. The NOₓ storage proceeded up to nearly steady-state, then the inlet NO concentration was stepwise decreased to zero. After a few minutes the O₂ concentration was also decreased in a stepwise manner to zero. This sequence does not modify the results if compared to the simultaneous NO and O₂ removal. The catalyst reduction was accomplished by imposing stepwise changes in the H₂ concentration (0 → 4000 ppm and 4000 → 0 ppm) at the reactor inlet with a second four-way valve. In each step the total gas flow was always maintained constant with He as balance. A stream of Ar was also present in the feed gases as inert tracer: accordingly the lag time of the system could be carefully evaluated, but it has always been found negligible. Note that the lean and rich phases have been separated with a He purge in between in order to analyze separately the catalytic performances of the investigated catalyst during the lean and rich phases, and to avoid any spurious effects due to temperature variations upon lean/rich switches. 1% v/v H₂O and 0.1% v/v CO₂ are always present in the feed; even if the CO₂ and H₂O concentrations are lower than in real applications, their effects are still representative [26]. On the other hand the use of such a low CO₂ concentration allowed us to detect even small quantities of CO₂ produced by soot oxidation.

The catalyst samples have been conditioned by performing a few lean-rich cycles in order to obtain a reproducible behaviour (typically 3-4 cycles). Since soot is progressively consumed during each test, several catalyst/soot batches have been used in order to allow a proper comparison among the
Effect of soot on the storage-reduction performances of LNT PtBa/Al$_2$O$_3$ catalyst various experiments. In particular all the data hereafter reported refer to a soot content near 7.8 % w/w, i.e. very close to the initial loading (10 % w/w).

Finally, in order to analyze the effect of soot on the thermal stability of the stored NO$_x$, TPD experiments of the stored NO$_x$ have been performed in the presence and in the absence of soot. For this purpose NO$_x$ have been stored onto the catalytic surface in the absence of soot, and then the NO$_x$-dosed catalyst has been mixed with soot. The storage phase has been carried out at 350°C with NO (1000 ppm) in He + O$_2$ (3% v/v), H$_2$O (1% v/v) and CO$_2$ (0.1% v/v) until a steady-state behaviour is attained; then the sample has been cooled at room temperature in He, extracted from the reactor and mixed with soot (10 % w/w) under atmospheric air. TPD experiments have been carried by heating the prepared catalyst-soot mixture at a rate of 10°C/min in He + H$_2$O (1% v/v) + CO$_2$ (0.1% v/v) from room temperature to 500°C. The results collected with the catalyst/soot mixture have been compared with those obtained in analogous experiments performed in the absence of soot.

Further details on the experimental procedure and apparatus can be found elsewhere [18,19,20].

3. Results and discussion

3.1. Effect of Temperature.

The NO$_x$ storage–reduction over PtBa/Al$_2$O$_3$ has been investigated in the temperature range 200–350°C in the absence and in the presence of soot, and the results are shown in Figures 1 and 2, respectively.

*Adsorption phase* – The NO$_x$ adsorption has been carried out with 1000 ppm of NO in the presence of O$_2$ (3 % v/v). At the lowest investigated temperature (200°C) and in the absence of soot (Fig. 1A), upon NO admission to the reactor (t = 0 s) NO is immediately observed at the reactor outlet. The NO concentration increases with time and eventually reaches the inlet NO concentration value after 1500 s. No significant NO$_2$ evolution is observed at this temperature. At t = 2200 s the NO inlet concentration is switched off; after the switch a tail is observed in the NO concentration profile, due to the desorption of weakly adsorbed NO$_x$ species. The amount of NO$_x$ stored at this temperature up to the end of the dose (steady-state) is near 0.29 mmol/g$_{cat}$, as apparent from Figure 3 (trace A, dotted line) which shows the amounts of NO$_x$ stored as a function of time-on-stream. These amounts are calculated from the NO$_x$ concentration curves showed in Figure 1A, taking into account the lag time of the apparatus which however has been found to be negligible (see experimental).
Effect of soot on the storage-reduction performances of LNT PtBa/Al$_2$O$_3$ catalyst

Upon NO admission, an increase in the CO$_2$ concentration is also observed, from the background level of 1000 ppm (Figure 1A). In particular a peak is initially observed; then the CO$_2$ concentration decreases to its background level at the end of the pulse. The increase in the CO$_2$ outlet concentration is due to the decomposition of surface carbonates upon NO$_x$ uptake [12], in line with the stoichiometry of the following reaction (3):

$$\text{BaCO}_3 + 2 \text{NO} + 3/2 \text{O}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2$$

(3)
Effect of soot on the storage-reduction performances of LNT PtBa/Al₂O₃ catalyst

As a matter of fact, by subtracting from the CO₂ concentration trace the concentration of CO₂ estimated from the NOₓ uptake according to the stoichiometry of reaction (3), a net CO₂ concentration trace is obtained (see Figure 1A) that closely resembles the inlet CO₂ concentration value (1000 ppm). This indicates that the evolution of CO₂ is uniquely related to the formation of nitrates species at the expense of carbonates, according to the stoichiometry of reaction (3). Along similar lines, after NO shutoff a small CO₂ uptake is observed, due to the occurrence of the reverse of reaction (3).

The NOₓ storage behaviour of the catalyst is affected by temperature. The NOₓ breakthrough increases from few seconds at 200 (Figure 1A) to 25 s at 300°C and 40 s at 350°C (Figures 1C and 1E). Besides the amounts of NOₓ stored up to steady-state increase with temperature, from 0.28 mol/g<sub>cat</sub> at 200°C to 0.34 mol/g<sub>cat</sub> at 300°C and 0.59 mol/g<sub>cat</sub> at 350°C (Figure 3 and Table 1).

Figure 2 - Lean-rich cycles performed over Pt-Ba/Al₂O₃/soot mixture at different temperatures in the presence of H₂O (1% v/v) and CO₂ (0.1% v/v): Lean phase (A, C, E): 1000 ppm NO + O₂ (3% v/v) in He; rich phase (B, D, F): 4000 ppm H₂ in He. Other experimental conditions: 60 mg of catalyst + 6 mg of soot, total flow rate 100 cc/min @ 0°C and 1 atm. panels A-B: T = 200°C; panels C-D: T = 300°C; panels E-F: T = 350°C.
Effect of soot on the storage-reduction performances of LNT PtBa/Al₂O₃ catalyst

Figure 3 – Amounts of adsorbed NOx versus time over Pt-Ba/Al₂O₃ (dotted lines) and over Pt-Ba/Al₂O₃/soot mixture (solid lines) at different temperatures

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<th>Desorbed NOₓ after NO shutoff</th>
<th>NOₓ/ Stored NOₓ</th>
<th>Stored NOx</th>
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</table>

Table 1. Stored NOₓ, desorbed NOₓ (1300s after NOₓ shutoff) and percentage of desorbed NOₓ / stored NOₓ ratio at different temperatures, in the absence and in the presence of soot.

The NO₂ concentration at the reactor outlet measured at the end of the NOₓ dose (steady-state) also increases with temperature. It has been suggested that NO₂ is precursor in the storage of NOₓ, in line with the occurrence of a “nitrate” pathway for the storage of NOₓ (i.e., NO oxidation to NO₂ followed by NO₂ adsorption in the form of nitrates via a disproportion reaction) [13]. Accordingly it is speculated that in the investigated temperature range the amounts of NOₓ adsorbed at steady-state are in thermodynamic equilibrium with the gas-phase NO₂ concentration, whose formation in our experimental conditions is kinetically controlled and hence increases with temperature (the reactor outlet NO₂ concentration is in all cases far from chemical equilibrium, being near 135 ppm at 350°C vs. the equilibrium value of 550 ppm at the same temperature). Accordingly in the investigated temperature range the amounts of stored NOₓ increases with temperature, as opposite to what expected from the thermodynamics of adsorption which is an exothermic process.
The hypothesis of a thermodynamic control on the amounts of NOx stored at steady state is also in line with data obtained with different inlet NO concentration (see later on). Indeed also in this case, as will be discussed below, the amount of NOx stored at steady state are related with the NO2 concentration. On the other hand, since other routes may be involved in the NOx adsorption process, e.g. direct NO uptake on the catalyst surface, etc., factors other than thermodynamics may govern the amounts of NOx stored at steady state. These aspects are still under debate and further studies are required for a better comprehension of the phenomena.

Finally, the increase in the NO2 concentration with temperature also leads to a decrease of the NO/NO2 ratio calculated at the end of the storage phase, from 59 at 200°C down to 6.4 at 350°C.

Temperature also affects the rate of adsorption, as expected. An indication of the average NOx adsorption rate can be derived from the slope of the adsorption curves in Figure 3. Notably, in the initial part the curves are almost superimposed since the rate of NOx adsorption is limited by the NO feed supply (almost complete NO uptake is initially observed at any temperature). Then the curves diverge and increase with a slope that, at fixed amounts of adsorbed NOx, increases with temperature.

The results obtained when the same experiments have been carried out in the presence of soot are shown in Figure 2A, 2C, 2E. Also in the presence of soot the NOx outlet concentration shows a dead time and then increases approaching the asymptotic values corresponding to the NO inlet concentration. The NOx breakthrough increases with temperature but it is always lower than in the absence of soot. Along similar lines the amounts of NOx stored up to steady-state (see Figure 3, solid lines) increase with temperature (from 0.20 mmol/gcat at 200°C, up to 0.40 mmol/gcat at 350°C), but the amounts of NOx stored in the presence of soot are always lower than those measured in the absence. At high temperatures the NO2 concentration measured at steady state is also lower in the presence of soot (e.g. 60 ppm vs. 140 ppm at 350°C in the presence and in the absence of soot, respectively) and accordingly higher NO/NO2 ratios are measured.

Hence the data clearly indicates that soot reduces the NOx storage capacity of the catalyst, in line with our previous data [23] and with results of Sullivan et al. [22] and Pieta et al. [29]. As previously suggested, the decrease in the NOx storage capacity of the catalyst at steady state is likely related to the decrease in the NO2 concentration.

Finally, the presence of soot also decreases the rate of NOx adsorption, as apparent from the comparison of the slopes of the adsorption curves collected at the same temperature in the
presence and in the absence of soot at fixed amounts of stored NO\(_x\) (Figure 3). This is likely associated to the decrease in the NO\(_2\) concentration, which hence influences the rate of the NO\(_x\) storage.

The presence of soot also influences the thermal stability of the adsorbed NO\(_x\) species. As indeed shown in Figures 1 and 2, upon NO shut off at the end of the adsorption phase (He purge) a tail is observed in the NO\(_x\) concentration and this decreases the amounts of NO\(_x\) which have been stored up to steady-state. The amounts of NO\(_x\) which have been desorbed at the various temperatures (calculated in all cases 1300 s after the NO shut off) are reported in Table 1. It is noted that in the absence of soot near 10% and 7% of the initially stored NO\(_x\) are decomposed after the NO shut off at 350 and 300°C, respectively; a higher fraction is calculated at 200°C (near 34%). In the presence of soot, the relative amounts of NO\(_x\) desorbed at 350°C and 300°C are 2-3 times higher than in its absence, being near 27.2 % (vs. 10 %) and 19.6 % (vs. 7.2 %) of those initially adsorbed, respectively. Relatively minor differences are observed at 200°C (43.8 % vs. 34%). Very similar conclusions are derived when the absolute amounts of NO\(_x\) are considered, instead of the percentage values (see table 1).

In spite of the fact that the data at 300°C seems to be slightly off-set since a minimum is observed in the absolute amounts of NO\(_x\) evolved at this temperature (see table 1), still the various effects are clearly visible. Indeed i) in all cases a significant NO\(_x\) desorption is observed, and ii) the presence of soot decreases both the amounts and the thermal stability of the NO\(_x\) adsorbed species. These points will be further discussed later in the following.

During NO\(_x\) storage in the presence of soot, the evolution of CO\(_2\) is also observed (Figure 2). As already discussed, this is due to the decomposition of surface carbonates on the catalytic surface upon nitrates formation in correspondence of the NO admission (reaction (3)). However, in the presence of soot, CO\(_2\) may also be formed due to soot combustion according to the stoichiometry of reactions (2) and/or (4a) and (4b):

\[
\text{NO}_2 + \text{C} \rightarrow \text{NO} + \text{CO} \quad (4a)
\]
\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad (4b)
\]

where NO\(_2\) and CO\(_2\) are formed upon NO and CO oxidation at Pt sites, respectively. As a matter of fact, soot oxidation experiments by NO\(_2\) carried out in the absence of the catalyst pointed out a relevant CO formation, in line with literature indications [30]. During our experiments CO formation is
not observed, likely because CO is oxidized to CO$_2$ by O$_2$ at Pt sites.

Accordingly reactions (2) and (4a-b) imply the consumption of NO$_2$ and a decrease of its concentration at the reactor outlet. In order to determine the amounts of CO$_2$ produced upon soot oxidation, the “net” CO$_2$ production has been calculated as previously indicated, and the results are shown in Figure 2. In the presence of soot a net CO$_2$ production is observed, which is negligible at 200°C (Figure 2A), but it is appreciable at 300°C and 350°C where the trace of the net CO$_2$ is roughly 50 ppm and 130 ppm above that of the background, respectively.

Notably, soot oxidation occurs only after NO addition to the reactor, since in the presence of oxygen alone no net CO$_2$ formation is observed. Hence NO$_2$, formed upon NO oxidation, is suggested to be the actual oxidizing agent of soot, accordingly to reactions (2) and (4a-b), and in line with many authors [16,22,31], although the participation of the stored NO$_x$ is also likely, as will be discussed later on.

**Regeneration phase** - After NO$_x$ adsorption and helium purge, the reduction of the stored NO$_x$ has been carried out at the same temperature of adsorption (200, 300 and 350°C) by admission of H$_2$ in He in the presence of CO$_2$ and H$_2$O. The results obtained upon reduction of the stored NO$_x$ at different temperatures in the absence and in the presence of soot are shown in Figures 1 and 2, respectively.

On the soot-free catalyst, upon the step addition of H$_2$ (at $t = 0$ s) at 200 °C (Figure 1B), the H$_2$ outlet concentration profile shows a dead time during which it is completely consumed and then it increases with time. During H$_2$ consumption, the evolution at first of N$_2$ and then of NH$_3$ is seen at the reactor outlet, together with a consumption of CO$_2$. No formation of other products (e.g. N$_2$O) has been detected in appreciable amounts. The evolution of N$_2$ and NH$_3$, and the consumption of CO$_2$ as well, are in line with the overall stoichiometry of the following reactions (5) and (6):

$$\text{Ba(NO}_3)_2 + 5 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{N}_2 + 5 \text{H}_2\text{O} \quad (5)$$

$$\text{Ba(NO}_3)_2 + 8 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NH}_3 + 5 \text{H}_2\text{O} \quad (6)$$

which consider the re-adsorption of CO$_2$ onto the Ba sites once NO$_x$ has been reduced to give gaseous products.

The observed temporal evolution of the reduction products (with nearly complete nitrogen selectivity at the beginning of the rich phase followed by ammonia formation) is due to the
occurrence of a two-steps in series process for the reduction of the stored \( \text{NO}_x \) by \( \text{H}_2 \) already proposed in previous studies of our group \([32, 33, 34]\). The suggested pathway involves a first fast step during which the stored \( \text{NO}_x \) react with \( \text{H}_2 \) to give \( \text{NH}_3 \), followed by the slower reaction of ammonia with residual nitrates to form nitrogen. The observed products evolution with time is due to an \( \text{H}_2 \) front which develops and travels along the reactor. Accordingly, \( \text{NH}_3 \) is formed at the \( \text{H}_2 \) front and reacts with the \( \text{NO}_x \) stored downstream the front, leading to \( \text{N}_2 \) formation, which accordingly is immediately detected at the reactor exit. When the front reaches the end of the catalytic bed, there are no \( \text{NO}_x \) stored downstream and this leads to the evolution of ammonia, which accordingly follows that of \( \text{N}_2 \).

Similar results have been obtained (in the absence of soot) at the other temperatures, i.e. 300°C and 350°C (Figure 1 D and F). However upon increasing the temperature it is observed that: i) the amounts of the evolved reduction products increase due to the larger amounts of stored \( \text{NO}_x \) with temperature (Figure 3); and ii) the nitrogen selectivity of the reduction process increases with temperature, from roughly 35% at 200°C up to 85% at 350°C. This is in line with the occurrence of the two-steps pathway previously suggested for \( \text{N}_2 \) formation \([34,35,36]\): by increasing the temperature the second step of the reaction which represents the r.d.s of the process (the reaction of ammonia with nitrates to give nitrogen) becomes faster and this drives the nitrogen selectivity of the reaction.

The results obtained upon reduction of the stored \( \text{NO}_x \) at the same temperatures in the presence of soot are shown in Figure 2 B, D and F. A comparison with the results obtained in the absence of soot (Figures 1 B, D and F) indicates that the presence of soot does not influences significantly the reduction of the stored \( \text{NO}_x \), although a slight increase of the \( \text{N}_2 \) selectivity is observed in the presence of soot in same cases (e.g. from 85.7% to 94.8% at 350°C).

3.2 Effect of NO inlet concentration on the \( \text{NO}_x \) storage/reduction and soot oxidation.

**Lean phase** - The effect of the NO inlet concentration on the simultaneous \( \text{NO}_x \) and soot removal over the model PtBa/Al\(_2\)O\(_3\) catalyst has been addressed by performing lean-rich cycles at 350°C in the presence of \( \text{CO}_2 \) (0.1% v/v) and \( \text{H}_2\text{O} \) (1% v/v) with 250, 500 and 1000 ppm of NO in the feed (\( \text{NO}_x \)) during the lean phase.

The results obtained in the case of 1000 ppm NO inlet concentration in the absence and in the presence of soot are shown in Figure 1E and 2E, respectively, and have been previously discussed. Figure 4 shows the results obtained at 350°C in terms of \( \text{NO}_x \) adsorbed during the lean phase as a function of time in the case of the different NO inlet concentrations both in the absence (dotted
lines) and in the presence (solid lines) of soot. As previously reported in the case of Figure 3, these amounts are calculated from the NO$_x$ concentration curves of Figure 1 and 2.

![Graph](image)

**Figure 4 – Amounts of adsorbed NOx versus time over Pt-Ba/Al2O3 (dotted lines) and over Pt-Ba/Al2O3/soot mixture (solid lines) at different NO inlet concentration**

As shown in Figure 4, in all cases the amounts of stored NO$_x$ increase with time reaching an asymptotic value corresponding to the steady-state conditions. In the absence of soot (dotted lines), the amounts of stored NO$_x$ decrease with the NO inlet concentration. A NO$_x$ storage capacity near 0.59 mmol/g$_{cat}$ has been measured at steady state when 1000 ppm of NO are fed to the reactor (trace A), which decreases to 0.37 mmol/g$_{cat}$ for a NO inlet concentration value of 200 ppm (trace C). The NO$_2$ outlet concentration at steady-state also decreases upon decreasing the inlet NO concentration. The lower NO$_x$ storage capacity which is observed upon decreasing the NO inlet concentration is likely related to lower concentration of NO$_2$ produced, as already discussed in the case of the effect of temperature. In fact, in line with the hypothesis of thermodynamic control of the NO$_x$ storage at steady state, the amounts of stored NO$_x$ are related to the NO$_2$ concentration. Also, the increase of the NO inlet concentration (and of NO$_2$ concentration as well) increases the rate of the NO$_x$ adsorption, as revealed by the slopes of the adsorption curves of Figure 4 (dotted lines) in the region where the storage is not limited by the supply of NO.

Finally, upon NO and O$_2$ shutoff a tail in the NO$_x$ concentration is observed, as already discussed in the case of the effect of temperature, indicating the decomposition of weakly adsorbed NO$_x$ species. The amounts of NO$_x$ desorbed after the NO shutoff (Table 2) decreases with the NO inlet
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concentration (6 and 3 µmol/g_cat for NO = 1000 and 250 ppm, respectively), but are very similar if normalized to the amounts of NOₓ initially stored (near 8-10%).

The presence of soot influences the storage of NOₓ as revealed by the comparison of the adsorption curves obtained in the absence and in the presence of soot (Figure 4, dotted lines vs. solid lines). In the presence of soot the amounts of adsorbed NOₓ decreases upon decreasing the NO inlet concentration, from 0.39 down to 0.27 mmol NOₓ/g_cat, and these amounts are always lower than those observed with the soot-free catalyst. The presence of soot also decreases the NO₂ concentration measured at steady-state at the exit of the reactor, if compared to the soot-free catalyst (data not shown). Accordingly in the presence of soot higher NO/NO₂ ratios are calculated at any investigated NO inlet concentration value. As previously discussed, this is related to the involvement of NO₂ in soot combustion according to reactions (2) and (4a-b). Along to the lines previously discussed, the decrease in the NOₓ storage capacity of the catalyst at steady state in the presence of soot is likely explained by the lower NO₂ concentrations obtained in these cases.

The rate of NOₓ adsorption also decreases upon decreasing the NO inlet concentration and upon addition of soot (compare the slopes of the adsorption curves at various NO inlet concentrations, and in the presence/absence of soot at fixed stored NOₓ, respectively). Again, this is likely associated to the effect of the NO₂ concentration on the rate of NOₓ adsorption.

Finally, also from these experiments it is clear that soot has a significant influence on the stability of the adsorbed NOₓ. In fact near 25-30 % of the NOₓ stored up to steady-state are desorbed in this case after NO shutoff (Table 2). These amounts are roughly 3 times higher than those calculated in the absence of soot.

<table>
<thead>
<tr>
<th>NO inlet concentration ppm</th>
<th>without soot</th>
<th>with soot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stored NOₓ</td>
<td>Desorbed NOₓ after NO shutoff</td>
</tr>
<tr>
<td></td>
<td>mmol/g_cat</td>
<td>mmol/g_cat</td>
</tr>
<tr>
<td>250</td>
<td>0.37</td>
<td>0.03</td>
</tr>
<tr>
<td>500</td>
<td>0.50</td>
<td>0.04</td>
</tr>
<tr>
<td>1000</td>
<td>0.59</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 2. Stored NOₙ, desorbed NOₓ (1300s after NOₓ shutoff) and percentage of desorbed NOₓ / stored NOₓ ratio at different NO inlet concentration, in the absence and in the presence of soot.
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*Regeneration phase* – The reduction of the NOₓ stored at 350°C by using different NO inlet concentration has been investigated as well. The results, here not shown for the sake of brevity, were in all cases very similar to those obtained in the case of Figure 1B (adsorption with NO = 1000 ppm at 350°C, absence of soot) and Figure 2B (adsorption with NO = 1000 ppm at 350°C, presence of soot). The results obtained in the absence and in the presence of soot point out that the presence of soot does not influence significantly the reduction of the stored NOₓ.

### 3.3 Interaction of the stored NOₓ with soot.

The results reported above pointed out that the presence of soot influences the storage of NOₓ over PtBa/Al₂O₃. In fact soot i) decreases the NOₓ storage capacity of the catalyst, and ii) favors the decomposition of the stored NOₓ species. These conclusions apply when NOₓ are stored at different temperatures and when different values of the NO inlet concentration are used. On the other hand, the reduction of the stored NOₓ (i.e. catalyst regeneration) is not significantly influenced by the presence of soot, if one neglect a small increase in the N₂ selectivity. During NOₓ storage, combustion of soot also takes place if the temperature is high enough, i.e. at 300°C and above. Evidence has been provided in this case for a soot oxidation pathway involving NOₓ, formed upon NO oxidation, that is well recognized in the literature [16,22,31]. However, the participation of adsorbed NOₓ species in the combustion of soot cannot be ruled out, as also suggested in previous papers [23]. In order to better analyze these aspects, experiments have been carried out in which the interaction of soot with NOₓ adsorbed on the catalyst surface is investigated. For this purpose TPD experiments have been carried out in which the thermal stability and reactivity of NOₓ species stored over the PtBa/Al₂O₃ catalyst has been studied in the presence and in the absence of soot. As previously discussed, the amounts of NOₓ that are stored at steady state on the catalyst in the presence and in the absence of soot are different. Accordingly, in order to compare catalyst samples with the same amounts of stored NOₓ, the NOₓ have been accumulated in the absence of soot in one batch of catalyst and then the sample has been divided into two portions: one has been mixed with soot prior the TPD experiment, while the second (not mixed with soot) has been used as a reference (see experimental). NOₓ have been stored by contacting the catalyst with NO/O₂ at 350°C up to steady-state; as indicated in previous studies only nitrates are formed in this case on the catalyst surface [13,35].

The results of the TPD runs (carried out in the presence of water and CO₂) are shown in Figure 5A (absence of soot) and 5B (presence of soot). In the case of the soot-free Pt-Ba/γ-Al₂O₃ catalyst (Figure 5A), decomposition of nitrates is observed starting from 260°C with the evolution of small
amounts of NO. Above 350°C (the adsorption temperature) the NO concentration rapidly increases and a maximum is observed at 500°C, i.e. corresponding to the end of the heating ramp. Accordingly this is not a genuine TPD peak but it is determined by the maximum temperature during the heating ramp. The catalyst has been kept at this temperature until complete evolution of the products.

Figure 5 - TPD run after NO adsorption at 350°C (lean phase 1000 ppm NO + O₂ (3% v/v) in He + H₂O (1% v/v) + CO₂ (0.1% v/v)) over (A) Pt-Ba/Al₂O₃ catalyst; (B) Pt-Ba/Al₂O₃ / soot mixture

Above 350°C the NO evolution is accompanied by that of O₂ in similar amounts; minor quantities of NO₂ are also observed with peak maximum of 65 ppm at 470°C. After the TPD run, a reducing treatment has been carried out with a stream of H₂ (0.4%v/v in He + 1%v/v H₂O+ 0.1% v/v CO₂) at 350°C to reduce the residual nitrates, if any. No reaction products have been detected, thus indicating that all the adsorbed nitrate species have been decomposed during the TPD run.

The overall amounts of NO, O₂ and NO₂ evolved, estimated by integration of the TPD peaks, are well in line with the stoichiometry of the following reactions:

\[
\text{Ba(NO}_3\text{)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NO} + \frac{3}{2} \text{O}_2 \quad (7)
\]

\[
\text{Ba(NO}_3\text{)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NO}_2 + \frac{1}{2} \text{O}_2 \quad (8)
\]

with reaction (7) prevailing over reaction (8). Besides, in line with the stoichiometry of reactions (7) and (8), an uptake of CO₂ is also observed in correspondence with nitrate decomposition, due to Ba-carbonates formation at the expense of nitrates. Worth to note that the presence of CO₂ (1000 ppm)
in the flowing gases does not appreciably affects the decomposition of the surface nitrates, as pointed out by dedicated TPD experiments carried out in the presence and in the absence of CO₂. This is in line with the lower acidity of CO₂ if compared to NOₓ towards adsorption onto the Ba sites.

The results of the TPD experiment of Figure 5A are very similar to those previously obtained over a similar catalyst sample, and reported elsewhere [23]. However, as opposite to the previous results, in this case a small NO evolution is observed below 350°C, i.e. below the temperature of NOₓ adsorption. This is likely related to the different procedure used in this case, which involves the exposure of the nitrated catalyst to air for several hours before the TPD run, leading to water/CO₂ adsorption from the atmosphere. This may have affected the stability of the stored nitrates: in fact in several TPD runs carried out with no exposure of the catalyst to the atmosphere after NOₓ adsorption, the nitrate decomposition onset was always observed very close to the temperature of adsorption. The reasons for which the thermal stability of nitrates is affected by exposure to the atmosphere are not well understood so far, although it has already been shown elsewhere that the features of the stored NOₓ are affected by surface hydration already at room temperature [36].

Figure 5B shows the results of the TPD experiments carried out after mixing the catalyst with soot. A comparison with Figure 5A clearly shows that the presence of soot favors the decomposition/reduction of the stored nitrates. Indeed in this case a significant release of NO and O₂ is observed in the temperature range 260°C-350°C, i.e. below the adsorption temperature of 350°C. The decomposition of nitrates is then completed above 350°C, with a peak maximum near 485°C. Notably, a different product distribution is observed in the presence of soot, since the amounts of oxygen are markedly lower if compared to that of NO; besides, no NO₂ evolution is observed. Finally, no significant CO₂ uptake is observed.

The data shown in Figure 5 clearly indicate that the presence of soot favors the reduction of the stored nitrates, while soot is being oxidized. In fact in the presence of soot the NO evolution is shifted to lower temperatures: based on the amounts of evolved NO it appears that roughly 20 % of the initially adsorbed nitrates have been decomposed below 350°C (i.e. the temperature of adsorption) in the presence of soot, while only 7 % in the case of the soot-free sample (Figure 5A). Besides, the NO peak maximum is observed at lower temperatures, i.e. near 485°C vs. above 500°C. The oxidation of soot upon nitrate decomposition leads to BaCO₃ which accordingly prevents the uptake of CO₂ from the gas phase (reactions (7) and (8)).
Effect of soot on the storage-reduction performances of LNT PtBa/Al₂O₃ catalyst

The effect of soot on the stability of the stored nitrates has also been pointed out by the ISC experiments discussed above (Figures 1 and 2) showing that the amounts of NOₓ released during the He purge, after the NO dose, are significantly higher in the presence of soot. These results imply a direct reaction between the stored nitrates and soot, which can be likely explained upon invoking a certain degree of mobility of the surface nitrates. In fact it has been suggested that nitrates, adsorbed on the Ba component of the catalyst, are rather mobile in the presence of a reducing center. Hence it may be argued that the soot particles may behave as reducing centers towards nitrates thus activating their surface mobility. When nitrates contact a soot particle carbon is oxidized according to the following reaction:

$$C + 2 \text{NO}_3^- \rightarrow \text{CO}_3^2^- + 2 \text{NO} + \frac{1}{2} \text{O}_2 \quad (9)$$

which results in the formation of NO and O₂, as indeed observed during the TPD experiment carried out in the presence of soot, and of carbonates species whose formation accounts for the lack of a significant CO₂ net uptake from the gas phase in the TPD experiment with the catalyst/soot mixture.

Reaction (9) obviously also implies a partial reduction of the stored nitrates. As a matter of fact, TPD data provide clear evidence for the occurrence of reduction of nitrates by soot (reaction (9)). In fact, below 350°C of the TPD run of Figure 5B (i.e. before the onset of nitrate thermal decomposition) the concentration of the evolved products obeys the stoichiometry of reaction (9), and the O/N atomic ratio in the evolved products is very close to the stoichiometric value. Besides no uptake of CO₂ is observed below 350°C (as expected from the occurrence of reactions (7) or (8)), due to CO₂ formation upon soot oxidation (reaction (9)).

Above 350°C, nitrate thermal decomposition also occurs, and hence the stoichiometry of reaction (9) is no longer respected. In fact above 350°C the evolved NOₓ species give to a O/N ratio in the product higher that that expected from the stoichiometry of reaction (9). As a matter of fact, the calculated oxygen/nitrogen atomic ratio of the gaseous products evolved during the entire TPD in the presence of soot (Figure 5B) is O/N = 1.7, which is lower than the stoichiometric O/N value of 2.5 of the nitrate decomposition (reactions (7) or (8)). This value is indeed calculated from the TPD of the stored nitrates without soot (Figure 5A, O/N = 2.6).

Accordingly TPD data indicates that adsorbed nitrates are able to oxidize soot below the temperature of their thermal decomposition, following the stoichiometry of reaction (9) which implies the direct reaction of the nitrates ad-species with soot. This pathway parallels the oxidation
of soot by NO\textsubscript{2} that occurs in the presence of gas-phase NO\textsubscript{2}, i.e. upon the NO\textsubscript{x} storage during lean/rich operation of the NSR catalyst.

The suggested mechanism implying the direct interaction between nitrate adspecies and soot has analogies with the pathway proposed for nitrate reduction during lean/rich operation of NSR catalysts. Indeed in that case it has been suggested that nitrates spill over the surface towards the Pt sites where they are reduced by the reductant \[^{38, 39}\], the driving force for this process being the presence of a reduced Pt site. Along similar lines, the presence of soot (a reductant) is believed to be the driving force for the mobility of the nitrates which may eventually oxidize soot according to the stoichiometry of reaction (9). Notably, in the suggested mechanistic proposals concerning the nitrate-soot interaction, the role of Pt (and of Pt-Ba couples) has not yet been clarified, and work is presently in progress in our labs to elucidate such aspects.

4. Concluding remarks

The present study pointed out that the presence of soot influences the NO\textsubscript{x} storage properties of the investigated PtBa/Al\textsubscript{2}O\textsubscript{3} catalyst, when estimated in the presence of water and CO\textsubscript{2}. In fact soot leads to an appreciable decrease both of the NO\textsubscript{x} storage capacity and of the rate of NO\textsubscript{x} adsorption. This effect is seen at different temperatures and when different values of the NO inlet concentration are used in the experiments. During NO\textsubscript{x} storage, soot oxidation also occurs at 300°C and above, thanks to the presence of NO\textsubscript{2} formed upon NO oxidation over Pt sites. In fact the NO\textsubscript{2} concentration at the reactor outlet in the presence of soot is significantly lower than that observed in the absence of soot, thus pointing out the involvement of NO\textsubscript{2} in soot oxidation. The decrease of the NO\textsubscript{2} concentration may likely explain also the observed decline in the NO\textsubscript{x} storage properties of the catalyst. In fact, in line with the occurrence of a “nitrate” pathway for the storage of NO\textsubscript{x} (i.e., NO oxidation to NO\textsubscript{2} followed by NO\textsubscript{2} adsorption in the form of nitrates via a disproportion reaction), Ba and soot compete for reaction with NO\textsubscript{2}, as suggested by Sullivan et al. \[^{23}\], leading to the observed decrease in the NO\textsubscript{x} storage properties. On the other hand, the reduction of the stored NO\textsubscript{x} is not significantly affected by the presence of soot, although some minor changes in the N\textsubscript{2} selectivity (a slight increase in the presence of soot) have been observed. These aspects deserve however further investigation.

Finally, it is worth of note that the adsorbed NO\textsubscript{x} oxidize soot at temperature well below those corresponding to their thermal decomposition originating NO\textsubscript{2} in the gas phase. This has been shown by TPD experiments in which the reactivity / thermal decomposition of nitrates has been
investigated in the presence and in the absence of soot. It has been found that the presence of soot favors the decomposition and the reduction of the stored nitrates, while soot is oxidized. In fact the presence of soot shifts the decomposition/reaction of the stored nitrates at lower temperatures, and the stoichiometry of the released products reflects the occurrence of a partial reduction of the initially stored NOx, as well as the oxidation of soot. Hence a direct reaction between the stored nitrates and soot has been suggested, that has been explained on the basis of the surface mobility of the adsorbed nitrates. This soot oxidation pathway involves surface species and parallels the NO2-soot oxidation that occurs in the presence of gas-phase NO2.

Acknowledgements

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References

Effect of soot on the storage-reduction performances of LNT PtBa/Al₂O₃ catalyst

Paper III

Interaction between soot and stored NOx during operation of LNT Pt–Ba/Al₂O₃ catalysts

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Abstract
The interaction of soot with nitrates stored on a model PtBa/Al₂O₃ LNT catalyst sample is here investigated under realistic conditions, i.e. upon lean/rich cycling in the presence of water and CO₂. The presence of soot inhibits the NOₓ storage capacity of the catalyst during the lean phase at different temperatures, in the range 200-350 °C, but does not affect significantly the regeneration process of the stored nitrates. Simultaneously with the NOₓ storage, soot is converted to CO₂ at temperatures above 300 °C. Soot is oxidized by NO₂ formed by NO oxidation on Pt sites, but the participation of the stored nitrates in the soot oxidation is also likely, as pointed out by TPD/TPO experiments showing the occurrence of a surface reaction involving soot and the stored nitrates.

Keywords
Soot oxidation, DPNR catalysts, simultaneous NOₓ and soot removal, Diesel Particulate NOₓ Reduction, NSR catalysts
1. Introduction

The reduction of both soot (particulate matter) and NOx emissions from diesel-equipped vehicles is nowadays mandatory to cope with the next coming emission standards [1]. The soot removal relies on the use of diesel particulate filters (DPFs) [2], that must be periodically regenerated to remove the entrapped soot avoiding excessive pressure drops at the exhaust. For this reason the filter may be catalyzed to promote soot combustion at lower temperatures.

Concerning NOx, either Selective Catalytic Reduction (SCR) [3,4] or Nitrogen Storage Reduction (NSR), also quoted as Lean NOx Trap (LNT) [5,6], represent the top contenders for reducing NOx concentrations in the exhausts from diesel and lean burn gasoline engines [1]. While the SCR technique is based on the reaction between injected NH3 and NO present in the flue gases on metal-substituted zeolites [1] or vanadia-tungsta-titania catalysts [8], NSR catalysts make no use of any external reductant. These catalysts operate the NOx reduction under cyclic conditions by alternating long lean phases during which NOx emitted in the exhaust gases are adsorbed on the catalyst, with subsequent short rich periods in which the stored NOx are reduced by H2, CO and Hydrocarbons (HC) present in the flue gases to produce nitrogen [5,6]. LNT catalysts are generally made by a high surface area support (such as γ-Al2O3), alkaline/alkaline-earth metal oxides (such as K2O and BaO) and precious metals like Pt, Rh, Pd; other components are also present in fully formulated catalysts (e.g. CeO2). Hybrid NSR + SCR configurations have also been proposed, since they guarantee higher NOx removal efficiencies [3,9-14].

Exhaust after-treatment systems able to cope with the next coming strict emission standards are rather complex. De-soot and De-NOx devices are used, along with a Diesel Oxidation Catalyst (DOC) as well. However the optimal design of the aftertreatment exhaust system is still a matter of debate: the DOC is generally placed upstream the DPF and SCR/LNT converters, while different solutions have been proposed for the DPF and the DeNOx catalyst. Integrated (or one-pot) solutions have been proposed, like Catalyzed Diesel Particulate Filters (CDPFs) which act as DOC but also remove soot, or the DPNR (Diesel Particulate-NOx Reduction) technology which has been recently proposed by the Toyota group [15,16]. The DPNR technique has the unique capacity to remove simultaneously soot and NOx, and is based on the use of a catalyzed filter on which a NSR catalyst is deposited. In this way soot is removed by the filter while NOx are reduced according to the NSR technology [15].

Despite DPNR systems are used at a commercial scale, still many aspects concerning their catalytic performances, the operating reaction mechanisms and the interactions between the De-soot and De-NOx functions are still under debate. This has motivated in recent years a number of studies concerning the reactivity of NSR catalysts in the presence of soot [17-20]. In previous works from our
group the behavior of model PtBa/Al₂O₃ and PtK/Al₂O₃ LNT catalysts in the simultaneous removal of soot and NOₓ has been investigated. It has been shown that during the lean phase NOₓ are being stored on the catalyst surface, while soot oxidation occurs involving primarily NO₂, formed upon NO oxidation [21,22]. However more recent studies have shown that NOₓ species, stored onto the trapping component of the catalyst, may participate in the combustion of soot by releasing gaseous NOₓ upon decomposition and/or by directly reacting with soot according to a surface reaction [23-26]. Besides, it has been shown that the presence of soot depresses the NOₓ storage capacity of the catalyst, in line with data obtained by Pieta et al. [27].

Along similar lines, Kustov et al. [28] showed that the stored nitrates may decrease the temperature of soot oxidation when nitrate decomposition occurs in a proper temperature range, due to the release of NOₓ in the gas phase. More recently studies carried out by Sanchez et al. [29, 30] on K/La₂O₃-based catalysts indicated that the reaction between soot and trapped NOₓ can proceed before the decomposition of nitrates.

Aim of the present work is to provide additional insights on the effects of the presence of soot on the catalytic behavior of a model PtBa/Al₂O₃ LNT catalyst, and in particular to gain further insight on the interaction between soot and the stored NOₓ on the de-soot and DeNOₓ activity of the catalyst. For this purpose, NOₓ storage/reduction experiments have been performed over the selected catalyst sample by alternating lean/rich cycles both in the presence and in the absence of soot. At variance with previous studies [21-23,25,26], in this study the absorption and reduction of the NOₓ has been investigated by alternating short lean and rich phases with no inert purge in between, thus providing results closer to the transient conditions adopted under real applications.

The interaction between soot and the stored NOₓ species has been further investigated by Temperature Programmed Methods under inert flow (TPD) and in the presence of oxygen (TPO) in which the stability/reactivity of the stored NOₓ species has been analyzed both in the presence and in the absence of soot. The experiments have also been carried out over a platinum-free catalyst in order to assess the role of Pt in the stability/reactivity of adsorbed nitrates as well.

2. Materials and methods

A model PtBa/Al₂O₃ (1/20/100 w/w) catalyst was used in this study. The sample was prepared by incipient wetness impregnation with dinitro-diammine platinum (Strem Chemicals, 5%) and then with barium acetate of an Al₂O₃ support, obtained by calcination at 700 °C of a commercial alumina (Versal 250 from UOP). After each impregnation steps, the powders was dried overnight in air at 80 °C and calcined at 500 °C for 5 h. The selected impregnation order (first Pt and then Ba) has been
adopted in order to ensure a good dispersion and stability of the noble metal on the alumina support, in line with the recipes of Toyota patents [31]. A Pt-free sample (Ba/Al₂O₃, 20/100 w/w) was also prepared by impregnation of alumina with an aqueous solution of barium acetate (Sigma Aldrich, 99%), followed by drying overnight in air at 80 °C and calcination at 500 °C for 5 h. Finally, for comparison purposes, a sample was also prepared in which a Ba(NO₃)₂ solution was directly impregnated over the calcined alumina support (Ba/Al₂O₃ ratio: 20/100 w/w). After impregnation, the sample was dried at 80°C overnight. In the following, this sample will be referred as Ba(NO₃)₂/Al₂O₃.

Surface area and pore size distribution of the prepared catalyst samples were determined by N₂ adsorption–desorption with the BET method using a Micromeritics TriStar 3000 instrument. The specific surface area of the ternary PtBa/Al₂O₃ sample is near 160 m²/g⁻¹; a lower surface area value was determined for the Ba/Al₂O₃ sample (105 m²/g⁻¹). The surface area contraction is accompanied by a slight reduction of the pore volume, from 0.80 cm³/g for the PtBa/Al₂O₃ catalyst down to 0.63 cm³/g for the binary Ba/Al₂O₃ sample. The Pt dispersion of the PtBa/Al₂O₃ sample was also estimated by hydrogen chemisorption at 0°C (TPD/R/O 1100 Thermo Fischer Instrument). The measured Pt dispersion value was near 60%.

The Ba/Al₂O₃ and PtBa/Al₂O₃ catalysts were characterized by XRD analysis (Brüker D8 Advanced Instrument equipped with graphite monochromator on the diffracted beam). The XRD patterns showed both the monoclinic (JCPDS 78-2057) and orthorhombic (Whiterite, JCPDS 5-378) polymorphic forms of BaCO₃, in addition to microcrystalline g-Al₂O₃ (JCPDS 10-425). Printex-U (Degussa) was used as model soot, whose properties are well addressed in literature [32]. Catalyst-soot mixtures were prepared by gently mixing in a vial the catalyst powder (74-105 µm) with the soot, thus realizing a loose contact which is representative of the soot/catalyst contact mode occurring in the DPNR system where soot is entrapped in the filter pores [15]. A soot loading (wₓ/ş) near 11 % has been typically employed. A sample with an intimate catalyst/soot interaction was also prepared by direct impregnation of the soot powder with aqueous solutions of Ba nitrate (“full contact” sample, [33]). After impregnation, the sample was dried overnight at 100 °C. In the following, this sample will be referred to as Ba(NO₃)₂/soot.

The reactivity experiments were performed in a flow micro-reactor system, consisting of a quartz tube (7 mm i.d.) equipped with a mass spectrometer (Omnistar 200, Pfeiffer Vacuum), a micro GC (Agilent 3000A) and an UV analyzer (Limas 11HW, ABB) for the on-line analysis of the reaction products. In each run 60 mg of catalyst have been used and the total flow rate was set at 100 cm³/min (at 0 °C and 1 atm). The catalytic De-NOₓ and De-soot activity was investigated by
performing lean-rich cycles at constant temperature alternating rectangular step feeds of NO (1000 ppm v/v) + 3% v/v of O₂ (lean phase) with feeds of H₂ (4000 ppm v/v, rich phase). The abrupt switches between the adsorption and the regeneration phase have been realized with the use of four-port valves. Experiments were performed in presence of 1% v/v H₂O and 0.1% v/v CO₂ at different temperatures, in the range 200 – 350 °C and with different NO inlet concentrations (500, 1000 ppm).

In order to analyse the interaction between soot and the stored NOₓ, TPD and TPO experiments were also performed over PtBa/Al₂O₃ and Ba/Al₂O₃ catalysts. Accordingly NOₓ have been stored onto the catalytic surface in the absence of soot at 350°C with NO or NO₂ (1000 ppm v/v) in He + O₂ (3% v/v) + H₂O (1% v/v) + CO₂ (0.1% v/v); then the catalyst has been cooled at room temperature in He, extracted from the reactor and mixed with soot (11 % w/w). TPD and TPO experiments have been carried by heating the so-prepared catalyst-soot mixture at a rate of 10°C/min in He + H₂O (1% v/v) + CO₂ (0.1% v/v) in the absence and in the presence of 3% v/v O₂, respectively, from room temperature to 500°C. The results collected with the catalyst/soot mixture have been compared with those obtained in analogous experiments performed in the absence of soot. TPD experiments have also been performed over Ba(NO₃)₂/Al₂O₃ (with and without soot) and over the “full contact” Ba(NO₃)₂/soot system.

3. Results and discussion

3.1 NOₓ storage/reduction cycles in the presence of soot

In order to study the effect of soot on the catalyst activity in the NOₓ adsorption and reduction, lean-rich cycles have been performed in the presence of soot over the model PtBa/Al₂O₃ NSR sample. Figure 1 shows a typical result, in term of NO, NO₂, CO₂, H₂ and N₂ outlet concentration vs. time, of a sequence of four lean-rich phases at 350 °C. For the sake of clarity, in the insert of the Figure an enlargement of the first cycle of the sequence can be seen, showing the concentrations of NO, NO₂, NOₓ (= NO + NO₂), CO₂, H₂, N₂ and ammonia. Upon NO and O₂ admission (at t = 0 s, insert of Figure 1) the NO outlet concentrations shows a delay of 100 s, and then increases to a steady level near 930 ppm. Also NO₂ formation is observed (with a time delay of 170 s), due to the occurrence of the oxidation of NO by O₂ at Pt sites according to the stoichiometry of reaction (1):

\[
\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2
\]

The outlet concentrations of both NO and NO₂ increase with time and eventually reach a steady state level, indicating that the maximum NOₓ storage capacity of the sample has been reached. The
area included between the NO inlet and NO\textsubscript{x} outlet concentration traces is proportional to the amount of NO\textsubscript{x} that have been stored onto the catalyst surface (4.04 x 10\textsuperscript{-4} mol/g\textsubscript{cat}).

Upon NO admission, the evolution of CO\textsubscript{2} is also observed. In fact the CO\textsubscript{2} concentration rapidly increases from its background level (1000 ppm) showing a maximum of 1800 ppm and then decreases approaching the constant value of 1450 ppm near the end of the pulse. As already reported elsewhere [21,25,26], the increase in the CO\textsubscript{2} outlet concentration results from two factors. One is related to the formation of Ba nitrates at the expenses of Ba-carbonates upon NO\textsubscript{x} adsorption, as described by the stoichiometry of reaction (2):

\[
\text{BaCO}_3 + 2 \text{NO} + 3/2 \text{O}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2 \quad (2)
\]

In reaction (2), formation of nitrates only is suggested as NO\textsubscript{x} adsorbed species, in line with many studies showing that at this temperature only nitrates are formed upon NO/O\textsubscript{2} adsorption [34]. Reaction (2) is responsible for the initial CO\textsubscript{2} peak; then the CO\textsubscript{2} concentration remains above its background level due to soot combustion. As a matter of fact, by subtracting from the CO\textsubscript{2} concentration trace the amounts of CO\textsubscript{2} resulting from the NO\textsubscript{x} uptake and calculated according to the stoichiometry of reaction (2), a net CO\textsubscript{2} concentration trace is obtained (see the insert) which refers uniquely to soot combustion. At the end of the lean phase, the rate of CO\textsubscript{2} formation due to soot combustion is near 3.35 x 10\textsuperscript{8} mol/s; roughly 13\% of the initial soot loading (11 % w/w) is consumed during the first lean/rich sequence. Since no appreciable CO\textsubscript{2} formation is seen before the
Interaction between soot and stored NOx during operation of LNT Pt–Ba/Al₂O₃ catalysts

lean-rich cycles, i.e. in the presence of O₂ only, NOₓ (either adsorbed or in the gas phase) are involved at the temperature of 350°C in the oxidation of soot, possibly according to the stoichiometry of reactions (3) and (4):

\[ \text{NO}_2 + \text{C} \rightarrow \text{NO} + \text{CO} \quad \text{(3)} \]
\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad \text{(4)} \]

Here, NO₂ formed upon NO oxidation at Pt sites oxidizes soot with formation of CO (and possibly of CO₂); CO is then oxidized to CO₂ by O₂ at Pt sites and/or by NO₂. As a matter of facts, studies on the non-catalytic oxidation of soot by NO₂/O₂ mixtures carried out elsewhere pointed out a relevant formation of CO upon soot combustion by NO₂ in line with literature indications [35]; this indicates that Pt is involved in the CO oxidation since no appreciable CO evolution is observed at the reactor outlet. The involvement of NOₓ (and more specifically of NO₂) in the oxidation of soot is also pointed out by the fact that when the NOₓ storage is carried out in the absence of soot, a higher NO₂ formation is observed (see below). This points out that NO₂ is involved in the removal of soot, although the participation of the stored nitrates cannot be ruled out, as will be discussed below.

At the end of the NOₓ adsorption (lean phase), the gas feed is switched to rich conditions to regenerate the catalyst surface from the stored NOₓ. Accordingly, 4000 ppm of H₂ have been fed to the reactor upon NO and oxygen shutoff. H₂ is completely consumed upon admission (see the insert of Figure 1) and a simultaneous N₂ evolution is observed at the reactor outlet. The N₂ concentration reaches a level of about 800 ppm, in line with the stoichiometry of reaction (5):

\[ \text{Ba(NO}_3)_2 + 5 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{N}_2 + 5 \text{H}_2\text{O} \quad \text{(5)} \]

The N₂ concentration keeps almost constant for several seconds; then it decreases and a peak of NH₃ is observed, according to the stoichiometry of reaction (6):

\[ \text{Ba(NO}_3)_2 + 8 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NH}_3 + 5 \text{H}_2\text{O} \quad \text{(6)} \]

In line with the stoichiometry of reactions (5) and (6), a decrease of the CO₂ inlet concentration is observed, due to the formation of Ba carbonates at the expenses of the stored nitrates. The N₂ selectivity of the regeneration process is high, being near 95 %. As detailed in previous studies [36-38], the observed sequence of reaction products has been explained on the basis of a two-step pathway involving at first the fast formation of ammonia upon reaction of nitrates with H₂ (reaction (6)), followed by the slower reaction of the so formed ammonia with the stored nitrates leading to the selective formation of N₂ (reaction (7)):

\[ 3 \text{Ba(NO}_3)_2 + 10 \text{NH}_3 \rightarrow 8 \text{N}_2 + 3 \text{BaO} + 15 \text{H}_2\text{O} \quad \text{(7)} \]

As discussed elsewhere [36-38], the observed temporal evolution of products during the reduction is due to the development of an H₂ front which travels along the reactor: NH₃ is initially formed in
correspondence with the $\text{H}_2$ front, and reacts with NO$_x$ stored downstream the front leading to N$_2$ evolution. Accordingly NH$_3$ evolution is observed at the reactor outlet after N$_2$ only when the nitrates are reduced and the $\text{H}_2$ front reaches the end of the catalyst bed.

The data described above clearly indicate that the catalyst system is able to simultaneously store/reduce NO$_x$ and oxidize soot. However, considering the whole sequence of the four NO$_x$ storage–reduction cycles (Figure 1), it appears that the behavior of the PtBa/Al$_2$O$_3$ catalyst is affected by the residual soot loading. In fact the NO$_x$ breakthrough progressively increases during the lean/rich sequence from $\sim$ 100 s to $\sim$ 140 s passing from the first to the fourth cycle, respectively, i.e. upon decreasing the soot loading. The increase in the dead time is accompanied by an increase of the amounts of NO$_x$ stored up to steady-state, from $4.04 \times 10^{-4}$ mol/g$_{\text{cat}}$ for the first cycle to $4.78 \times 10^{-4}$ mol/g$_{\text{cat}}$ for the fourth cycle (Figure 2).

Figure 2 also shows the amounts of soot which is oxidized during the lean phase as a function of the cycle number, estimated from the amounts of evolved CO$_2$. During the lean phase of the first cycle, roughly 13 % of the initial soot loading is oxidized, which reduces to 8 % during the fourth cycle. At the end of the sequence the residual soot loading is near 3.9 % w/w. In fact the CO$_2$ concentration measured at steady-state at the end of the lean phase decreases from 1450 ppm of the first cycle to 1250 ppm of the fourth cycle, indicating a progressive decrease of the rate of soot combustion. Of note, the NO$_2$ concentration is similar for all cycles during the whole experiment, as well as the NO/NO$_2$ ratio, although the progressive decrease of the soot combustion rate and the involvement of NO$_2$ in the oxidation of soot.
Figure 2. Amounts of stored NOx (mol/gcat) and of soot oxidized (% w/w) during lean-rich cycles at 350 °C over PtBa/Al2O3-soot mixture. Exp. conditions: see caption Fig. 1. These results are in line with our data discussed elsewhere [21] obtained during isothermal soot oxidation over PtBa/Al2O3 at 350 °C in presence of O2 and NO and showing that the NO2 concentration exhibits a remarkable increase only when the soot loading is very low (near 1 % w/w). Finally, considering the reduction phase, no significant changes both in the products formation and in their temporal evolution are observed during the cycles. N2 selectivity values near 95 % have been calculated in lean/rich cycles, thus indicating a negligible effect of soot on the regeneration of the stored NOx.

A comparison of the catalytic behavior of the PtBa/Al2O3 catalyst during a lean-rich cycle in the presence and in the absence of soot is shown in Figures 3 A and B, respectively (a concentration of 500 ppm of NO has been used during the lean phase). In the presence of soot (6.2 % w/w in the case shown in Figure 3 A) a shorter dead time for NOx breakthrough is observed during the lean phase (240 vs 280 s); the amounts of NOx stored at the end of the lean phase is also lower (3.8 x 10⁴ vs 4.9 x 10⁴ mol/gcat). Besides, a lower NO2/NO ratio is measured in the presence of soot due to the involvement of NO2 in the soot oxidation. On the other hand, no appreciable changes in the behavior of the sample during the rich phase are observed.

Fig. 3. Lean–rich cycles at 350 °C over PtBa/Al2O3 catalyst in the presence (A) and in the absence of soot (B). Lean phase: 500 ppm NO + O2 (3%, v/v) in He, CO2 (0.1%, v/v) and H2O (1%); rich phase: 4000 ppm H2 in He, CO2 (0.1%, v/v) and H2O (1%).

Soot is oxidized during the lean phase: as seen in figure 3 A, the steady state level of the CO2 concentration at the end of the lean phase is higher than the inlet value (1140 ppm vs. 1000 ppm), corresponding to a rate of soot oxidation of 1.04 x 10⁸ mol/s. This value is lower than that observed in the case of the run carried out with 1000 ppm NO during the lean phase likely due to the lower NO2 concentration observed with 500 ppm of NO in the feed [26].
In conclusions the results showed in Figures 1 - 3 point out that the presence of soot affects the NO\textsubscript{x} storage behavior of the investigated LNT system and in particular decreases the NO\textsubscript{x} storage capacity of the catalyst, in line with the results reported in our previous works [23,25,26] and by other authors as well [27]. On the other hand the presence of soot does not impact significantly the catalyst behavior during the rich phase.

In order to investigate more in details the effect of soot on the behavior of the model PtBa/Al\textsubscript{2}O\textsubscript{3} sample, lean-rich cycles have been performed at other temperatures, in the temperature range 200-350 °C, both in the absence and in the presence of soot. The results (here not reported for brevity) indicate that in the absence of soot the amounts of NO\textsubscript{x} stored during the lean phase decrease upon decreasing the temperature from 5.6 \times 10^{-4} \text{ mol/g\textsubscript{cat}} at 350 °C to 2.6 \times 10^{-4} \text{ mol/g\textsubscript{cat}} at 200 °C. The presence of soot has a negative impact on the NO\textsubscript{x} storage at all the investigated temperatures, in that it decreases the amounts of NO\textsubscript{x} stored during the lean phase. Soot is oxidized during the lean phase, but soot oxidation is appreciable only at 300 °C and above.

Concerning the rich phase, it is noted that in the absence of soot the N\textsubscript{2} selectivity of the reduction process increases with temperature, as already pointed out in other studies and in line with the two-steps mechanism for NO\textsubscript{x} reduction [36-38]. The presence of soot does not affect significantly the reduction process, as already observed at 350 °C (see above). These results parallels those obtained under different experimental conditions (lean and rich phases separated by an inert purge in between) and already reported elsewhere [26].

3.2 Soot reaction with adsorbed NO\textsubscript{x} species: TPD experiments

3.2.1 PtBa/Al\textsubscript{2}O\textsubscript{3} catalyst

To gain further insight into the effect of soot on the adsorbed NO\textsubscript{x} species (nitrates) and in particular on their stability/reactivity, TPD experiments of the stored nitrates in the presence and in the absence of soot have been carried out. Since soot affects the NO\textsubscript{x} storage on the PtBa/Al\textsubscript{2}O\textsubscript{3} system, NO\textsubscript{x} have been stored at 350°C in the absence of soot, and then the sample has been mixed with soot before the TPD runs (see the experimental section), thus realizing a loose contact between soot and the nitrated catalyst. A reference TPD run has also been carried without mixing with soot.

The results of the TPD runs carried out the absence and in the presence of soot (dashed and solid lines, respectively) are shown in Figure 4 in terms of NO, \textsubscript{x}O\textsubscript{2} and CO\textsubscript{2} concentrations.

In the absence of soot (dashed lines) the nitrate decomposition is observed above 350 °C (i.e. the adsorption temperature), although very small amounts of NO\textsubscript{x} are also seen at lower temperatures. Nitrate decomposition occurs with evolution mainly of NO (along with minor amounts of NO\textsubscript{2}) and of
O$_2$. These results perfectly match those already published elsewhere [26] and confirm that the thermal stability of stored NO$_x$ is ruled by their adsorption temperature. The nitrate decomposition is not completed at the end of the heating rate at 500 °C, but is completed during the subsequent hold at this temperature. It is noteworthy that the overall amounts of evolved NO, O$_2$ and NO$_2$, estimated by integration of the TPD peaks, are well in line with the stoichiometry of nitrates decomposition reactions (8) and (9):

$$\text{Ba(NO}_3\text{)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NO} + 3/2 \text{O}_2 \quad (8)$$

$$\text{Ba(NO}_3\text{)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2 \text{NO}_2 + 1/2 \text{O}_2 \quad (9)$$

In fact the measured O/N atomic ratio in the evolved products (i.e. (NO + 2 NO$_2$ + 2 O$_2$)/(NO + NO$_2$)) is 2.6, very close to the theoretical value of 2.5.

![Fig. 4. TPD after NOx adsorption at 350 °C over PtBa/Al$_2$O$_3$ in the absence (dashed lines) and in the presence of soot (solid lines).](image)

Finally, a decrease of the CO$_2$ concentration (contained in the feed stream with a level of 1000 ppm) is observed in correspondence with the nitrate decomposition, due to the re-adsorption of CO$_2$ on the Ba sites leading to the formation of Ba carbonates at the expenses of Ba nitrates (reactions (8) and (9)).

Solid lines in Figure 4 show the results of a TPD run performed in the presence of soot (i.e., after mixing the nitrated catalyst sample with soot). The decomposition of nitrates is shifted at lower temperatures if compared to the soot-free sample, in that a significant release of NO$_x$ is observed already in the temperature range 260 – 350°C. The nitrate decomposition is then completed at
higher temperatures, with NOx (only NO) and O2 peaking near 485 °C. Besides, no a net CO2 uptake is observed. It is suggested that in this case a surface reaction takes place involving nitrates and the soot particle:

\[ C + Ba(NO_3)_2 \rightarrow BaCO_3 + 2 \text{NO} + \frac{1}{2} \text{O}_2 \] (10)

which results in the release of NO and O2 and in the formation of carbonates whose formation accounts for the lack of a significant CO2 net uptake from the gas phase in the TPD experiment with the catalyst/soot mixture.

These results clearly indicate that the presence of soot decreases the thermal stability of the stored nitrates. Moreover, if compared to the soot-free sample, a different distribution of the evolved products is also observed: in fact the calculated O/N atomic ratio of the gaseous products evolved during the entire TPD in the presence of soot is near 1.7, well below the stoichiometric O/N value of 2.5 for the nitrate decomposition. This indicates that nitrates and/or their decomposition products oxidize soot to CO2, in line with the absence of a net CO2 uptake (reaction (10)).

Based on the above observation, it clearly appears that soot promotes the decomposition of the NOx adsorbed species, which is in fact observed at lower temperature if compared to the soot-free sample. This calls for the existence of a surface reaction involving the stored nitrates and the soot particles. As a matter of fact, studies on the reduction of the stored nitrates with several reductants suggested that nitrates are rather mobile on the surface [39,40], the driving force for the mobility of nitrates being the presence of reduced Pt sites (leading to nitrate decomposition/reduction). The role of the reductant in the process is to kept Pt in a reduced form. It is speculated that the soot particles, acting as reducing center for the NOx species, provide the driving force for the process leading to nitrate reduction/decomposition (and soot oxidation). A similar nitrate destabilizing effect has been attributed to Pt in PtBa/Al2O3 catalysts, in order to explain the decrease in the decomposition temperature of nitrates which is observed upon Pt addition to Ba/Al2O3 [41].

3.2.2 Ba/Al2O3 catalyst

**TPD runs over nitrated samples** - In order to check whether Pt has a role in the soot-nitrate surface reaction, TPD experiments have been carried out over the binary Ba/Al2O3 catalyst in the absence and in the presence of soot after NO2 adsorption at 350 °C. The obtained results are shown in Figure 5 A and B (absence and presence of soot, respectively) in terms of concentration traces of the various evolved products (NO, NO2, O2, CO2 and CO). In the case of the soot-free Ba/Al2O3 sample (Figure 5A), nitrates decompose above 350 °C (i.e. the adsorption temperature) with evolution mainly of NO2. Evolution of O2 is also observed while that of NO is very small. Worth to note that in spite of the long isothermal period at 500 °C, nitrate decomposition is not yet completed at the end
of the TPD run: in fact the NO$_2$ concentration shows a very long tail which extends for more than 4 h (not shown in the Figure). At the end of the run, only a portion of the stored nitrates have been decomposed.

![Figure 5](image)

Fig. 5. TPD after NOx adsorption at 350 °C over Ba/Al$_2$O$_3$ catalyst in the absence (A) and in the presence of soot (B).

The TPD profile obtained in the presence of soot (Figure 5B) is very different: the decomposition onset of the stored NO$_x$ is observed near 300°C, that is roughly 50 °C below that observed in the case of the soot-free sample, and is almost completed after the 4 h isothermal period at 500 °C. Also the distribution of the evolved products is different: in fact NO represents the major decomposition product and no significant amounts of NO$_2$ or O$_2$ are observed. Moreover, in correspondence with the NO evolution, a significant production of CO$_2$ is detected above the inlet value of 1000 ppm. Formation of significant amounts of CO (75 ppm) are also observed in this case, in line with other studies showing the formation of CO along with that of CO$_2$ during the non-catalytic soot oxidation by NO$_2$ [35].
These results indicate that the surface reaction between soot and the stored nitrates is not catalyzed by Pt: even in the absence of the noble metal, soot reacts with the NO$_x$ ad-species which in fact decompose at lower temperatures if compared to the soot-free sample. This is in line with previous suggestions indicating that the soot particles may provide the driving force for nitrate mobility and reduction/decomposition.

**Effect of the soot/nitrate contact** - To further investigate the interaction between soot and nitrates, and in particular the effect of the soot/nitrate contact, TPD experiments were performed with samples with a loose and a full contact between soot and the nitrates. In the first case (loose contact) nitrates were deposited over alumina by impregnation with an aqueous solution of Ba(NO$_3)_2$ (Ba(NO$_3)_2$/Al$_2$O$_3$ sample) followed by drying at 80 °C and gently mixing with soot; in the other case (full contact) the soot was directly impregnated with Ba(NO$_3)_2$ (Ba(NO$_3)_2$/soot sample). The obtained results are shown in Figures 6 and 7, where the heating ramp was ended at 800 °C.

![Fig. 6. TPD over Ba(NO3)2/Al2O3 catalyst in the absence (A) and in the presence of soot (B).](image)

In the case of the loose contact system, a reference TPD run was also carried without mixing the Ba(NO$_3)_2$/Al$_2$O$_3$ sample with soot (Figure 6 A). In this case the decomposition of the Ba nitrate species is apparent above 300 °C with the initial evolution of NO$_2$ (and O$_2$), showing a maximum near 500 °C. Then a decomposition peak centered near 600 °C is observed, accompanied by the evolution of NO, O$_2$ and NO$_2$. In correspondence with the nitrate decomposition a decrease of the CO$_2$
concentration is also observed, from the inlet value (1000 ppm) to a minimum of 200 ppm, due to readsorption for carbonates formation onto the catalytic surface. Complete decomposition of the NO₃ adsorbed species is achieved at temperatures slightly below 700 °C. This result is in line with the decomposition of nitrates formed upon NO₃ adsorption (Figure 5 A); however in the case of Figure 5 A only the first NO₂ peak could be observed, since the heating ramp of the TPD run was limited at 500 °C.

A different picture is apparent in the presence of soot (Figure 6B): the temperature onset for nitrate decomposition is observed near 230 °C, i.e. more than 70 °C below that of the soot-free system. The evolution of mainly NO is observed in this case, with much lower amounts of NO₂ and O₂. Besides, in correspondence with the NO evolution, a significant CO₂ production is observed, along with CO (maximum 260 ppm). These results resemble those obtained in the case of the sample obtained by NO₃ adsorption (Figure 5 B) and confirm the capability of nitrates to oxidize soot at temperature well below that of their decomposition (being reduced to NO).

Finally, worth to note that in the presence of soot (Figure 6B) the production of 300 ppm of H₂ is also evident at temperature above 700 °C, accompanied by the evolution of CO. This is due to the occurrence of the carbon gasification reaction (11):

\[
C + H₂O \rightarrow CO + H₂ \quad (11)
\]

due to the presence of water (1 % v/v) in the feed stream. CO₂ formation is also observed likely due to the occurrence of the water gas shift reaction (12):

\[
CO + H₂O \rightarrow CO₂ + H₂ \quad (12)
\]

The carbon gasification reaction is catalyzed by Ba, in line with the well known effect of alkaline/alkaline-earth oxides on this reaction [42,43]. In fact TPD experiments carried out over bare soot (here not shown) indicate that the carbon gasification reaction (11) takes place appreciably only at temperatures above 700 °C with very small production of CO and H₂.

The results of the TPD experiment carried out over the “full contact” sample is shown in Figure 7. When Ba(NO₃)₂ is directly deposited onto soot (i.e., when an intimate contact is provided between nitrates and the soot particle) significant changes in the TPD profile are observed with respect to the loose contact sample (compare Figure 7 and 6B). In fact in this case the temperature threshold for the nitrate decomposition significantly decreases with respect to that of the corresponding loose contact system (Figure 6B), being NO evolution observed at temperatures as low as 150 °C. Moreover complete nitrate decomposition is obtained near 550 °C (vs. 700 °C of Ba(NO₃)₂/Al₂O₃- soot system). The production of CO₂ in correspondence with NO evolution points out also in this case the soot oxidation by the nitrates. Finally also in this case at temperature above 700 °C the simultaneous
production of H$_2$, CO and CO$_2$ is observed due to the occurrence of reaction (11) and (12). Notably in this case a much higher soot gasification rate is measured: as matter of fact the maximum production of 3000 and 600 ppm is measured for H$_2$ and CO, respectively. The high H$_2$ and CO production is due to the catalytic effect of Ba (in close-contact with the soot) on the carbon gasification reaction.

Fig. 7. TPD over Ba(NO$_3$)$_2$/soot “full contact” system.

**Effect of the presence of oxygen** – Finally, the effect of the presence of oxygen on the nitrate-soot interaction has also been addressed. For this purpose TPO runs have been performed with the Ba(NO$_3$)$_2$/Al$_2$O$_3$ sample in the absence and in the presence of soot, and results are shown in Figures 8 A and 8 B, respectively. In the case of the soot-free sample (Figure 8 A), the results closely resemble those obtained during the TPD experiments (Figure 6 A), with nitrate decomposition apparent above 300 °C with the evolution of NO$_2$, NO and O$_2$, showing maxima near 500 °C and 600 °C, and the uptake of CO$_2$. These results show that the decomposition of the nitrates is not significantly affected by the presence of oxygen in the feed stream.

In the presence of soot (Figure 8 B), the temperature onset for nitrate decomposition is observed well below that of the soot-free system, like during the TPD experiment. Accordingly the soot-nitrate interaction is not significantly affected by the presence of oxygen. The evolution of NO is observed in this case, with much lower amounts of NO$_2$. Formation of CO$_2$ (and of CO as well) is also detected above 300 °C, with a maximum near 700 °C and a shoulder at 550 °C. The shoulder of the CO$_2$ concentration at 550 °C is associated with the soot oxidation by nitrates, whereas the maximum at 700 °C is due to soot oxidation by O$_2$ as confirmed by blank TPO experiments carried out in the absence of the catalyst (here not reported). Worth to note that a shoulder is observed at 550 °C in the O$_2$ concentration trace, corresponding to the maximum in the NO concentration and to the
shoulder in the CO₂ concentration traces. This suggests the participation of O₂ also during the soot oxidation by nitrates, in line with literature reports showing the participation of O₂ during the soot oxidation by NOₓ [44].

Fig. 8. TPO over Ba(NO₃)₂/Al₂O₃ catalysts in the absence (A) and in the presence of soot (B).

4. Conclusions

In the present study the interaction of soot with nitrates stored on a model PtBa/Al₂O₃ LNT catalyst sample has been investigated under realistic conditions, i.e. upon cycling under lean/rich conditions and in the presence of water and CO₂ in the feed stream. The results pointed out that the presence of soot decreases the NOₓ storage capacity of the catalyst during the lean phase. The inhibiting effect of soot on the NOₓ storage capacity increases with the soot amount, up to 11 % w/w (the maximum investigated soot loading), and is observed at different temperatures in the range 200-350 °C. However, the presence of soot does not affect significantly the catalyst behavior during the rich phase, i.e. during the regeneration of the stored nitrates.

Simultaneously with the NOₓ storage, at temperatures above 300 °C soot is oxidized to CO₂ during the lean phase. Soot oxidation occurs through the participation of NO₂ formed by NO oxidation on Pt sites; in fact the NO₂ concentration measured at the reactor outlet is significantly lower in the presence of soot than in its absence. However, in parallel with this NO₂-soot oxidation pathway, the
participation of the stored nitrates in the soot oxidation is also likely. This has been shown by TPD/TPO experiments carried out over both the model PtBa/Al₂O₃ and Ba/Al₂O₃ samples in which the reactivity / thermal decomposition of nitrates has been investigated in the presence and in the absence of soot. Clear indication on the occurrence of a surface reaction involving soot and the stored nitrates has been pointed out, leading to soot oxidation (and nitrate reduction). In fact the stored nitrates are able to oxidize soot at temperatures well below those corresponding to their decomposition in the absence of soot. This reaction possibly involves the surface mobility of the stored nitrates, soot particles being the driving force for the process and acting as reduced centers. This process does not require the presence of the noble metal (Pt) in that it occurs in the case of the Ba/Al₂O₃ catalyst sample as well; as expected, it is favored by the contact between the nitrates and soot. In fact when nitrates are stored onto the soot, the nitrate/soot reaction is monitored at lower temperatures.

**Acknowledgements**

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**References**

Paper III

Interaction between soot and stored NOx during operation of LNT Pt–Ba/Al2O3 catalysts

Paper IV

Diesel soot and NOx abatement on Pt-K/Al2O3 LNT catalyst: influence of temperature and ageing

R. Matarrese, N. Artioli, L. Castoldi, L. Lietti, E. Finocchio, P. Forzatti

In preparation
Abstract
Soot particles and nitrogen oxides are the main pollutants emitted by diesel engines. The Pt-K/Al₂O₃ catalyst is active for soot combustion and it is also able to work as lean NOₓ trap. In this work, the effect of the reaction temperature on the catalytic activity is addressed. Both, the soot combustion and the NOₓ storage are studied and a comparison with another LNT system Pt-Ba/Al₂O₃ is attempted.

Keywords
Soot oxidation, DPNR catalysts, simultaneous NOₓ and soot removal, Diesel Particulate NOₓ Reduction, LNT catalysts
1. Introduction
The main pollutants emitted by diesel engine exhausts are nitrogen oxides and soot particles. For this reason, the simultaneous abatement of NOx and particulates from diesel exhaust gas represents an outstanding issue. The current three-way technology used near stoichiometric conditions is unable to meet upcoming regulations in Europe, United States, and Japan. The existing technical solutions involving an exhaust gas recirculation to get an optimal NOx/particulates compromise by controlling the recirculated gas rate or modifying the distribution channel will likely be unable to fulfill the next Euro 6 standard regulation. The implementation of an optimal strategy is not an easy task because a reduction of NOx induces an increase in particulate emission and reversibly subsequent reduction of particulate matter will induce an increase in NOx emission. Consequently such a situation implies to reconsider the actual end-of-pipe technologies commercially available combining diesel particulate filter (DPF) and DeNOx catalysts [1].

Commercial NOx abatement technologies are actually available. They are essentially developed for heavy-duty vehicles such as the urea selective catalytic reduction (SCR). For the light vehicles a competition between SCR and NOx storage and reduction after-treatment systems exist. In this complex technological context, the development of integrated De-NOx and De-soot after-treatment technologies have also been proposed. One example is the Diesel Clean Advanced Technology (D-CAT) emission control system recently proposed by the Toyota group. Its Avensis model is equipped with the D-CAT package which includes the DPNR (Diesel PM and NOx Reduction) system, a combination of a diesel particulate filter with a NOx adsorber-catalyst [2]. The DPNR converter features a newly developed, highly porous ceramic filter coated with a catalyst exclusively developed by Toyota for its NOx storage reduction catalytic converter (NSR catalysts), initially designed for use with Toyota’s lean-burn (high-oxygen) gasoline engines [3]. The NSR catalysts are generally composed of precious and base metal supported catalysts such as Pt-Rh/Ba-Al2O3 and Pt-Rh/K-Al2O3 [4]. During longer lean period NO in the exhaust gas is oxidized to NO2 over Pt and NO2 is stored as nitrates over Ba and K. Under rich conditions the stored nitrates are released as NOx, which is further reduced to N2 by CO, H2 and HC over Pt/Rh. Various surface compounds such as nitrates and active oxygen generated during storage and reduction steps are proposed as active soot oxidation species and, thereby, decreasing the oxidation temperature. NO2 produced over noble metals of NSR catalysts can be trapped as nitrates and can also react with soot generating NO again [5]. Under lean conditions NSR system can be expected to function as catalyzed soot filter (CSF). It is also proposed that under rich conditions active oxygen generated on the catalyst can oxidize the trapped soot. DPNR or NSR catalysts in this respect will have obvious advantages as it can reduce emission of both the pollutants and acts as ‘4-way’ catalyst.

Only a few studies over ‘4-way’ catalytic materials that can store NOx, such as CeO2, Ba and K-containing catalysts, for soot oxidation are reported [5,6]. In our previous works [1,8], it has been shown that soot...
oxidation occurs during the lean phase only, while NO is being oxidized to NO₂ and nitrites/nitrates are being stored on the catalyst surface. NO₂ is an efficient and well recognized oxidizing agent for soot, but surface nitrates may have a role as well according to that proposed by Makkee et al. [9]. In particular, in [15] the reactivity of model Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ catalysts in the simultaneous removal of NOₓ and soot has been investigated under a variety of experimental conditions (NO concentration, temperature, and particulate loading).

In this paper similar experiments have been performed over Pt-K/Al₂O₃ catalyst under more realistic conditions (i.e. in the presence of CO₂ and H₂O) in the range 250-350°C, both in the absence and in the presence of soot, and a comparison with Pt-Ba/Al₂O₃ catalyst is presented.

It is well known that the high mobility of some K compounds improves the effective contact with soot and, consequently, K-promoted catalysts have good activity in the soot combustion. However, the high mobility causes K to present a technological problem associated with its interaction with the monolith support, and looses due to volatilization and/or stripping by condensed water. For this reason, in this paper attention has been paid to how the Pt-K/Al₂O₃ catalyst modify its catalytic activity during lean-rich cycles, studying the effect of soot on the NOₓ storage activity and in particular on the stability of the Pt-K/Al₂O₃ catalyst. ISC experiments and FT-IR analysis have been used in this case has complementary techniques.

2. Experimental

2.1. Catalysts preparation and characterization

A homemade Pt-K/Al₂O₃ (1/5.4/100 w/w/w) catalyst has been prepared by incipient wetness impregnation of a commercial alumina sample (Versal 250 from UOP) with aqueous solutions of dinitro-diammine platinum (Strem Chemicals, 5% Pt in ammonium hydroxide) and subsequently with a solution of potassium acetate (Aldrich, 99%). The powder has been dried at 80 °C and calcined in air at 500 °C for 5 h after each impregnation step. The impregnation order (first Pt and then K) has been selected in order to ensure a good dispersion and stability of the noble metal and of the alkaline component on the alumina support, in line with recipes of Toyota patents [3]. This sample has molar amount of K comparable to that contained in the Pt-Ba/Al₂O₃ (1/20/100 w/w/w) model catalyst previously used for similar studies (0.146 mol K or Ba/100 g of Al₂O₃) and reported here for comparisons [10]. The catalyst was characterized by XRD analysis (Brüker D8 Advanced Instrument equipped with graphite monochromator on the diffracted beam), surface area and pore size distribution by N₂ adsorption-desorption at 77K (Micromeritics TriStar 3000 instrument) and Pt dispersion by hydrogen pulse chemisorption at 0°C (TPD/R/O 1100 Thermo Fischer Instrument). The Pt-K/Al₂O₃ sample presents a surface area near 167 m²/g_cat and pore volume of 0.90 cm³/g_cat, while the Pt dispersion is close to 30%. Printex-U (Degussa) was used as model soot [9]. Catalyst-soot mixtures were
prepared by gently mixing in a vial the catalyst powder with soot (9:1 catalyst/soot ratio), thus realizing a loose contact.

Further details of catalyst preparation and characterization are reported elsewhere [11, 12].

2.2. Catalytic tests

All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7mm i.d.) connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum), a micro-GC (Agilent 3000A) and an UV analyzer (Limas 11HW, ABB) for the on-line analysis of the outlet gases (NO, NO₂, N₂, O₂, CO, CO₂, N₂O and NH₃). 66 mg of the soot-catalyst mixture (or 60 mg of bare catalyst) was used in each run. Prior catalytic activity runs, the catalyst sample has been conditioned by performing few storage/regeneration cycles. For this purpose, Isothermal Step Concentration (ISC) experiments have been performed at 350°C by imposing a rectangular step feed of NO (1000 ppm) + 3% v/v O₂ in flowing He + 1% H₂O + 0.1% CO₂ (lean phase) until catalyst saturation. Then the NO and O₂ concentrations have been stepwise decreased to zero, and a He purge at the same temperature (350°C) has been performed. This leads to the desorption of weakly adsorbed NOₓ species. After the He purge, catalyst regeneration (rich phase) has been carried out with H₂ (3500 ppm) in flowing He + 1% H₂O + 0.1% CO₂. Conditioning lasted until a reproducible behavior was obtained; this typically required 3-4 adsorption/reduction cycles.

After catalyst conditioning at 350°C, the catalytic activity of Pt-K/Al₂O₃ has been tested with typical ISC run in the range 250-350°C, both in the absence and in the presence of soot. A comparison with Pt-Ba/Al₂O₃ is addressed at 300°C.

Finally, the effect of soot on the stability of the Pt-K/Al₂O₃ catalyst has been studied. The fresh catalyst has been mixed with soot (9:1 w/w ratio) and ISC experiment has been performed at 350°C. During this first run (Run 1 in the Figures), soot has been progressively consumed. After the complete consumption of soot, the clean catalyst has been mixed again with soot (in the same ratio) (Run 2) and further lean-rich cycle at 350°C have been carried out until the complete oxidation of particulate. The soot mixing and the catalyst cycling have been replicated another time (Run 3).

3. Results and discussion

3.1. Effect of temperature on the NOₓ storage-reduction

The storage/reduction of NOₓ activity over Pt-K/Al₂O₃ catalyst in the absence of soot has been investigated in the 250-350°C temperature range. The NO, NO₂, NOₓ and CO₂ concentration profiles measured during the lean phase when 1000 ppm NO are fed to the reactor in the presence of O₂, H₂O and CO₂ are shown in Figure 1.
Diesel soot and NOx abatement on Pt-K/Al2O3 LNT catalyst: influence of temperature and ageing

Fig. 1 - Adsorption phase over Pt-K/Al2O3 catalyst in the absence of soot at different temperatures (A 250°C, B 300°C, C 320°C, D 350°C) with 1000 ppm NO + O2 (3% v/v) in He + H2O (1% v/v) + CO2 (0.1% v/v)

At the highest investigated temperature (350 °C, Fig. 1D), upon NO admission to the reactor (t = 0 s) a delay near 200s is observed in the NO detection at the reactor outlet. Then, the NO concentration increases with time and reaches the steady state value of 645ppm. NO2 breakthrough is observed with a delay of 50s respect to NO and increases until its asymptotic level of 375ppm. As well known, NO2 production is related to the NO oxidation on Pt sites (reaction 1):

\[
\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2
\]  

(1)

The amount of NOx stored at this temperature up to the stationary level is near 0.56 mmol/gcat, as apparent from Fig. 2A which shows the amounts of stored NOx as a function of time-on-stream. When the NO inlet concentration is switched off (2000 s), a tail is observed in the NOx concentration profile, due to the desorption of weakly adsorbed NOx species \(^{[13]}\). The net amount of stored NOx has been calculated by difference of the NOx adsorbed during NO feeding and the NOx desorbed and it is close to 0.42 mmol/gcat, that corresponds to a decrement of roughly 25% respect to the storage capacity (see Table 1).
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Upon NO admission, an increase in the CO₂ concentration is also observed. A peak is initially detected in correspondence to NOₓ breakthrough; then, the CO₂ concentration gradually decreases to its background level until NOₓ reach their stationary level. The increase in the CO₂ outlet concentration is due to the decomposition of surface carbonates upon NOₓ uptake according to the stoichiometry of the following reaction:

\[ K_2CO_3 + 2 \text{NO} + 3/2 \text{O}_2 \rightarrow 2 \text{KNO}_3 + \text{CO}_2 \] (2)

It is possible calculate the amount of CO₂ evolved due to carbonate decomposition considering the stoichiometry of reaction (2) and the amount of stored NOₓ. By subtracting from the CO₂ concentration trace this estimated CO₂ amount, a net CO₂ concentration trace is obtained \cite{14}. In Fig. 1D this curve closely resembles the inlet CO₂ concentration value (1000 ppm), indicating that the evolution of CO₂ is uniquely related to the formation of nitrates species at the expense of carbonates, according to the stoichiometry of reaction (2). After NO shutoff, a small CO₂ uptake is observed, due to the occurrence of the reverse of reaction (2).

ISC experiments have been performed in similar condition varying the reaction temperature in the range 250-350°C and the results are reported in Fig. 1A-C. As clearly appear from the Figures, the NOₓ storage behavior of the catalyst is affected by the temperature. In fact, the NOₓ breakthrough increases from 90 s at 250°C (Fig. 1A) to 180 s at 300°C (Fig. 1B) and 200 s at 320°C (Fig. 1C). Besides the amounts of NOₓ stored...
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up to steady state increase with temperature, from 0.52 mmol/gcat at 250°C to 0.62 mmol/gcat at 300°C (Fig. 2A and Table 1); above this temperature the amounts of stored NOx slightly decrease.

Finally, the NO2 concentration measured at the reactor outlet at the end of the NOx dose (i.e. at steady-state) increases with temperature. In fact under our experimental conditions NO2 formation is far from chemical equilibrium and the observed increase with temperature of the NO2 concentration is hence expected being the reaction kinetically controlled. Accordingly, the NO/NO2 molar ratio calculated at the end of the storage phase decreases with temperature from 9.8 at 250°C to 1.72 at 350°C.

Temperature also affects the rate of NOx adsorption, as expected. As shown by the slope of the adsorption curves in Fig. 2A, in the initial part the curves are almost superimposed since an almost complete NO uptake is initially observed at all temperatures (i.e. NOx uptake is initially limited by the NO feed). After 200s the adsorption curves slightly diverge and the steady-state loadings of the stored NOx are reached earlier upon increasing the temperature. A similar effect has been observed in the case of Pt-Ba/Al2O3 catalysts as well [14], since also for this catalyst the rate of adsorption increases with temperature. A direct comparison between the amounts of NOx stored at steady-state on the Pt-K/Al2O3 and Pt-Ba/Al2O3 catalyst samples is shown in Fig. 3.

![Fig. 3](image)

**Fig. 3 – Amounts of stored NOx versus time over Pt-K/Al2O3 and Pt-Ba/Al2O3 catalysts (A) in the absence of soot and (B) in the presence of soot**

It appears that the amounts of NOx stored on Pt-K/Al2O3 are higher than those on Ba-based catalyst, although at 350°C the storage capacity of the two catalysts is very similar. Finally, the amounts of NOx desorbed upon NO shutoff are higher over Pt-K/Al2O3 than over Pt-Ba/Al2O3 (see Table 1).

Table 1 resumes the quantitative analysis discussed above. In the Table are also reported the amounts of NOx desorbed in correspondence of NO shutoff. As may be seen, this contribute is more significant at
higher temperature and at 350°C corresponds to the 25% of the total amount of NO\textsubscript{x} stored during NO pulse.

<table>
<thead>
<tr>
<th>Pt-K/Al\textsubscript{2}O\textsubscript{3} catalysts</th>
<th>Without soot</th>
<th>With soot</th>
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<tbody>
<tr>
<td>Stored NO\textsubscript{x} up to steady state</td>
<td>Desorbed NO\textsubscript{x} upon NO shutoff</td>
<td>Desorbed NO\textsubscript{x}/Stored NO\textsubscript{x}</td>
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<tr>
<td>mmol/g\textsubscript{cat}</td>
<td>mmol/g\textsubscript{cat}</td>
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<tr>
<td>300°C</td>
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<td>320°C</td>
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<tr>
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<table>
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<tr>
<th>Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalysts</th>
<th>Without soot</th>
<th>With soot</th>
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<tr>
<td>Stored NO\textsubscript{x} up to steady state</td>
<td>Desorbed NO\textsubscript{x} upon NO shutoff</td>
<td>Desorbed NO\textsubscript{x}/Stored NO\textsubscript{x}</td>
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<tr>
<td>mmol/g\textsubscript{cat}</td>
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<tr>
<td>300°C</td>
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<tr>
<td>350°C</td>
<td>0.59</td>
<td>0.06</td>
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</tbody>
</table>

Table 1 – Stored NO\textsubscript{x} up to steady state, desorbed NO\textsubscript{x} and percentage of desorbed NO\textsubscript{x}/stored NO\textsubscript{x} ratio at different temperatures, in the absence and in the presence of soot over Pt-K/Al\textsubscript{2}O\textsubscript{3} and Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalysts (NO 1000 ppm, O\textsubscript{2} 3% v/v, H\textsubscript{2}O 1% v/v, CO\textsubscript{2} 0.1% v/v).

The NO\textsubscript{x} stored at different temperatures are then reduced under isothermal conditions by admitting H\textsubscript{2} (3500 ppm) in He + H\textsubscript{2}O (1% v/v) + CO\textsubscript{2} (0.1% v/v) and the results are shown in Fig. 4.

At 350°C (Fig. 4D), upon the addition of H\textsubscript{2} (at t= 0 s) N\textsubscript{2} is immediately observed at the reactor outlet along with a CO\textsubscript{2} consumption. This uptake of CO\textsubscript{2} is in line with the occurrence of reaction (3) which consider the
re-adsorption of CO$_2$ onto the K sites once NO$_x$ has been reduced:

\[ 2 \text{KNO}_3 + 5 \text{H}_2 + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{N}_2 + 5 \text{H}_2\text{O} \] (3)

The H$_2$ consumption is initially nearly complete and after a delay near 200 s its concentration increases with time until the initial value of 3500 ppm. Furthermore, no production of ammonia or other byproducts like N$_2$O is observed. Only a small amount of NO is detected along with nitrogen and this leads to a N$_2$ selectivity of 95%. At the end of the reduction phase (t = 300 s) the nitrates are all reduced and the catalytic surface is fully regenerated, as confirmed by N-balance.

The reduction pathway over Pt-K/Al$_2$O$_3$ catalyst has been recently studied by some of us [13] and carefully compared with that already proposed in the case of Pt-Ba/Al$_2$O$_3$ catalyst [15]. Both studies have pointed out that under nearly isothermal conditions N$_2$ formation occurs via an in series two-steps Pt-catalyzed molecular process involving the formation of ammonia as an intermediate. The first step of the series is ammonia formation through the reaction of H$_2$ with stored nitrates; ammonia then reacts with the nitrates left on the catalyst surface leading to the formation of nitrogen. The higher N$_2$ selectivity observed in the case of the Pt-K/Al$_2$O$_3$ catalyst is due to the fact that the onset for the H$_2$ + nitrate reaction leading to ammonia occurs at temperatures very close to the threshold for the NH$_3$ + nitrate reaction leading to N$_2$.

Accordingly, ammonia, once formed, readily reacts with surface nitrates to give N$_2$, and this drives the selectivity of the reduction process to N$_2$ [13].

Similar results have been obtained (in the absence of soot) at the other temperatures, i.e. 250, 300, 320°C (Fig. 2A-C): the main reduction product is nitrogen and only small amounts of NO are detected as byproduct. However, upon increasing the temperature from 250 to 300°C it is observed that the amounts of the evolved reduction products increase due to the larger amounts of stored NO$_x$ with temperature in the adsorption phase (see also Fig. 1).

The overall nitrogen selectivity is in all cases higher than 95% and slightly increases with temperature (in the range 250-300°C). At all the investigated temperatures, the catalyst is fully regenerated at the end of the reduction phase, as pointed out from the N-balance.

### 3.2. NO$_x$ storage-reduction in the presence of soot

The results obtained when the same experiments have been carried out in the presence of soot in the 250-350°C temperature range are shown in Fig. 5 A-D, respectively, in terms of NO, NO$_2$, NO$_x$ and CO$_2$ concentration profiles measured during the lean phase when 1000 ppm NO (+O$_2$ + H$_2$O + CO$_2$) are feed to the reactor.

Inspection of Fig. 5D, referring to 350°C, shows that in the presence of soot the NO$_x$ outlet concentration shows a dead time lower than in the absence of soot (90 s vs 210 s); then, its curve increases approaching
the asymptotic values corresponding to 880 ppm. The NO$_2$ concentration measured at steady state is roughly 100 ppm.

![Graph showing adsorption phase over Pt-K/Al$_2$O$_3$ catalyst in the presence of soot at different temperatures (A 250°C, B 300°C, C 320°C, D 350°C) with 1000 ppm NO + O$_2$ (3% v/v) in He + H$_2$O (1% v/v) + CO$_2$ (0.1% v/v).

Fig. 5 - Adsorption phase over Pt-K/Al$_2$O$_3$ catalyst in the presence of soot at different temperatures (A 250°C, B 300°C, C 320°C, D 350°C) with 1000 ppm NO + O$_2$ (3% v/v) in He + H$_2$O (1% v/v) + CO$_2$ (0.1% v/v).

The amounts of NO$_x$ stored at steady-state in the presence of soot are near 0.38 mmol/g$_{cat}$, i.e. much lower if compared to those measured in the absence of soot (0.58 mmol/g$_{cat}$). Similar results have been obtained at the other investigated temperatures, as apparent upon comparison of the data shown in Fig. 2A and 2B (and Table 1).

The effect of soot on the storage capacity of LNT catalyst has also been investigated on Ba-based systems [14, 16], and similar results have been obtained. In fact also in the case of Ba-based catalysts, the data clearly indicated that soot reduced the NO$_x$ storage capacity of the catalyst, in line with the results of Sullivan et al. [17] and of Pieta et al. [18]. The decrease in the NO$_x$ storage capacity of the catalyst at steady state is primarily related to the decrease in the NO$_2$ concentration. In fact the NO$_2$ concentration at the reactor outlet in the presence of soot is significantly lower than that observed in the absence of soot (compare with Fig. 5D vs 1D); this could be explained with a participation of NO$_2$ in the combustion of soot according to the following reaction:

$$2 \text{NO}_2 + \text{C} \rightarrow \text{CO}_2 + 2 \text{NO}$$

Accordingly, in the presence of soot the NO/NO$_2$ molar ratio is higher than on the soot - free catalyst (near 8.8 vs 1.72).

The low NO$_2$ concentration explicates also the lower storage capacity of the catalyst - soot mixture. In fact, also over Pt-K/Al$_2$O$_3$ catalyst, like over Ba-based LNT system, operates the “nitrate” pathway for the storage of NO$_x$ [13] which involves a direct adsorption of NO$_2$ over K sites in the form of nitrates via a disproportion...
reaction. Accordingly, K and soot compete for reaction with NO\textsubscript{2} leading to the observed decrease in the NO\textsubscript{x} storage properties.

The presence of soot also influences the stability of the adsorbed NO\textsubscript{x} species. As shown in Fig. 5D, upon NO shutoff at the end of the adsorption phase (He purge) a tail is observed in the NO\textsubscript{x} concentration indicating the desorption/decomposition of the NO\textsubscript{x} previously stored; a significant effect is detected in correspondence of the O\textsubscript{2} shutoff as well. These effects decrease the amounts of NO\textsubscript{x} which have been stored up to steady-state from 0.38 mmol/g\textsubscript{cat} to 0.18 mmol/g\textsubscript{cat}, i.e. the amounts of stored NO\textsubscript{x} decrease roughly by 50\% during the purge. Inspection of Table 1 shows that in the absence of soot the amount of NO\textsubscript{x} desorbed is lower (25\%) and no significant contribution of desorption in correspondence of O\textsubscript{2} shutoff is detected.

This destabilizing effect of soot on the stored NO\textsubscript{x} was already observed in the case of Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalyst [14]. In fact, in the absence of soot near 10\% of the initially stored NO\textsubscript{x} are decomposed after the NO shut off at 350°C, whereas in the presence of soot, the relative amounts of NO\textsubscript{x} desorbed at the same temperature are 2-3 times higher than in its absence, being near 27\% of those initially adsorbed (see Table 1).

During NO\textsubscript{x} storage in the presence of soot, the evolution of CO\textsubscript{2} is also observed (Fig. 5D). The CO\textsubscript{2} curve shows a very complex trend. In correspondence of NO feeding, the CO\textsubscript{2} increases from the inlet value up to 1700 ppm at the end of NO pulse. Then its concentration slowly decreases and tends to reach the inlet value (1000 ppm) after O\textsubscript{2} shutoff.

The CO\textsubscript{2} production is due to two contributions: i) the decomposition of surface carbonates on the catalytic surface upon nitrates formation (reaction (3)); ii) soot combustion according to the reaction (4) previously reported. Note that reaction (4) is a global reaction; two steps could be considered:

\[
\text{NO}_2 + C \rightarrow \text{CO} + \text{NO} \quad (5)
\]

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad (6)
\]

During our experiments CO formation is not observed, likely because CO is oxidized to CO\textsubscript{2} by O\textsubscript{2} at Pt sites, as reported elsewhere [14].

In order to determine the amounts of CO\textsubscript{2} produced upon soot oxidation, the net CO\textsubscript{2} production has been calculated as previously indicated, and the results are shown in Fig. 5D. In the presence of soot a net CO\textsubscript{2} production is observed, not only in the presence of NO but also after NO shutoff, i.e. in the presence of O\textsubscript{2} only. Since the soot combustion in Fig. 5 D is apparent only after NO addition to the reactor (i.e. in the presence of O\textsubscript{2} only no CO\textsubscript{2} production is observed), it could be speculated that O\textsubscript{2} does not act as direct oxidizing agent of soot at these temperatures. Notably, the tail in NO\textsubscript{x} concentration suggests that adsorbed NO\textsubscript{x} species are involved in the combustion of soot as also suggested in previous papers [14] and
according to reaction (7):

\[ \text{C} + 2 \text{NO}_3^- \rightarrow \text{CO}_3^{2-} + 2 \text{NO} + \frac{1}{2} \text{O}_2 \]  

(7)

At 350°C roughly 50% of the total amount of CO₂ produced after NO and O₂ shutoff is due to the nitrates oxidation. ISC experiments in the presence of soot have been performed in similar condition varying the reaction temperature in the range 250-350°C and the results are reported in Fig. 5A-D. In analogy to that observed in the case of soot-free catalyst, in all cases NO₃⁻ breakthrough increases with temperature but it is always lower than in the absence of soot (50s at 250°C, 75s at 300°C, 120s at 320°C) and also the amounts of NO₃⁻ stored up to steady-state increase with temperature until 300°C, as appears from Fig. 2B and Table 1. At temperature higher than 300°C the amounts of stored NO₃⁻ decreases. The data clearly show a more pronounced trend to a maximum in the amounts of stored NO₃⁻ and indicate that the amounts of NO₃⁻ stored in the presence of soot are always lower than those measured in its absence.

The temperature affects also the rate of NO₃⁻ adsorption, as already observed in the absence of soot. Indeed, in Fig. 2B the slope of stored NO₃⁻ curves is equal up to 130 s, then the curves diverge. As observed in the absence of soot, the stored NO₃⁻ curves increase with a slope that, at fixed amounts of adsorbed NO₃⁻, increases with temperature with a maximum at 300°C. In the presence of soot this effect of temperature is much more pronounced.

The amounts of desorbed NO₃⁻ after NO shutoff increase with temperature and are always higher than in the absence of soot. It is noted that in the presence of soot near 27% (vs. 8%) and 40% (vs. 20%) of the initially stored NO₃⁻ are decomposed after the NO shutoff at 300°C and 320°C, respectively. This confirm the destabilizing effect of soot on the stored species, that is more evident at high temperature.

Also the amounts of NO₂ increases with temperature, but its concentration at steady state is always lower than in the absence of soot (155 ppm vs. 256 ppm at 300°C and 134 ppm vs. 305 ppm at 320°C). Accordingly, higher NO/NO₂ ratios are measured (5.6 vs. 2.9 at 300°C, 6.4 vs. 2.3 at 320°C). This trend is related to the participation of NO₂ in soot oxidation that became significant at temperature higher than 300°C. In fact, at each temperature a CO₂ evolution is always observed (see Fig. 5A-C) during the NO adsorption (occurrence of reaction (3)) but only above 300°C the trace of net CO₂ reveals a contribute to soot oxidation (reaction (4)). Note that by increasing the temperature the contribute of adsorbed NO₃⁻ species to the soot combustion increases as well. After NO and O₂ shutoff, the occurrence of reaction (7) represents the 20% and 30% of the total amount of CO₂ produced.

The data herein presented well parallel those obtained over Pt-Ba/Al₂O₃ [14] where a detrimental effect of soot on the NO₃⁻ storage capacity has been observed to increase with temperature in the range 250-350°C. As reported in Fig. 3 and Table 1 the performances of Pt-K/Al₂O₃ keep higher than that of Ba-based catalyst also in the presence of soot. Finally, inspection of Table 1 shows that at temperature higher than 300°C a
larger amounts of NO\textsubscript{x} are desorbed from Pt-K/Al\textsubscript{2}O\textsubscript{3} than from Pt-Ba/Al\textsubscript{2}O\textsubscript{3}. This is accompanied by an increased production of CO\textsubscript{2} after NO shutoff, indicating a greater contribution of reaction (7) to soot combustion.

Fig. 6A-D show data collected during the rich phase of cycling in the presence of soot in the range 250-350°C. The products evolution is similar to that previously described for the regeneration phase in the absence of soot (Fig. 2), being nitrogen the main reduction product; negligible amounts of NO are detected only at high temperature (i.e. 350°C). A comparison with the results obtained in the absence of soot indicates that the presence of soot does not influence significantly the reduction of the stored NO\textsubscript{x} at any temperature.

![Graph](image)

**Fig. 6 - Reduction phase over Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst in the presence of soot at different temperatures (A 250°C, B 300°C, C 320°C, D 350°C) with 3500 ppm H\textsubscript{2} in He + H\textsubscript{2}O (1% v/v) + CO\textsubscript{2} (0.1% v/v)**

### 3.3 effect of soot loading and stability of the Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst

The results herein presented point out that the presence of soot affects the catalytic performance of the Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst by lowering not only the amount but also the stability of the NO\textsubscript{x} adsorbed species. In order to investigate more in details the effect of the soot loading on the catalyst behaviour, and the stability of the Pt-K/Al\textsubscript{2}O\textsubscript{3} upon repeated soot oxidation cycles, several lean-rich cycles have been carried out over the same sample. For this purpose a sequence of NO\textsubscript{x} adsorption and reduction cycles (6-7 cycles) has been performed in the presence of soot over a fresh Pt-K/Al\textsubscript{2}O\textsubscript{3} at 350°C until the complete consumption of soot (run 1); after that, the clean catalyst has been mixed again with soot and has been again cycled under the same experimental conditions until complete soot oxidation (Run 2). This procedure has been repeated three times.
The amounts of NO\textsubscript{x} stored at steady-state during the various lean-rich cycles are shown in Figure 7 as function of the residual soot. During the first run (black squares) with the full soot loading (near 11 % w/w) roughly 0.31 mmol/g\textsubscript{cat} of NO\textsubscript{x} could be loaded on the catalyst. The amounts of NO\textsubscript{x} stored on the catalyst increase upon decreasing the soot loading; roughly 0.46 mmol/g\textsubscript{cat} of NO\textsubscript{x} could be stored at the end of Run 1, on the soot-free sample (point 3 in Fig. 7).

After that, the clean catalyst has been mixed again with soot and has been again cycled in the same conditions (Run 2, points 4-5 in Fig. 7) until the complete oxidation of particulate. Finally the procedure has been repeated for the third time (Run 3, points 6-7 in Fig. 7).

The clean catalyst has been mixed again with soot (point 4 in Fig. 7) and Run 2 has been performed; at the end of this run the the storage capacity is further decreased. A new mixing and a new run (Run 3) show that the clean catalyst (point 7 in Fig. 7) has lost its storage capacity, which is about half of that of the fresh catalyst.

![Fig. 7 – Stored NOx as function of residual soot in subsequent lean-rich cycles over Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst during three different runs](image)

The data point out that ageing the LNT Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst by repeated soot oxidation cycles, the NO\textsubscript{x} storage capacity decreases; indeed, the amount of NO\textsubscript{x} stored on aged Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst (i.e. clean catalyst) is lower than that on the fresh catalyst. This is in line with the results obtained by Krishna et al. [S].

The soot oxidation activity of Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst has also been evaluated calculating the soot conversion in the lean phase of such Run (Fig. 8). Comparing the amount of soot oxidized in the tree different runs after the same number of lean phase, it clearly appears that second and the third cycle are almost identical and lower that the first one. On the other hand, the NO/NO\textsubscript{2} molar ratio (Fig. 9) strictly depends on the soot present; the amount of soot decreases the ratio decreases since NO\textsubscript{2} is not involved in the soot
combustion. Notably, the same NO/NO₂ molar ratio is calculated on the fresh and aged catalyst, indicating the ageing process does not involve Pt sites.

Fig. 8 - Cumulative conversion of soot (%) in subsequent lean phases (1000 ppm NO + O₂ (3% v/v) in He + H₂O (1% v/v) + CO₂ (0.1% v/v) at 350°C) during three different runs

Fig. 9 - NO/NO₂ molar ratio as function of residual soot over Pt-K/Al₂O₃ catalyst at NO shutoff

The observed decrease in soot oxidation activity over aged K-containing catalyst can be attributed to the volatile nature of K-active species, like nitrates (melting point 334°C) [5, 19, 20]. The mobility of such compounds is expected to be high, leading to good contact with soot and bringing an additional activity. The degradation of catalyst should be due to the sublimation of K during soot combustion [21]. The loss of K have as consequence a lower amount of storage sites; accordingly, the storage capacity of system decreases and a lower amount of K-nitrates are available to oxidize soot. This also in line with that reported by Wu et al. [22].
On the other hand, after the first run the catalyst seems to stabilized its oxidation activity. Also Gross has observed a similar behaviour \(^{23}\) studying the catalyst stability. Based on the results collected the Authors conclude that during the ageing the catalyst reaches a steady-state concerning the most relevant species, for example, carbonates or carbonate-type compounds produced via chemisorbed CO\(_2\). These compounds could be formed and decomposed in a range of intermediate temperatures, such as the soot oxidation temperatures. This is a key point, since if these compounds do not decompose, the catalytic surface would be enriched in carbonates composition and a deactivation could be observed.

Bibliography

Paper V

The NO\textsubscript{x} reduction by CO on Pt-K/Al\textsubscript{2}O\textsubscript{3} Lean NO\textsubscript{x} Trap Catalyst

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The NOx reduction by CO on Pt-K/Al$_2$O$_3$ Lean NOx Trap Catalyst

ABSTRACT

The reduction by CO under dry condition of NO$_x$ species stored at 350 °C onto a Pt-K/Al$_2$O$_3$ Lean NO$_x$ Trap catalyst is investigated by means of transient response methods (CO-TPSR and CO-ISC experiments) and complementary FT-IR spectroscopy. The results show that the pathway for the reduction of stored NO$_x$ by CO under dry and near isothermal conditions is the same proposed by some of us in a previous work for Pt-Ba/Al$_2$O$_3$ catalyst. In particular: i) the reduction of stored NO$_x$ by CO occurs according to a Pt catalyzed surface pathway that does not involve as a first step the release of NO$_x$ in the gas phase, is effective already at low temperature and leads to nitrogen; ii) the reaction scheme implies the formation of surface isocyanate species followed by the reaction of these species with residual NO$_x$ to give nitrogen; iii) the reaction of NCO species with nitrates to give nitrogen is slightly slower than the reduction of nitrates to give NCO species; but on Pt-K/Al$_2$O$_3$ catalyst this last step is faster than on Pt-Ba/Al$_2$O$_3$ system. As a consequence, the amount of isocyanates species present on the surface at the end of the reduction is lower for Pt-K/Al$_2$O$_3$ then Pt-Ba/Al$_2$O$_3$ catalyst.

Keywords: Lean NO$_x$ Trap - Pt-K/Al$_2$O$_3$ - Reduction by CO - Transient Response Methods – FTIR – Nitrates – Nitrites – Isocyanates - Reaction Pathway
INTRODUCTION

Commercial vehicles and diesel passenger cars will be subjected in a near future to very stringent emission regulations regarding nitrogen oxides (NO$_x$). In fact EU emission standards coming in force in 2014 (Euro 6) impose strict emissions limits on these pollutants, in addition to hydrocarbon, carbon monoxide and particulate matter (soot): accordingly improved and viable solutions for NO$_x$ reduction under lean conditions are required.

Different strategies have been proposed to handle the strict NO$_x$ limits in lean-burn automotive emissions. One such strategy is the NO$_x$ Storage-Reduction (NSR) system, or Lean NO$_x$ traps (LNTs) $^{[1,2,3]}$. This technique is based on the use of a catalyst containing precious metals such as Pt, Pd and Rh for the reduction and oxidation reactions, and alkali or alkaline-earth metal components such as Ba or K that store NO$_x$ as nitrite and nitrate species $^{[4,5]}$. Overall, NO$_x$ are reduced to N$_2$ over NSR catalyst by alternating lean and rich periods, i.e. a lean period of 30-90 s during which the NO$_x$ emitted in the exhaust gases are stored on the catalyst surface, and a short 3-5 s rich period during which the stored NO$_x$ are reduced to N$_2$ by H$_2$, CO and unburned hydrocarbons.

Several studies deal with the reactivity and characteristics of Ba containing catalysts (see for example Refs. $^{6,7,8,9}$), but reports on the specific behaviour of K-based catalysts are scarce in the literature, particularly on the reduction step. In this respect, the reactivity of different reducing agents (e.g. H$_2$, CO, C$_2$H$_6$ and C$_3$H$_8$) has been investigated in the case of Ba-containing catalysts; these studies indicate that hydrogen is the most effective reductant for lean NO$_x$ traps $^{[10,11,12,13,14]}$.

In recent papers of various research groups, including ours, mechanistic aspects of the reduction of NO$_x$ stored over Ba-based NSR catalytic systems have been reported when H$_2$ is used as a reductant $^{[15,16,17]}$. It has been shown that the reduction by H$_2$ under near isothermal conditions of NO$_x$ stored onto Pt-Ba/Al$_2$O$_3$ (and onto Pt-K/Al$_2$O$_3$ as well) is not initiated by the thermal decomposition of nitrates/nitrates ad-species with release of NO$_x$ in the gas phase, but involves a Pt catalyzed surface pathway which is active at low temperature and leads to nitrogen $^{[18,19]}$. It has also been proposed that under near isothermal conditions N$_2$ is formed exclusively via a consecutive reaction scheme which involves the fast reaction of H$_2$ with stored NO$_x$ to give ammonia followed by the slower reaction of ammonia with residual stored NO$_x$ to give N$_2$ $^{[15,16,17,20]}$. However, it has been also pointed out that the reaction of ammonia with residual stored NO$_x$ to give N$_2$ is slower over Pt-Ba/Al$_2$O$_3$ than over Pt-K/Al$_2$O$_3$.

In general, the reduction by CO of NO$_x$ stored on LNT catalysts has attracted lower interest. In a very recent paper, some of us have performed a systematic and quantitative study of the reduction by CO under dry conditions of NO$_x$ stored onto a Pt-Ba/Al$_2$O$_3$ LNT catalyst in order to clarify the reaction pathway and the mechanism of the reaction $^{[21]}$. By using transient reactivity methods and complementary FT-IR spectroscopy, it was shown that also in the case of CO and under nearly isothermal conditions the
The NOx reduction by CO on Pt-K/Al2O3 Lean NOx Trap Catalyst

Reduction of nitrates stored onto Pt-Ba/Al2O3 occurs through a Pt-catalyzed surface pathway. A mechanism was proposed for the reduction of surface nitrates by CO under dry conditions which proceeds through a stepwise reduction of nitrates with formation of nitrites and then of surface isocyanate/cyanate species followed by the reaction of these species with residual nitrites to give nitrogen. This last reaction is slower than the reduction of nitrates to give nitrites and then NCO species. Dedicated experiments have also shown that NCO species can be re-oxidized to surface nitrites at first and then to surface nitrates upon contact with oxygen at increasing temperature. This explains the formation of nitrogen observed during the reduction of stored NOx by CO, and during the oxidation of surface NCO species upon oxygen addition and upon admission of NO in the presence of excess O₂.

The work here presented focuses on the study of the reduction steps when K replaces Ba as the storage component and CO is used as a reductant. For this purpose, the reduction with CO under dry conditions of NOx stored onto a model Pt-K/Al2O3 catalyst has been analyzed. For this purpose NOx have been adsorbed on the catalyst surface starting from NO/O2; then the reactivity of the stored NOx with CO has been investigated by means of Temperature Programmed Surface Reaction experiments (TPSR). Isothermal Step Concentration experiments (ISC) have also been performed in which the storage and the reduction phases have been carried out under nearly isothermal conditions, i.e. in the absence of significant temperature effects during cycling. These conditions have been accomplished by using low CO concentration and by separating the lean and the rich phases by an inert purge in between. Accordingly a more precise rationalization of the catalytic behaviour and a better understanding of the chemical uncontrolled thermal effects.

In parallel with reactivity experiments, FT-IR spectroscopy has been employed as complementary technique to obtain information about the nature, reactivity and evolution of surface species. The results collected over the Pt-K/Al2O₃ catalyst sample in this study have been compared with those collected in the case of a Pt-Ba/Al₂O₃ catalyst [21] in order to highlight possible similarities and differences.

EXPERIMENTAL

1. Materials

K/Al₂O₃ and Pt-K/Al₂O₃ catalysts were prepared by the incipient wetness impregnation method, using aqueous solutions of CH₃COOK (Sigma Aldrich, 99%) and Pt(NH₃)₃(NO₃)₂ (Strem Chemicals, 5% Pt in ammonium hydroxide) to impregnate the γ-alumina support calcined at 700°C (Versal 250 from UOP, surface area of 207 m²/g and pore volume of 0.96 cm³/g). In the case of the Pt-K/Al₂O₃ catalyst the impregnation was carried out in sequential manner: the alumina support was first impregnated with the Pt dinitrodiammine solution, and then with the K acetate solution. After each impregnation step the catalysts
were dried at 80°C overnight and then calcined at 500°C for 5 h. The final loading was 5.4/100 w/w for the K/Al₂O₃ catalyst and 1.5/4.100 w/w for the Pt-K/Al₂O₃ catalyst. The following surface areas and pore volumes were measured by N₂ adsorption-desorption at 77K: 179 m²/g and 0.84 cm³/g for the K/Al₂O₃ sample; 176 m²/g and 0.9 cm³/g for the Pt-K/Al₂O₃ sample. The Pt dispersion, as determined by H₂ chemisorption at 0°C, was ≈ 65 %. Mean Pt particle size measured by HRTEM was 1.5 nm [22], in good agreement with the mean Pt particle sizes (dp) calculated from the empirical relationship often used for monometallic catalysts, doi

\[ dp(nm) = 1.1/(H/Pt), \]

where H/Pt is the Pt dispersion measured from H₂ chemisorption.

2. Reactivity tests

The reactivity tests were performed over the Pt-K/Al₂O₃ and the K/Al₂O₃ samples previously conditioned. In the case of the Pt-K/Al₂O₃ catalyst, conditioning involved few adsorption/reduction cycles with NO/O₂ (1000 ppm NO and 3% v/v O₂ in He) and H₂ (2000 ppm in He) at 350 °C, respectively, with an inert purge (He) between the two phases. Conditioning was done until a reproducible behavior was obtained, and this typically required 2 or 3 lean-rich cycles [19,20]. For the K/Al₂O₃ binary catalyst, which does not adsorb significant amounts of NO in line with previous observations for the homologous Ba/Al₂O₃ [9] and does not react with H₂, the adsorption was carried out with NO₂ (1000 ppm in He), and the adsorbed NOₓ were removed by heating at 400°C. Like Pt-K/Al₂O₃, also in the case of K/Al₂O₃ NOₓ are stored on the catalyst surface in the form of nitrates [20,22].

Temperature Programmed Surface Reaction experiments (TPSR) were carried out in the presence of CO as reducing agent to analyze the reactivity of adsorbed nitrates. For this purpose NOₓ were stored at 350°C with NO/O₂ mixtures (1000 ppm NO, 3% v/v O₂ in He). For the K/Al₂O₃ catalyst the adsorption was carried out with NO₂ (1000 ppm in He). The NO + O₂ (or NOₓ) flow was maintained up to adsorption equilibrium; then the inlet NO + O₂ (or NO₂) concentration was decreased to zero. After storage, the samples were kept under inert He flow at the same temperature to provoke the desorption of weakly adsorbed species (He purge). Afterwards, the samples were cooled down to RT under flowing He and the CO-TPSR experiment was started by heating the catalyst at 10°C/min up to 400°C in He + 6500 ppm CO.

The storage/reduction of NOₓ over Pt-K/Al₂O₃ was also investigated at constant temperature by imposing stepwise changes in the inlet concentration of the reagents (Isothermal Step Concentration experiments, ISC), according to the following sequence. After catalyst conditioning (see above), the storage of NOₓ (Lean phase) was accomplished at 300°C by admitting NO (1000 ppm) in He+ 3 % v/v O₂. After storage, the NO + O₂ concentration was decreased to zero, while maintaining the catalyst at the same temperature (He purge). The reduction of the stored NOₓ was then carried out by imposing a stepwise change in the CO.
inlet concentration \((0 \rightarrow 2000 \text{ ppm} \rightarrow 0)\) in flowing He (Rich phase). Three or four cycles have been carried out until a reproducible catalytic behaviour was attained.

All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7 mm i.d.) directly connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum) and to a micro GC (Agilent 3000A) for the on-line analysis of the outlet gases \((\text{N}_2, \text{O}_2, \text{CO}, \text{CO}_2, \text{N}_2\text{O})\). The outlet NO, NO\textsubscript{2}, NH\textsubscript{3} concentrations were also detected by a UV analyzer (Limas 11HW, ABB).

60 mg of catalyst with small particle diameter (100-120 μm) and a total flow rate of 100 cc/min (at 1 atm and 0°C) were used in each run in order to minimize intra- and inter-particle diffusion limitations. The flow rates of the gases were measured and controlled by mass-flow controllers (Brooks 5850 TR), and the gases were mixed before entering the reactor. The reactor was inserted into an electric furnace driven by a PID temperature controller/programmer. A K-type thermocouple (outer diameter 0.5 mm) directly immersed in the catalyst bed was used to measure and control the catalyst temperature.

Further details about the experimental apparatus and procedures can be found elsewhere [8-9,15,20,21].

### 3. FT-IR study

Absorption/transmission IR spectra were run on a Perkin-Elmer FT-IR System 2000 spectrophotometer equipped with a Hg-Cd-Te cryo-detector, working in the range of wavenumbers 7200-580 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\). For IR analysis powder samples were compressed in self-supporting discs (10 mg cm\(^{-2}\)) and placed in a commercial heated stainless steel cell (Aabspec) allowing thermal treatments \textit{in situ} under vacuum or controlled atmosphere and the simultaneous registration of spectra at temperatures up to 600°C.

Before the NO\textsubscript{x} storage, the samples were conditioned by \textit{i)} outgassing at 500°C for 30 min, \textit{ii)} one or two cycles consisting of NO\textsubscript{2} adsorption at 350°C and reduction with H\textsubscript{2} at 350°C (for Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst) or outgassing at 500°C (for K/Al\textsubscript{2}O\textsubscript{3} sample), necessary to eliminate the carbonates present on calcined powder \cite{23}, \textit{iii)} oxidation at 500°C for 30 min and cooling in oxygen down to the temperature requested.

NO\textsubscript{x} storage was carried out at 350°C by admitting, on the Pt-K/Al\textsubscript{2}O\textsubscript{3} disc, freshly prepared NO/O\textsubscript{2} mixtures \((p_{\text{NO}} = 5 \text{ mbar}, p_{\text{O}_2} = 20 \text{ mbar})\) or, on the K/Al\textsubscript{2}O\textsubscript{3} disc, NO\textsubscript{2} \((p_{\text{NO}_2} = 5 \text{ mbar})\) up to catalysts saturation (ca. 20 min), and outgassing at the same temperature. The spectra of the stored NO\textsubscript{x} were collected at 350°C or after cooling down the discs at the chosen temperature. The reduction was accomplished in CO \((p_{\text{CO}} = 10 \text{ mbar})\) and was performed both in isothermal conditions and at increasing temperature. The reduction in isothermal conditions was accomplished at 280°C and 350°C: at each temperature the spectra were run at increasing exposure times. For the reduction experiments at increasing temperature, the samples were cooled down at 100°C under vacuum, then heated in CO in the range 100-400°C. NO (Praxair, purity ≥ 99.0 %) was freshly distilled before use. Conversely, NO\textsubscript{2} (Praxair, purity ≥ 99.5 %), O\textsubscript{2} (Praxair, purity ≥ 99.999 %) and CO (Praxair, purity ≥ 99.9 %) were directly used.
RESULTS AND DISCUSSION

1) K/Al₂O₃ sample.

**CO-TPSR experiments and FT-IR study** - The reactivity of CO towards NOₓ species stored at 350°C onto K/Al₂O₃ was investigated by performing a CO-TPSR experiment and the results are presented in Figure 1A.

CO is consumed above ~ 330°C while CO₂ and NO are simultaneously formed, along with trace amounts of N₂. The concentrations of the products increase up to 400°C, and then slowly decrease to 0 ppm while the system is held at this temperature (400°C); in the meantime the concentration of CO slowly approaches the inlet value.

It is worth noticing that CO reacts with stored NOₓ at temperatures (330°C) near to the onset temperature for nitrates thermal decomposition (~ 340°C), as appears from the He-TPD experiment reported in the insert of Figure 1A. In this experiment the thermal decomposition of nitrates species present on the catalyst surfaces results in the initial evolution of NO₂, followed by O₂ and NO. The process is not complete at temperatures as high as 500°C; the catalyst was then kept at 500°C until desorption of NOₓ was complete. The comparison between He-TPD and CO-TPSR experiments points out that the presence of CO in the feed does not affect appreciably the temperature threshold of nitrate thermal decomposition. In contrast, decomposition under a reducing atmosphere leads to a different product distribution, with the lack of any significant NO₂ evolution, and a corresponding increase in NO concentration. Besides, also oxygen evolution was not observed, whereas the formation of nitrogen was seen together with that of CO₂. These results well parallel those obtained in the case of Ba/Al₂O₃ catalyst [¹⁸,²¹].

The reduction of the NOₓ stored onto K/Al₂O₃ catalyst at 350°C with CO has also been investigated by in situ FT-IR spectroscopy and the spectra obtained at increasing exposure times are reported in Figure 1B. In particular curve a is the spectrum of NOₓ species previously stored at 350°C, i.e. ionic nitrates (related bands at 1375 and 1033 cm⁻¹, assigned to ν(NO₃)asym and ν(NO₃)sym modes, respectively) and bidentate nitrates (related bands at 1550, 1306 and 1006 cm⁻¹, assigned to ν(N=O), ν(NO₂)asym and ν(NO₂)sym modes, respectively) [²⁰,²²]; curves b and c correspond to the spectra recorded during the interaction with CO at increasing exposure times at 350°C. The extent of nitrates reduction is nihil after 20 min of exposure (not reported). After 40 min of exposure (curve b) small amounts of ionic nitrates are consumed and it needs 3 hs of exposure (curve c) to further reduce the ionic nitrates and to reveal minor amounts of reaction products (carbonate species, shoulder at 1620 cm⁻¹, corresponding to ν(C=O) mode, [²²]) along with minor amounts of isocyanate species (weak band at 2235 cm⁻¹) [²³].

In line with CO-TPSR experiment reported in Figure 1A, FT-IR data show that the reduction by CO of
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Nitrates stored onto K/Al₂O₃ sample is extremely slow at 350°C and only occurs to a rather limited extent.

Figure 1 - A) CO-TPSR (6500 ppm CO in He) after NO₂ adsorption at 350°C over the K/Al₂O₃ catalyst. The results of the TPD run in He after NO₂ adsorption at 350°C over the same catalyst is shown in the insert. B) FT-IR spectra of NOₓ reduction at 350°C in CO (10 mbar) at increasing exposure time over the K/Al₂O₃ catalyst. Curve a, spectrum of NOₓ stored at 350 °C by NO₂ adsorption; curves b and c, spectra after reduction for 40 min and 3h, respectively.

2) Pt-K/Al₂O₃ catalyst

**CO-TPSR experiment and FT-IR study** - The reactivity of CO towards NOₓ species previously stored at 350°C over the Pt-K/Al₂O₃ sample was investigated by performing a CO-TPSR experiment (CO inlet 6500 ppm) and the results are presented in Figure 2A.
CO consumption starts near 210°C: the CO trace shows a minimum of \(~ 4150\) ppm at 270°C and then slowly increases approaching at 340°C an asymptotic value which is slightly below the inlet concentration. A shoulder in the CO consumption peak is observed near 315°C. The formation of CO2 is detected simultaneously with the consumption of CO, showing a maximum of \(~ 1420\) ppm in the temperature range where the CO trace shows its minimum. At the same time nitrogen is formed at slightly higher temperature, starting from 230°C; its concentration gradually increases up to 340 ppm at 280°C, then slowly decreases. A shoulder in N2 and CO2 traces is observed corresponding to the shoulder of CO peak at 315°C. Finally, very small amounts of NO are also detected near 235°C.

From \(~ 330\)°C, when the nitrogen concentration is close to zero, hydrogen is detected in the gaseous products together with CO2.

The production of H2 and CO2 at high temperature, jointly with a constant consumption of CO, suggests
the occurrence of the Water Gas Shift (WGS) reaction:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad (1) \]

Indeed, inspection of Figure 2A shows the presence of small amounts of water starting from 250°C; according to that observed during the He-TPD (not reported), the water concentration trace increases with temperature, suggesting that it is likely related to a desorption from the catalyst surface. The desorption of H₂O could be likely associated to the presence of trace amounts of water in the feed that causes the surface catalyst rehydration at the low temperatures (RT-200 °C) and is released at the high temperature (250-350°C). It is worth to note that the occurrence of the WGS reaction occurs over the Pt-K/Al₂O₃ sample starting from 180°C in the absence of stored nitrates (data not reported), but is observed at higher temperature (330°C) when the stored nitrates are almost completely depleted. A similar behavior has been observed over the Pt-Ba/Al₂O₃ sample \[^{[21]}\]; in addition it has also been shown in the past that the catalyst promotes the Reverse Water Gas Shift (RWGS) reaction as well and also in this case the reaction was seen to take place after stored NOₓ groups have been depleted \[^{[8]}\].

It is concluded that over Pt-K/Al₂O₃ the consumption of CO occurs at temperatures well below that of NOₓ thermal desorption over the same catalyst. In fact in the absence of CO nitrates stored at 350°C decompose only starting from the temperature of adsorption, as pointed out by dedicated He-TPD experiments where the stability of nitrates stored at 350°C over the Pt-K/Al₂O₃ sample has been investigated (data not reported). Moreover, a comparison with the results of CO-TPSR experiments carried out over the Pt-free sample (Figure 1) pointed out that the reduction of the stored nitrates is catalyzed by Pt, since over K/Al₂O₃ the reduction is only observed starting from the temperature of the thermal decomposition of stored NOₓ. This clearly indicates that over Pt-K/Al₂O₃ a Pt-catalysed surface route is responsible for the reduction of the stored nitrates, similarly to the case of Pt-Ba/Al₂O₃ \[^{[15,21]}\].

Notably, the CO trace is complex, with a first peak at about 270°C and a shoulder near 315°C. This may suggest the involvement of stored NOₓ species with different reactivity. These features have been observed also when H₂ is used as a reductant instead of CO \[^{[19,20]}\]: also in that case two major H₂ consumption peaks were apparent in the TPSR experiments, associated with the formation of different products, i.e. N₂ in the first peak and NH₃ in the shoulder at higher temperature. As will be discussed later on, FT-IR measurements pointed out that this is possibly related to the presence of NOₓ adsorbed species having different reactivity, i.e. ionic and bidentate nitrates.

The moles of CO consumed and of the different products formed during CO-TPSR were calculated from Figure 2A and are reported in Table 1 for different temperature ranges. 1.90 × 10⁻⁴ moles/\(B_{\text{cat}}\) of N₂ and 0.12 × 10⁻⁴ moles/\(B_{\text{cat}}\) of NO are released in the gas phase during the whole TPSR run. Since 4.33 × 10⁻⁴ moles/\(B_{\text{cat}}\) of NOₓ species have been previously stored onto the catalyst, ~ 90 % of the stored nitrates are reduced to gaseous N-containing products. Accordingly small amounts of N-containing species could be present at the
The NOx reduction by CO on Pt-K/Al2O3 Lean NOx Trap Catalyst

catalyst surface at the end of the CO-TPSR experiment. In fact, as it will be shown in the following, FT-IR spectra show that NCO species still remain onto the catalyst surface at the end of the reduction phase.

<table>
<thead>
<tr>
<th>reagent and product species (moles/g_cat)</th>
<th>Temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RT - 250°C</td>
</tr>
<tr>
<td>CO consumed</td>
<td>2.91 $10^{-4}$</td>
</tr>
<tr>
<td>CO2 formed</td>
<td>1.49 $10^{-4}$</td>
</tr>
<tr>
<td>N2 formed</td>
<td>0.08 $10^{-4}$</td>
</tr>
<tr>
<td>NO formed</td>
<td>-</td>
</tr>
<tr>
<td>H2 formed</td>
<td>-</td>
</tr>
<tr>
<td>NH3 formed</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Moles/g_cat of CO consumed and of products formed during CO-TPSR over Pt-K/Al2O3 (NOx stored at 350°C in NO/O2 are 4.33 $10^{-4}$ moles/g_cat).

The features herein discussed suggest that the reduction of stored NOx species primarily occurs according to the reactions:

\[
2 \text{KNO}_3 + 5 \text{CO} \rightarrow \text{K}_2\text{CO}_3 + \text{N}_2 + 4 \text{CO}_2 \quad (2)
\]

\[
2 \text{KNO}_3 + 8 \text{CO} \rightarrow 2 \text{KNCO} + 6 \text{CO}_2 \quad (3)
\]

Close inspection of Figure 2A shows that in the low-T region (below 250°C) the consumption of CO is accompanied by the evolution of CO2 and of a very small quantity of N-containing species (0.08 $10^{-4}$ moles/g_cat of N2; Table 1). This points out that the initial step in the reduction of stored nitrates is described by reaction (3), as also confirmed by FT-IR study (see infra).

A similar TPSR experiment performed over Pt-Ba/Al2O3 catalyst demonstrated that at the end of the CO-TPSR experiment only ~ 43 % of the stored nitrates were reduced to gaseous N-containing products and consequently N-containing species were still present at the catalyst surface \textsuperscript{[21]}. Also in that case in the low temperature region (below 250°C) the CO consumption is higher than that expected from N2 and CO2 production and the formation of isocyanates species has been pointed out by FT-IR experiments, according to the stoichiometry of the following reaction:

\[
\text{Ba(NO}_3)_2 + 8 \text{CO} \rightarrow \text{Ba(NCO)}_2 + 6 \text{CO}_2 \quad (4)
\]

As shown in the following, FT-IR measurement reveals that the formation of isocyanates ad-species is effective in the case of Pt-K/Al2O3 catalyst as well. However, as opposite to the homologous Pt-Ba/Al2O3 catalyst \textsuperscript{[21]}, over Pt-K/Al2O3 the amounts of NCO species left onto the catalyst surface at the end of the reduction are small, in line with the observation that ~ 90 % of the stored nitrates are reduced to gaseous N-containing products (see above).
The NOx reduction by CO on Pt-K/Al₂O₃ Lean NOx Trap Catalyst

The reduction by CO of NOₓ species previously stored at 350°C onto the Pt-K/Al₂O₃ catalyst investigated by means of in situ FT-IR spectroscopy is reported in Figure 2B. In this Figure curve a is the spectrum of NOₓ species stored at 350°C and cooled down to 100°C, and curves b-e correspond to the spectra recorded during interaction with CO at increasing temperature up to 400°C. The stored nitrates are not perturbed in the range 100-200°C (not reported), at 250°C the bidentate nitrates become to be reduced (curve b, bands at 1550, 1314, 1006 cm⁻¹) and completely removed at 350°C (curve d). Starting from 300°C (curve c) also the ionic nitrates (band at 1375, 1033 cm⁻¹) start to be reduced and their reduction is complete at 400°C. It is worth noting that ionic nitrates are more resistant to the reduction with respect to the bidentate ones, but ionic nitrates start to react before the complete removing of bidentate species: this justifies the presence of the two contributions of CO consumption in TPSR measurement (Figure 2A), with a minimum near 270°C and a shoulder at 315°C.

Simultaneously to the nitrate reduction, increasing amounts of NCO surface species (band at 2225 cm⁻¹ and a very weak one at 2163 cm⁻¹) and of surface carbonates (bands at 1604, 1320 and 1066 cm⁻¹, corresponding to ν(C=O), ν(CO₂)asym and ν(CO₂)sym modes, respectively [24]) are also revealed. Actually, up to 350°C the ν(CO₂)asym mode of carbonates is superimposed with some of nitrate modes. The NCO species responsible for the band at 2163 cm⁻¹ appear only by reduction at 350°C. The two bands at 2225 and 2163 cm⁻¹ are in the same positions of the bands related to isocyanate species formed in a similar experiment accomplished (i.e. reduction with CO of stored NOₓ) on a Pt-Ba/Al₂O₃ catalyst [21]. In the literature, these bands have been assigned to isocyanate species coordinated to Al³⁺ in tetrahedral coordination and on the Ba phase, respectively [24,25,26]. However, our results obtained from experiments performed with assignment purposes do not match with literature. We found that both the bands are related to different isocyanate species on the Ba-phase [21,27,28]. For the same reasons, and on the basis of dedicated experiments (not reported because out of the aim this work), we assign both the bands found on Pt-K/Al₂O₃ catalyst to different NCO species on the K-phase.

In line with TPSR data, FT-IR experiments confirm that nitrates stored onto Pt-K/Al₂O₃ catalyst are reduced by CO at temperatures lower than that corresponding to their thermal decomposition. However, FT-IR measurements reveal a beginning of the reduction at temperatures slightly higher (250°C) than that found in the TPSR experiment (210°C). This can be related to the different operating conditions: vacuum pretreatment and static conditions for FT-IR measurements and flow conditions for TPSR ones. Moreover, FT-IR experiments confirm that onto Pt-K/Al₂O₃ catalyst a certain amount of nitrogen is still present on the surface as isocyanate species after reduction of stored nitrates with CO up to 400°C. As already mentioned, the formation of strongly adsorbed NCO species justifies the absence of N₂ evolution at the beginning of the TPSR experiment, while CO is being consumed. NCO species might be involved in N₂ formation, as
Isocyanate species formed on Pt-K/Al₂O₃ catalyst at the end of the reduction (see Figure 2B, curve e) are in very low amounts if compared with those formed in similar conditions by reduction with CO of NOₓ stored on the Pt-Ba/Al₂O₃ [21]. This statement needs some considerations. The more correct mode to support the statement should be an evaluation of the ratio between the integrated intensities of absorption bands related to NCO at the end of the reduction and of nitrate absorption bands before the reduction. In this way should be possible to evaluate the ratio between the total amount of nitrogen stored as nitrates and of nitrogen that remains at the surface after the reduction step on the two catalysts. However, while on Pt-Ba catalyst practically only ionic nitrates are presents, on Pt-K catalyst both ionic (with different spectroscopic features with respect to Pt-Ba system) and bidentate nitrates are present. The different distribution of nitrate types with different absorption coefficients on the two systems makes this kind of evaluation not feasible.

Conversely, having the NCO species the same spectroscopic features on Pt-K/Al₂O₃ and Pt-Ba/Al₂O₃ systems, it is reasonable to assume that they have the same absorption coefficients. Moreover, we have to take into account that: i) the molar amounts of K and Ba per gram of catalyst are similar on both the systems; ii) the dispersion of the basic phase is high on both the catalyst [22,29]; iii) we used discs with comparable weights; iv) the ratio between the specific surface areas of Pt-K/Al₂O₃ (176 m²/g) and Pt-Ba/Al₂O₃ (137 m²/g) is 1.3; v) the amounts of NOₓ stored at 350°C on the two systems are comparable (4.33 × 10⁻⁴ mol/g_cat. for Pt-K/Al₂O₃ and 5.8 × 10⁻⁴ mol/g_cat. for Pt-Ba/Al₂O₃) [20,21]. On the basis of these considerations, it is possible to directly compare the integrated intensities (normalized to the surface areas of the catalysts) of the isocyanate species formed in similar experiments to make an evaluation of the difference in the amounts of isocyanates formed on the two systems. These calculations suggest that the amount of isocyanates formed on Pt-K catalyst is roughly 5 times lower than that formed on Pt-Ba catalyst.

Another possibility is considering the ratio between the integrated intensities of the bands related to isocyanate species and to the carbonate species formed at the end of the reduction. In this case, no assumptions about surface areas, discs weights, amount and dispersion of the storage phase are necessary. However, it is necessary to assume: i) the same absorption coefficients for the carbonates on the surface of Pt-K and Pt-Ba systems. This is reasonable, since they show same spectroscopic features for the two catalysts; ii) a similar equilibrium between CO₂ in the gas phase and CO₂ adsorbed as carbonates on the surface of Pt-K/Al₂O₃ and Pt-Ba/Al₂O₃. Another crucial assumption is that the carbonate amounts for gram of catalyst should be the same, even if carbon consumed from CO to form NCO species is surely higher for
Pt-Ba than for Pt-K catalyst. However, the reaction pathway proposed (see infra) show the formation of an high CO₂ excess with respect to isocyanates, ensuring a negligible error in the evaluation here proposed. On the basis of these considerations, the ratio between the amounts of NCO (in the range 2330-2080 cm⁻¹) and CO₃²⁻ species (in the range 1800-1160 cm⁻¹) formed at the end of the nitrate reduction at increasing temperature is 0.27 for Pt-K/Al₂O₃ and 1.4 for Pt-Ba/Al₂O₃. This calculation suggest that, assuming constant the amount of carbonates formed on the two catalysts, the quantity of isocyanates on Pt-K system is roughly 5 times lower than that on Pt-Ba one, perfectly in line with the previous evaluation.

The calculated values are in agreement with data obtained from TPSR experiments over both Pt-K/Al₂O₃ and Pt-Ba/Al₂O₃ catalysts. In fact for Pt-Ba/Al₂O₃ catalyst [21] 43% of the stored nitrates are reduced to gaseous N-containing products and consequently 57% of nitrogen remains on the surface as isocyanates, whereas for Pt-K/Al₂O₃ 90% of the stored nitrates are reduced to gaseous N-containing products and consequently only 10% of nitrogen remains on the surface as isocyanates. This means that the quantity of isocyanates present on Pt-K system is roughly 5-6 times lower than that on the Pt-Ba one.

Finally, it is also worth noticing that, after CO interaction at 250°C up to 300°C FT-IR spectra showed two weak bands at 2052 and 2017 cm⁻¹ (Figure 2B) related to the stretching modes of linear carbonyls adsorbed on reduced Pt sites [22], indicating that the platinum is already reduced by CO at 280°C. Actually, these bands start to decrease at 350°C for carbonyl desorption with a contemporary shift to lower frequencies, as expected on decreasing the CO coverage.

**CO-ISc experiment and FT-IR study** - The reactivity towards CO of NOₓ stored at 300°C over the Pt-K/Al₂O₃ sample was investigated by performing isothermal reactivity experiments.

The results of a CO-ISc experiment run at 300°C reported and discussed in the following are collected over a sample that showed reproducible cyclic behavior, i.e. after performing few lean rich cycles (i.e. NOₓ storage and reduction by CO with an inert purge in between).

Figure 3 shows the results of a lean-rich cycle at 300°C (storage and reduction) over the Pt-K/Al₂O₃ catalyst performed by admitting 1000 ppm of NO in the presence of O₂ (3% v/v in He), followed by reduction of the stored NOₓ by admission of 2000 ppm of CO (in He). An helium purge was fed between the lean and rich phases.

As shown in Figure, the admission of 3% v/v O₂ (Figure 3, t = - 1000 sec) causes the evolution of small amount of N₂, produced by the oxidation of surface N-containing species that remain adsorbed at the catalyst surface after the previous reduction with CO. Then, upon the NO step addition (at t = 0 s) NO and NO₂ show a dead time of about 30 and 100 s respectively; their concentration rapidly increases with time approaching the asymptotic concentrations corresponding to the NOₓ feed concentration.
(NO + NO$_2$) after about 2000 s. Accordingly, significant amounts of NO$_x$ were stored (5.41 $10^{-4}$ moles/g$_{cat}$). Formation of NO$_2$ in the gas phase indicates that Pt is active in the NO oxidation reaction; as indicated in a dedicated FT-IR analysis, nitrates are the major adsorbed species present after adsorption in NO/O$_2$ at 300°C [$^{19,20}$].

![Figure 3 - ISC experiments at 300°C over the Pt-K/Al$_2$O$_3$ catalyst (storage phase: NO 1000 ppm + O$_2$ 3 % v/v in He; reduction phase: CO 2000 ppm in He).](image)

Upon admission of CO ($t = 4114$ s), ~360 ppm of N$_2$ and ~1730 ppm of CO$_2$ are immediately produced, together with negligible amounts of NO (30 ppm). CO is completely consumed for about 200 s; afterwards CO is detected at the reactor outlet: its concentration increases and approaches the inlet value within ~1700 s after CO admission. After CO breakthrough the N$_2$ and CO$_2$ concentrations (and NO production) decrease. When the nitrogen concentration is close to zero (i.e., when stored NO$_x$ are almost depleted) H$_2$ production is observed as in the case of the CO-TPSR experiment.

Worth to note that a very small increase in the catalyst temperature ($\leq 2^\circ$C) is measured upon CO admission, so that the reduction is performed under nearly isothermal conditions.

When the CO feed is stopped (after 1700 s from the CO admission), a small amount of nitrogen is produced, along with CO$_2$ (see Table 2).

The moles of CO consumed and of the different products formed during CO-ISC experiment over Pt-K/Al$_2$O$_3$ were calculated from Figure 3 and reported in Table 2. From the amounts of CO consumed and of evolved N$_2$ and CO$_2$ it appears that the reduction of the stored NO$_x$ roughly obeys the stoichiometry of reaction (2):

$$2 \text{KNO}_3 + 5 \text{CO} \rightarrow \text{N}_2 + \text{K}_2\text{CO}_3 + 4 \text{CO}_2 \quad (2)$$
The NOx reduction by CO on Pt-K/Al₂O₃ Lean NOx Trap Catalyst

<table>
<thead>
<tr>
<th>reagent and product species (moles/(g_{\text{cat}}))</th>
<th>(O_2) admission (t = -1000 s)</th>
<th>(CO) admission (t = 4114 - 5770 s)</th>
<th>(CO) shutoff (t = 5770 - 6600 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO consumed</td>
<td>-</td>
<td>(16.2 \times 10^{-4})</td>
<td>-</td>
</tr>
<tr>
<td>(CO_2) formed</td>
<td>-</td>
<td>(13.9 \times 10^{-4})</td>
<td>(0.334 \times 10^{-4})</td>
</tr>
<tr>
<td>(N_2) formed</td>
<td>(0.035 \times 10^{-4})</td>
<td>(2.61 \times 10^{-4})</td>
<td>(0.024 \times 10^{-4})</td>
</tr>
<tr>
<td>(NO) formed</td>
<td>-</td>
<td>(0.09 \times 10^{-4})</td>
<td>-</td>
</tr>
<tr>
<td>(NH_3) formed</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Moles/\(g_{\text{cat}}\) of CO consumed and of different products formed during CO-iSC carried out at 300 °C over Pt-K/Al₂O₃ (NOₓ stored at 300°C in NO/O₂ are \(5.41 \times 10^{-4}\) moles/\(g_{\text{cat}}\)).

Besides, the N-balance is almost satisfied, thus suggesting that almost all the stored NOₓ have been removed by CO. As a matter of fact, FT-IR results pointed out that only small amount of N-containing species remains onto the catalyst surface after reduction with CO (see below), but this is within the experimental error of our experiments.

The interaction of CO with the NOₓ species stored on Pt-K/Al₂O₃ catalyst in isothermal condition followed by FT-IR spectroscopy and obtained at 280°C and 350°C is presented in Figure 4 A and 4B, respectively. In Figure 4A curve a is the spectrum of NOₓ species previously stored at 350°C, whereas curves b-i correspond to the spectra recorded during interaction with CO at increasing exposure times at 280°C. As expected on the basis of the results obtained at increasing temperature, the reduction of bidentate nitrates starts before (after 30 seconds, Fig. 4A, curve b, bands at 1550, 1314, 1006 cm⁻¹) than the reduction of ionic ones (after 1 min., Fig. 4A, curve c, band at 1375, 1033 cm⁻¹). At 280°C the reaction evolves slowly and it is not completed even after 2 hours (Fig. 4A, curve i). This can be evinced by the linear intensity of the carbonate band at 1320 cm⁻¹ formed during the reduction: it should be almost the same of that of the band at 1604 cm⁻¹ (as evidenced in the experiment at increasing temperature, Fig. 2B), but this is not the case, revealing the contribution of residual ionic nitrates under the band at 1320 cm⁻¹. NCO species formed are practically only those responsible of the absorption at 2225 cm⁻¹. Furthermore, also in this kind of FT-IR experiments it is possible to observe the presence of bands in the region 2090-1880 cm⁻¹ related to the presence of carbonyls onto reduced Pt sites.

In Figure 4B curve a is the spectrum of NOₓ species previously stored at 350°C, while curves b-f correspond to the spectra recorded during CO interaction at increasing exposure times at 350°C. The reduction of nitrates is very fast since the band intensities of both bidentate and ionic nitrate are reduced markedly after 30 s of CO contact, even more after 1 min. of contact (Fig. 4B, curve c). Their consumption is complete after 4 min. (Fig. 4B, curve f), even if already at 2 min. of contact their amounts are really low, being revealed by a very weak shoulder on the high wavenumber side of the carbonate band at 1320 cm⁻¹.
Simultaneously to the nitrate reduction, the carbonate species appear, due to the adsorption of CO₂ produced during the reduction, along with NCO species (bands at 2225, 2163 cm⁻¹).

As observed for FT-IR experiment at increasing temperature, also isothermal measurements confirm that onto Pt-K/Al₂O₃ catalyst after NOₓ reduction in CO, only small amounts of nitrogen are still present on the surface as isocyanate species. Indeed, isocyanate species formed on Pt-K/Al₂O₃ catalyst at 350°C (at 280°C the reduction is not complete) are in very low amounts if compared with those formed in the same condition by reduction with CO of NOₓ stored on the Pt-Ba/Al₂O₃ catalyst [21]. As already performed for experiments at increasing temperature, it is possible to coarsely evaluate the integrated intensities of absorption bands related to NCO, or the ratio between the integrated intensities of NCO band (in the range 2330-2080 cm⁻¹) and of CO₃²⁻ absorptions (in the range 1800-1160 cm⁻¹), taking into account the same assumptions already mentioned. Whatever of the two methods of calculation is employed, the result is that the quantity of isocyanates on Pt-K system is roughly 4 times lower than that on Pt-Ba/Al₂O₃ catalyst. CO-ISC data performed on Pt-Ba/Al₂O₃ catalyst [21] showed that 58% of the stored nitrates is reduced to
gaseous N-containing products and consequently 42% of nitrogen remains on the surface as isocyanates. On this basis, we can estimate that about 10% of nitrogen, stored in form of nitrates, remains on the surface as NCO species for Pt-K/Al₂O₃.

At the end of the FT-IR reduction experiment at 350°C, the thermal stability of NCO species was also investigated by FT-IR analysis, and results are shown in Figure 5A. The prolonged outgassing at 350°C and 400°C (Figure 5A) indicates that NCO species are very stable at these temperatures; notably, on the basis of the integrated intensity of the band at 2225 cm⁻¹, 57% of the NCO species is still present after 2h of outgassing at 350°C (Fig. 5A, curve d) and 39% after 1h of outgassing at 400°C (curve e). It is also possible to evaluate the carbonate thermal stability (bands at 1600, 1320, 1064 cm⁻¹), which results lower than that of isocyanates: 31% of carbonates remains on the surface after 2h of outgassing at 350°C (Fig. 5A, curve d) and 24% after 1h of outgassing at 400°C (curve e).

![Figure 5](image_url)

**Figure 5** - A) FT-IR investigation of the thermal stability of NCO species under evacuation at 350°C and 400°C. Curve a, spectrum of NCO species formed in CO at 350°C; curves b-d, spectra after evacuation at 350°C for 10 min, 30 min and 2h, respectively; curve e, spectrum after evacuation at 400°C for 1h. B) FT-IR investigation on the reactivity of NCO species toward oxygen. Curve a, spectrum of NCO species formed at 350°C and cooled down to RT; curves b-f, spectra during treatment in O₂ (10 mbar) at 240, 280, 320, 360 and 400°C, respectively (heating at 10°C/min, spectrum recording each 2 min).
Oxidation measurements of NCO species were also performed after NO\textsubscript{x} reduction in CO at 280°C (Figure 5B): after reduction, the sample was outgassed at 350°C and then cooled down at 100°C (Fig. 5B, curve a). Then oxygen was admitted at 100°C: the sample was heated in O\textsubscript{2} at 10°C/min and the spectra were run at intervals of 2 min up to 400°C. The isocyanates are not perturbed in the range 100-240°C (not reported). Their erosion starts at 240°C (curve b) and it is complete only at 400°C (curve f). This justifies N\textsubscript{2} evolution in the ISC experiment, when oxygen is admitted after a reduction step in CO.

**Mechanistic aspects** - The results collected during CO-TPSR over K/Al\textsubscript{2}O\textsubscript{3} (Figure 1A) and over Pt-K/Al\textsubscript{2}O\textsubscript{3} (Figure 2A) highlight that in the presence of Pt the reduction of nitrate species by CO is faster considering that the onset temperature of the reaction is lower (~ 210°C vs 340°C), and the conversion of CO is higher. Besides, it appears that the reduction does not require as first step the thermal release of NO\textsubscript{x} in the gas phase since the reaction is seen at temperatures well below that of the thermal decomposition of adsorbed NO\textsubscript{x} (340°C).

The results collected during CO-ISC experiment over Pt-K/Al\textsubscript{2}O\textsubscript{3} (Figure 3) are in line with the results of CO-TPSR experiments and further indicate that the reduction at 300°C by CO of NO\textsubscript{x} stored onto the Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst is very fast and controlled by the concentration of CO. It is possible to conclude that the reduction by CO under nearly isothermal conditions of nitrates stored onto Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst at high temperature (i.e. 300°C) occurs according to a Pt catalyzed surface pathway. As it is apparent from Figure 3, this catalytic route of nitrates reduction by CO leads mainly to nitrogen and CO\textsubscript{2} in the gas phase.

It is worth noticing that a low temperature Pt-catalyzed surface pathway has already been demonstrated for the reduction by H\textsubscript{2} of NO\textsubscript{x} stored over the same catalyst used in this study \(^{[10]}\), leading mostly to nitrogen; hydrogen is more effective than CO since the onset temperature of the reduction is lower (120°C vs. 210°C). The same conclusions apply to a Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalyst used in previous works \(^{[15,21]}\) and this suggests that the reduction of stored NO\textsubscript{x} with H\textsubscript{2} and with CO over LNT catalysts might present analogies that are worth to be investigated.

The results of CO-TPSR and CO-ISC experiments over Pt-K/Al\textsubscript{2}O\textsubscript{3} (Figure 2A and 3) and of the complementary FT-IR study (Figure 2B and 4) indicate that the reduction by CO of nitrates stored onto the Pt-K/Al\textsubscript{2}O\textsubscript{3} catalyst occurs under dry conditions according to the stoichiometry of the following overall reactions:

\[
\begin{align*}
2 \text{KNO}_3 + 5 \text{CO} & \rightarrow \text{K}_2\text{CO}_3 + \text{N}_2 + 4 \text{CO}_2 \quad (2) \\
2 \text{KNO}_3 + 8 \text{CO} & \rightarrow 2 \text{KNCO} + 6 \text{CO}_2 \quad (3)
\end{align*}
\]

Reactions (2) and (3) account for the consumption of CO and of nitrates, and for the formation of CO\textsubscript{2}. In particular, reaction (3) accounts for the consumption of nitrates with formation of isocyanates (revealed by
FT-IR) and CO$_2$; reaction (2) accounts for the formation of N$_2$, CO$_2$ and carbonates at the catalyst surface, as revealed by FT-IR. The formation of isocyanates and carbonates at the surface explains the fact that the N balance and the C balance in the gas phase do not close at the end of CO-TPSR experiment. In particular, reaction (2) does not occur in the low temperature range (210-250°C) where N$_2$ is not detected.

FT-IR spectra reveal also that bidentate nitrates stored onto the catalytic surface are reduced at first and ionic ones start to be reduced later on, resulting more resistant to the CO reduction. Similar results have been obtained when H$_2$ was used as a reductant instead of CO $^{[19,20]}$; also in that case, FT-IR measurements put in evidence a different reactivity between ionic and bidentate nitrates towards H$_2$. These features well agree with TPSR data where two contribution of reductant (H$_2$ and/or CO) consumption are apparent.

The data herein discussed are consistent with the reaction pathway already proposed for N$_2$ formation in the case of Pt-Ba/Al$_2$O$_3$ $^{[21,28]}$. In that case ISC, TPSR and FT-IR results have demonstrated that large amounts of NCO species are left at the catalyst surface after reduction of CO under dry conditions; these species can be oxidized to give N$_2$ during the subsequent lean phase either by oxygen or by NO+O$_2$, NO$_2$, surface nitrites and/or surface nitrates. N$_2$ is formed primarily according to an in series two steps process where NCO species are formed first and then are converted to nitrogen upon reaction with NO$_x$ stored species. In analogy with the reaction pathway for the reduction by CO of nitrates stored over Pt-Ba/Al$_2$O$_3$ under dry conditions, the reduction by CO of nitrates stored onto the Pt-K/Al$_2$O$_3$ catalyst occurs according to the stoichiometry of the following overall reactions:

$$2 \text{KNO}_3 + 8 \text{CO} \rightarrow 2 \text{KNCO} + 6 \text{CO}_2$$

$$6 \text{KNO}_3 + 10 \text{KNCO} \rightarrow 8 \text{N}_2 + 8 \text{K}_2\text{CO}_3 + 2 \text{CO}_2$$

Hence NCO species are considered intermediates in the formation of N$_2$, whose formation occurs exclusively according to the stoichiometry of the reactions (3) + (5) (the sum giving the overall reaction (2)). Besides, analogies could be found for both the catalytic systems also with the reduction of stored nitrates by H$_2$, where an in series 2-steps molecular pathway has been proposed for N$_2$ formation involving at first the formation of ammonia upon reaction of nitrates with H$_2$, followed by the reaction of the so-formed ammonia with the residual stored nitrates leading to the formation of N$_2$ $^{[15,16,19,20]}$. The following overall reactions are involved:

$$2 \text{KNO}_3 + 8 \text{H}_2 \rightarrow 2 \text{NH}_3 + \text{KOH} + 4 \text{H}_2\text{O}$$

$$6 \text{KNO}_3 + 10 \text{NH}_3 \rightarrow 8 \text{N}_2 + 6 \text{KOH} + 12 \text{H}_2\text{O}$$

In the case of reduction by CO, NCO ad-species play as intermediate in the reduction instead of NH$_3$.

The reduction by CO of NO$_x$ stored over Ba- and K-containing catalyst shows slightly distinct features. Over Pt-Ba/Al$_2$O$_3$ only ionic nitrates were observed, giving during the CO reduction two FT-IR bands at 2222 and 2164 cm$^{-1}$ related to NCO species, whereas both bidentate and ionic nitrates are present on Pt-K/Al$_2$O$_3$ and mainly the band at 2225 cm$^{-1}$ is detected.
The CO-TPSR experiment over Pt-Ba/Al₂O₃ has shown [21,28] that the reaction of surface nitrates to give nitrogen (analogous of reaction (2)) is slower than that responsible for the initial reduction of nitrates to give NCO species (analogous of reaction (3)). The formation of nitrogen in this case via the reduction of nitrates by CO is explained as the sum of the reduction of nitrates by CO to give surface NCO species (analogous of reaction (3)) and the subsequent oxidation of these species by surface nitrates to give nitrogen (analogous of reaction (5)).

Also in the case of Pt-K/Al₂O₃ the reaction of surface nitrates to give nitrogen seems to be slower than that responsible for NCO species formation. In fact, the formation of nitrogen is observed only above 250°C while evidence for the formation of N-containing species from 210°C is provided by the consumption of CO and by the simultaneous evolution in the gas phase of CO₂ with no N-containing species. Accordingly, FT-IR measurement shows that isocyanates are formed and their storage on the surface is higher in the low temperature range. However, in this case the reaction between surface nitrates and surface NCO species to give nitrogen is faster and more efficient than over Ba-containing system. Accordingly, at the end of the CO-ISc experiments both the C and N balances close in the case of K-containing catalyst (300°C) but not over Pt-Ba/Al₂O₃ (350°C).

The reason for the higher NOₓ reduction efficiency to N₂ pointed out by the Pt-K/Al₂O₃ catalyst may be related to the higher mobility of the adsorbed surface species. It has been speculated that the reduction of the stored NOₓ implies the surface mobility of these species towards Pt, where they are reduced by the reductant [21]. In the case of CO as reductant, isocyanate species are formed as intermediates. In the suggested pathway of the reduction of stored NOₓ by CO, the rate determining step is the slow reaction between nitrates and isocyanates (reaction (5)) which involves two surface species; hence the surface mobility of the species is expected to play a major role on the reaction. It is known that K-nitrates have a melting point lower than of Ba-nitrates (334°C vs. 592°C). Along this line, K-nitrates might have a higher surface mobility that facilitate their spillover from the K component onto the Pt particles and as consequence their reaction with K-NCO species. As result, the CO reduction is more efficient over Pt-K/Al₂O₃ catalyst than over Pt-Ba/Al₂O₃ catalyst.

CONCLUSIONS
In this paper the reactivity of NOₓ stored at 350°C onto Pt-K/Al₂O₃ LNT catalyst in the reduction by CO under dry conditions was investigated by means of transient experiments (CO-TPSR and isothermal CO-ISc) and complementary FTIR study.

It was shown that the reduction by CO of nitrates stored onto Pt-K/Al₂O₃ at high temperature under nearly isothermal conditions occurs through a Pt catalyzed surface pathway, which does not involve the thermal decomposition of stored NOₓ with release of NOₓ in the gas phase and leads mainly to
nitrogen and CO₂. The reaction scheme already proposed in the case of Pt-Ba/Al₂O₃ catalyst operates also in the case of Pt-K/Al₂O₃ system and implies the formation of surface isocyanate species at first and in the second step the reaction of these superficial species with residual nitrates to give nitrogen. Over Pt-K/Al₂O₃ system this last surface reaction is more efficient than over the Ba-containing catalyst, so at the end of the reduction the amount of isocyanates species present on the surface is lower for Pt-K/Al₂O₃ then Pt-Ba/Al₂O₃ catalyst. A different mobility of the surface species involved in these reactions is invoked, having K-containing species higher mobility than Ba ones.

References

Paper V
The NOx reduction by CO on Pt-K/Al2O3 Lean NOx Trap Catalyst


Paper VI

FT-IR study of the surface redox states on platinum-potassium-alumina catalysts

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Abstract

Pt-K/Al2O3 (Pt 1%; K 5.4% wt/wt) catalyst active for the simultaneous Diesel particulate oxidation and NOx reduction have been characterized in comparison with 1% Pt/Al2O3 catalyst. IR spectra of adsorbed CO at −140 °C and at room temperature allowed the detection of oxidized Pt centers and of their very strong oxidizing ability. TPD and IR spectra of adsorbed CO2 allowed to characterize the basicity of the samples.

The data indicate that Pt centers lie in close proximity of potassium oxide species generating basicity.
1. Introduction

Platinum/alumina based catalysts are largely used in industry for several reactions, such as hydrogenations and dehydrogenations. As examples, Pt/Al₂O₃ is used in the BenSat process to hydrogenate benzene to cyclohexane in gasoline fractions [1], in the Oleflex light paraffin dehydrogenation technology and in the Pacol long linear paraffin dehydrogenation technology, all from UOP [2]. Such catalysts may also contain alkalis and additional activator metals, such as Sn [3]. Pt/Al₂O₃ based catalysts are also applied to reactions where water acts as a reactant, like for water gas shift reaction for fuel cell applications [4], and act as of promising catalysts for dry reforming of methane [5].

Platinum/alumina represents also an important system for catalytic oxidation, like the SELECTOXOTM process for the preferential oxidation of CO in the presence of hydrogen (PROX) [6]. For this reaction K is reported to act as a promoter of Pt/Al₂O₃ [7]. Pt/Al₂O₃ based catalysts containing also base metals are patented for ammonia selective oxidation (SCO) to N₂ [8], and are used as VOC catalytic oxidation catalysts [9]. For this reaction potassium may act as a promoter as well [10].

Generally speaking, alkali ions are frequently added as dopants at the surface of metal catalysts to introduce basicity or to reduce acidity, and in catalysis “assisted by basicity” [11]. Potassium is frequently preferred to sodium possibly because of its larger ionic size that limits reactivity towards supports and the formation of bulk salts, as well as results in higher basicity.

Pt-K/Al₂O₃ sorbents-catalysts, typically containing ~1 and 8%wt/wt of Pt and K have also been proposed for the “NOx storage reduction” (NSR) reaction, a recent technology developed by Toyota in the early nineties [12,13] to reduce the NOx content in the exhaust gases of lean-burn gasoline engines. A further evolution of this technology is the DPNR (Diesel particulate-NOx reduction) process, for the simultaneous NOx and soot removal [14,15]. This catalytic system works alternatively in oxidizing (lean burn) condition (where Pt is supposed to catalyze the oxidation of NO to NO₂, favouring NOx storage and soot combustion) and in reducing conditions (where Pt is supposed to catalyze the reduction of adsorbed NOx to N₂). Potassium acts as the sorbent for NOx storage [16].

While most characterization studies concern reduced noble metal catalysts, much less is known about Pt/Al₂O₃ in oxidized or unreduced state. According to some of us [17], the location of Pt species on the alumina surface is “selective”, substituting or exchanging the OH sites located on tetrahedral Al species, giving rise to isolated oxidized Pt ions, while they only perturb the OHs located over octahedral Al species. Quite in contrast with this, Kwak et al. proposed that bulk-like PtO layers form at the surface of γ-Al₂O₃ by interacting with pentacoordinated Al³⁺ species [18].

The IR spectroscopy of low temperature adsorption of CO is today a very popular technique for the characterization of solid surfaces, both of metallic and of oxide nature [19,20]. This is because CO, if adsorbed at low temperature (350–423 °C), is a very good and gentle probe for surface hydroxy-groups, cationic and
metallic centers, with small or not surface perturbation nor reactivity. When dealing with noble-metal based oxidation catalysts, this technique allows the detection of oxidized ions, which is not always an easy matter [22,24].

In this paper we will summarize our data concerning IR spectroscopy of low temperature adsorption of CO on catalysts belonging to the Pt-K/Al₂O₃ system, with the aim to clarify the role of potassium in modifying the behavior of Pt/Al₂O₃ catalysts. This characterization study has been performed with and without previous reduction, just because Pt-K/Al₂O₃ catalysts work in oxidizing conditions when working as NOx traps as well as total oxidation catalysts, while they work in reducing conditions in the short step needed to reduce adsorbed NOx.

2. Experimental

Pt-K/Al₂O₃ catalyst (Pt: ~1 wt.%, K: 5.4 wt.%) was obtained by impregnation in two sequential steps of a commercial γ-Al₂O₃ carrier (Versal 250 from UOP, surface area of 200 m²/g and pore volume near 1 cm³/g), as follows: the γ-Al₂O₃ powder was at first impregnated with a solution of Pt(NH₃)₂(NO₃)₂ (Strem Chemicals, 5% Pt in ammonium hydroxide) with an appropriate concentration so as to yield 1 wt.% Pt metal loading. After drying in air for 12 h at 80 °C and calcination at 500 °C for 5 h, the sample was impregnated with CH₃COOK (Sigma Aldrich, 99%) solution so as to yield a K content equal to 5.4 wt.%. After that, the sample was dried for 12 h at 80 °C and then calcined at 500 °C for 5 h (sample denoted as prepared, a.p. in the following). For comparative purposes, two reference binary systems, Pt/Al₂O₃ (Pt: 1 wt.%) and K/Al₂O₃ (K: 5.4 wt.%), were also prepared using the same precursors and procedures. The Pt dispersion on samples activated by heating in vacuo and subsequently in dry oxygen at 1096 °C and finally reduced in H₂ at 896 °C was estimated by hydrogen chemisorption to be 64.8% on Pt/Al₂O₃ and 71.7% on Pt-K/Al₂O₃.

IR skeletal studies have been performed using KBr pressed disks. For IR adsorption studies, pressed disks of the pure catalysts powders were activated “in situ” by using an infrared cell connected to a conventional gas manipulation/outgassing ramp. All catalysts were first submitted to a treatment in oxygen (200 Torr) at 350 °C, for 1 h, followed by evacuation at the same temperature before the adsorption experiments. In order to obtain the reduced catalysts, after the mentioned evacuation, they were put in contact with a H₂ pressure (~400 Torr) at 350 °C, two cycles for 30 min, and successively outgassed at the same temperature. CO adsorption was performed at −140 °C by the introduction of a known dose of the gas (1 Torr) inside the low temperature infrared cell containing the previously activated wafers. IR spectra were collected evacuating at increasing temperatures between −140 °C and room temperature (r.t.). Spectra have been recorded in the same temperature range by a Nicolet Nexus FT instrument.

The thermal stability of carbonate species formed on K/Al₂O₃ and Pt–K/Al₂O₃ was analyzed by thermal decomposition in inert flow (temperature programmed desorption, TPD) in a flow-reactor apparatus.
Paper VI

FT-IR study of the surface redox states on platinum-potassium-alumina catalysts

consisting of a quartz tube reactor (7mm i.d.) connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum) and to a microGC (Agilent 3000A) for the on-line analysis of the outlet gases. For this purpose after CO2 adsorption (3000ppmv/v in flowing helium) at 100 °C the sample was then heated (10 °C/min) in He up to 500 °C. 60mg of catalyst was used in each run, and the total gas flow was always set at 100cm³/min (at 0 °C and 1 atm). Before catalytic tests, the samples have been heated at 500 °C in He to remove any adsorbed species on the catalytic surface.

3. Results and discussion

3.1. Surface hydroxyl groups

The spectra of the pure powder pressed disks of both K/Al₂O₃ and Pt-K/Al₂O₃ samples before any activation treatment are very similar (see Fig. 1 for Pt-K/Al₂O₃) and show the strong bands of carbonate and hydroxide species with additional features at 3443, 3411, 1550, 1406, 997cm⁻¹. The absence of evident scissoring mode of water suggests that this species is essentially an hydroxy carbonate species. A similar spectrum was found previously for a 12% wt/wt K₂CO₃-Al₂O₃ catalyst [25]. Outgassing at 350 °C of both K/Al₂O₃ and Pt-K/Al₂O₃ samples causes the almost complete disappearance of these bands, suggesting that such species are decomposed with release of CO₂ and water. Both samples show, after activation at 350 °C, only weak bands in the region 1700–1200cm⁻¹ (see Fig. 1 for Pt-K/Al₂O₃), due to surface impurities (carbonates and/or carboxylates).

Fig. 1. FT-IR spectra of pure powder pressed disk of the Pt-K/Al₂O₃ sample after brief outgassing at r.t. and after activation at 350 °C.
As expected, all samples show bands in the region 3800–3400 cm⁻¹ (Fig. 2), due to OH stretchings of surface hydroxy groups. In the case of alumina support we find maxima at 3726, 3675 and 3575 cm⁻¹, with additional shoulders at 3765 cm⁻¹ and near 3500 cm⁻¹. This spectrum is quite typical for γ-Al₂O₃ samples outgassed at medium temperature. Our previous studies [26] suggested that the higher frequency component at 3765 cm⁻¹ is due to terminal hydroxy-groups bonded to Al ions in a tetrahedral-like environment, the splitting being associated to vacancies with respect to the spinel-type composition. The band at 3725 cm⁻¹, instead, is present also at the surface of α-Al₂O₃ and of stoichiometric spinels, and is consequently likely due to terminal OHs on Al ions in octahedral-like environment. The additional components at 3675 and 3575 cm⁻¹ are assigned to bridging and triply bridging OHs, respectively.

![FT-IR spectra](image)

Fig. 2. FT-IR spectra of pure powder pressed disks of the catalysts after activation at 350 °C (OH stretching region).

The Pt/Al₂O₃ sample shows, in these conditions, a quite similar spectrum with respect to the support, but the intense band at 3725 cm⁻¹ on alumina is shifted a bit upwards and significantly weakened in intensity. A similar result was observed previously with respect to another Pt/Al₂O₃ catalyst [17]. The K/Al₂O₃ sample shows the lower frequency feature broadened and shifted to near 3500 cm⁻¹, while all higher frequency features are definitely weaker than on the support. This is likely due to partial K⁺ for H⁺ cationic exchange. Here we find very sharp a band at 3719 cm⁻¹ with a shoulder at 3750 cm⁻¹. The position of this band is similar to that reported previously for different K-Al₂O₃ samples (3715 cm⁻¹ [27]) and for a 12% wt/wt K₂CO₃-Al₂O₃ catalyst (3710 cm⁻¹ [25]). On titania, K doping causes the formation of a band at 3720–3712 cm⁻¹ [28]. The spectrum of the Pt-K/Al₂O₃ sample is very similar to that of K/Al₂O₃.
3.2. IR study of the adsorption of carbon monoxide

In Fig. 3 the spectra of carbon monoxide adsorbed on the support γ-Al₂O₃ (upper spectra, A–C) as well as on the K/Al₂O₃ (lower spectra, D–F) are reported and compared. In the left parts of the figure the spectra are recorded during adsorption after admission of CO into the cell, in the right section the spectra recorded during outgassing upon warming. At the highest coverages the main maximum on alumina is at 2153 cm⁻¹. Looking at the OH stretching region (see the insert C in Fig. 3) it is evident that this band is associated to the H-bonding of CO with surface hydroxygroups. Upon this interaction, the band at 3725 cm⁻¹ is involved partially, being shifted in part to near 3600 cm⁻¹. The component at 3675 cm⁻¹ seems almost not involved, being still evident. The shift of the OH stretching band is, consequently, in the range ΔνOH ~ 125 cm⁻¹, which allows to denote the alumina’s OH as medium strength Brønsted acid sites. Thus the band at 2153 cm⁻¹ is attributed to CO H-bonded on the terminal hydroxy groups of alumina on Al ions in octahedral-like environment. In agreement with this assignment, this band disappears fast upon outgassing at low temperature.

![FT-IR spectra](image)

**Fig. 3.** FT-IR spectra of Al₂O₃ (A–C) and of K/Al₂O₃ (D–F) at −140 °C after admission of CO gas into the cell until saturation (A and D) and upon outgassing at increasing temperatures from −140 to −90 °C (B and E). In the inserts C and E: OH stretching region of the samples at −140 °C before (a) and after (b) saturation with CO, and the corresponding difference (after saturation−before saturation).

A weaker feature, more resistant to outgassing, is observed at higher frequencies, shifting from near 2180 cm⁻¹ to 2192 cm⁻¹ upon outgassing. It does not correspond to any perturbation of the νOH bands. It is assigned to CO species interacting with Lewis acidic Al³⁺ cations. The shift with respect to νCO of gas or liquid CO is relatively weak, and this shows that after outgassing at 350 °C the strongest Lewis sites of alumina are still not produced, being the surface still in a highly hydroxylated state.
In the low section of Fig. 3 the spectra of carbon monoxide adsorbed on sample K/Al₂O₃ are reported. At the highest coverages the main maximum is at 2144cm⁻¹, i.e. definitely lower than in the case of pure alumina. The height of the band is similar in the two cases. However, the shape of the band is different, being definitely broader for K/Al₂O₃. A deconvolution of this spectrum is shown in Fig. 4, where it is superimposed to the band observed on alumina. At least two components are evident in the deconvolution of the spectrum observed on K/Al₂O₃, located at 2149cm⁻¹, less intense, and at 2139cm⁻¹, more intense. Looking at the OH stretching region (compare inserts C and d in Fig. 3) we note here that the spectrum is, in this region, less perturbed. The sharp band at 3714cm⁻¹ is shifted up to 3723cm⁻¹, certainly due to a secondary interaction. No H-bonding with CO is found in this case. Our data support the assignment of this band to CO adsorbed on two different families of K⁺ ions. In fact, the position of this band is at slightly lower frequency than that found on K-zeolites (2170–2150cm⁻¹ [29]) where K ions are bonded to a less basic structure. Low temperature CO adsorption on K₂O–TiO₂ was reported previously to produce a band at 2148cm⁻¹ [28]. At least two different families of potassium ions are formed, differing in their Lewis acidity.

The data reported here show that, over this heavily K-doped alumina, the surface hydroxy groups have totally lost their Brønsted acidity and K⁺ ions display very weak Lewis acidity, although they appear to be well exposed at the surface. The weaker feature, more resistant to outgassing, found near 2175cm⁻¹, is assigned to CO species interacting with residual Lewis acidic Al³⁺ cations. The position of this band, shifted downwards with respect to pure alumina, and the intensity, definitely weaker than on pure alumina (compare Fig. 3, A and B, with Fig. 3, C and D, and see Fig. 4), show that potassium species cover the surface, mainly interacting with the strongest Lewis sites.

Thus only part of weaker Lewis sites of alumina are residual, in small amounts. This result is quite similar to that reported previously for K-doped alumina using pyridine and nitrile as the probes [27].
In Fig. 5 the spectra of carbon monoxide adsorbed on the Pt/Al₂O₃ catalyst are reported. In the upper part of the figure (A) the spectra are recorded during adsorption after admission of CO into the cell, in the lower section (B) the spectra recorded during outgassing upon warming. At the highest coverages the main maximum is at 2158 cm⁻¹, i.e. 5 cm⁻¹ higher than on pure alumina. Looking at the OH stretching region (see the insert C in Fig. 5) it is evident that this band is associated to the H-bonding of CO with surface hydroxy-groups. Upon this interaction, the band at 3735 cm⁻¹ is involved partially, being shifted in part to near 3600 cm⁻¹. Actually, we find two unresolved components at 3610 and 3540 cm⁻¹. The component at 3675 cm⁻¹ seems again almost not involved, being still evident. The shift of the OH stretching band is, consequently, in the range ΔvOH ~ 125–200 cm⁻¹. In any case it seems that the Brønsted strength of alumina’s OH is not much perturbed by addition of Pt, being perhaps a little strengthened, in agreement also to the slight shift up of the corresponding νCO.

![FT-IR spectra](image)

**Fig. 5.** FT-IR spectra of unreduced Pt/Al₂O₃ at −140 °C after admission of CO gas into the cell until saturation (A) and upon outgassing at increasing temperatures from −140 to −90 °C (B). In the inserts: (C) OH stretching region of unreduced Pt/Al₂O₃ at −140 °C before and after saturation with CO, and the corresponding difference (after saturation–before saturation); (D) the spectrum of CO adsorbed just after admission (lowest coverage); (E) the spectrum of residual CO adsorbed after outgassing at −90 °C.

On the other hand, a weak tail at lower frequency is observed on the spectrum recorded during adsorption, which is more clearly evident upon desorption as a single band centred at 2085 cm⁻¹. This absorption is typical for terminal carbynls on Pt° particles whose average size is of the order of few nanometers [30]. Upon outgassing and warming, a band also grows at 2346 cm⁻¹, due to OCO asymmetric stretching of adsorbed CO₂. This reactivity is not found on pure alumina. This shows that unreduced Pt centers exist and are able to oxidize CO to CO₂. Quite obviously, the second oxygen atom comes from the oxide species balancing Pt cations.
Also on Pt/Al$_2$O$_3$ a band more resistant to outgassing is observed at higher frequencies, shifting from near 2188 cm$^{-1}$ to 2195 cm$^{-1}$ upon outgassing. This absorption is in the region of bands typically assigned to CO species interacting with Lewis acidic Al$^{3+}$ cations.

The same experiment has been performed with pre-reduced Pt/Al$_2$O$_3$, as shown in Fig. 6. In this case the main band is in the same position than on pure alumina (2153 cm$^{-1}$). The formation of CO$_2$ is much lower, confirming that our mild reduction pre-treatment reduced a large part of cationic Pt. The carbonyls on zerovalent Pt are evident but the maximum is at a definitely higher frequency (2098 cm$^{-1}$), suggesting that larger metal particles are formed by reduction. However, the band is large with components at lower frequency suggesting a large distribution of particle size. On the other hand, in agreement with the well-known preference of CO adsorbed over metallic Pt for on-top position, due to electronic factors [3], we do not find evidence of bands of bridging species, in fact usually not observed or extremely small in low loading Pt- Al$_2$O$_3$ [30,32].

![Fig. 6. FT-IR spectra of prereduced Pt/Al$_2$O$_3$ at −140 °C after admission of CO gas into the cell until saturation (A) and upon outgassing at increasing temperatures from −140 to −90 °C (B). In the inserts: (C) OH stretching region of prereduced Pt/Al$_2$O$_3$ at −140 °C before and after saturation with CO, and the corresponding difference (after saturation–before saturation); (D) the spectrum of CO adsorbed just after admission (lowest coverage); (E) the spectrum of residual CO adsorbed after outgassing at −90 °C.](image)

In Fig. 7 the spectra of CO adsorbed on Al$_2$O$_3$, unreduced Pt/Al$_2$O$_3$ and reduced Pt/Al$_2$O$_3$ and their deconvolutions are reported. The deconvolution of the spectrum of CO adsorbed on alumina allows to only separate the component due to CO interacting with Al$^{3+}$, found at 2183 cm$^{-1}$, from that due to CO H-bonded on OHs, found at 2152 cm$^{-1}$. In the case of the spectrum of CO adsorbed on unreduced Pt/Al$_2$O$_3$ the higher frequency band increases in intensity and shifts up to 2186 cm$^{-1}$, the most intense band shifts up a little bit to 2155 cm$^{-1}$ while a new absorption appears clearly centered at 2135 cm$^{-1}$. In the case of reduced Pt/Al$_2$O$_3$
the higher frequency band shifts back down to 2183cm⁻¹ and decreases in intensity, the most intense band shifts also back to 2153cm⁻¹, while the new absorption increases in intensity and shifts up to 2139cm⁻¹.

Fig. 7. FT-IR spectra of CO adsorbed on Al₂O₃, on unreduced and prerduced Pt/Al₂O₃ at −140 °C at saturation (pointed lines), and deconvolution of the spectra.

These data suggest that highly oxidized and oxidizing Pt ions contribute to the band at 2186cm⁻¹, and are reduced in the reduced sample. We assign the band at 2186cm⁻¹ predominantly to Pt⁻¹–CO (with n = 4 or 2). The band at 2135–2139cm⁻¹ should be assigned to another form of Pt⁻¹–CO, less oxidized and less oxidant, with n = 2 or 1. The amount of the latter species should increase by reduction of the former one. These assignments are consistent with data arising from different authors (reviewed in Ref. [20]) as well as with a previous study from one of our laboratories [17].

In Figs. 8 and 9 the spectra of carbon monoxide adsorbed on the Pt-K/Al₂O₃ catalyst unreduced and reduced, respectively, are reported. At the highest coverage the spectrum is dominated by the band assigned to carbonyl species on K⁺ centers. In this case, as for the experiment done with K/Al₂O₃, this band is evidently split into two partially resolved components, as shown by the deconvolutions reported in Fig. 4, located at 2149–2150 and near 2139–2140cm⁻¹. It seems that the intensity of the higher frequency components increases for the unreduced Pt-K/Al₂O₃ sample with respect to K/Al₂O₃, but decreases back for reduced Pt-K/Al₂O₃. Maybe carbonyls of cationic Pt may contribute to the higher frequency component here. In any case the quality of the two K⁺ sites is fully unchanged as an effect of the presence of small amounts of platinum. Also in these cases, like for K/Al₂O₃, the adsorption of CO does not result in any direct interaction with surface OHs. In fact the only perturbation of the OH stretching band consists in a very slight shift up of the band observed at 3719cm⁻¹. This confirms that, at these high K loading levels, surface OHs exist but do not show any Brønsted acidity.

The presence of reduced zerovalent Pt centers is evident on the unreduced Pt-K/Al₂O₃ sample, due to the presence of a broad band of carbonyl species at 2075–2065cm⁻¹. The lower frequency observed for these Pt⁺ carbonyls with respect to those observed on Pt/Al₂O₃ is likely due to the effect of the increased basicity of the neighbouring [23]. On the other hand, reductions seem to give rise to better defined Pt particles, where CO adsorbs on-top producing a sharp maximum at 2072cm⁻¹ with a tail at lower frequencies.

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FT-IR study of the surface redox states on platinum-potassium-alumina catalysts
FT-IR study of the surface redox states on platinum-potassium-alumina catalysts

Fig. 8. FT-IR spectra of unreduced Pt-K/Al$_2$O$_3$ at –140 °C after admission of CO gas into the cell until saturation (A) and upon outgassing at increasing temperatures from –140 to –90 °C (B). In the inserts: (C) OH stretching region of unreduced Pt-K/Al$_2$O$_3$ at –140 °C before and after saturation with CO, and the corresponding difference (after saturation–before saturation); (D) the spectrum of CO adsorbed just after admission (lowest coverage); (E) the spectrum of residual CO adsorbed after outgassing at –90 °C.

Fig. 9. FT-IR spectra of prereduced Pt-K/Al$_2$O$_3$ at –140 °C after admission of CO gas into the cell until saturation (A) and upon outgassing at increasing temperatures from –140 to –90 °C (B). In the inserts: (C) OH stretching region of prereduced Pt-K/Al$_2$O$_3$ at –140 °C before and after saturation with CO, and the corresponding difference (after saturation–before saturation); (D) the spectrum of CO adsorbed just after admission (lowest coverage); (E) the spectrum of residual CO adsorbed after outgassing at –90 °C.

In this experiment the oxidation of CO to CO$_2$ is more limited than on the K-free catalyst, but is not much affected by pre-reduction, suggesting that Pt is more reduced already in the unreduced sample. This may be associated to a higher reactivity of Pt cations as an effect of the presence of potassium, that
consequently reduces by decomposition already during outgassing at 350 °C. To reveal whether CO adsorption is able to detect unreduced Pt centers on Pt-K/Al₂O₃ sample, we analyzed the subtraction spectra of CO adsorbed on reduced and unreduced sample (Fig. 10) after outgassing at −130 °C. While the absorption of CO on metallic Pt is well evident only on the reduced sample, as expected indeed, and appears as a negative peak in the subtraction, in the higher frequency region a small peak at 2150cm⁻¹ is evident as a positive peak, together with an even smaller feature near 2120cm⁻¹. It is possible that these very weak bands arise from Pt⁺⁺–CO species over the unreduced sample, although a small perturbation of the K⁺–CO band could also be responsible for them.

Fig. 10. FT-IR spectra of CO adsorbed on unreduced and pre-reduced Pt-K/Al₂O₃ at −140 °C at saturation, and subtraction of the spectra.

The spectra we report in Fig. 9 are well different with respect to those reported in the literature for CO adsorption on similar catalysts [34,36], which have, however, been recorded at r.t. To compare better with spectra reported in the literature, we also performed experiments of CO adsorption at room temperature. The spectrum obtained on reduced Pt-K/Al₂O₃ sample, after room temperature adsorption of CO and short room temperature outgassing is reported in Fig. 11a. The band due to CO interacting with K⁺ ions as well as with Al³⁺ and Pt⁺⁺ ions (i.e. at νCO > 2100cm⁻¹) cannot be observed at r.t., as indeed expected to the weakness of these interactions which are only detectable at low temperature. However, a stronger band is observed in the field of terminal carbonyls on platinum, centred at 2056cm⁻¹, with a prominent shoulder centred at 2008cm⁻¹, while an additional band is found at 1800cm⁻¹, in the typical region of bridging carbonyls. Additionally, also very strong bands are observed at 1580 and 1332cm⁻¹, that should be assigned to carbonate ions, which are observed much weaker at low temperature, in parallel to the formation of CO₂. The spectrum we observe in these conditions is similar to those reported by other authors at room or
higher temperatures, on similar catalysts. Derrouiche et al. [34] with a 2.9% Pt-10%K-Al₂O₃ catalyst observe at room and higher temperatures bands at 2050, 1950 and 1763 cm⁻¹, assigned to linear and bridging CO on Pt⁺, and species adsorbed on a Pt-K site, respectively. Prinetto et al. [35,36] at room temperature find a similar spectrum, with a band in the region 2045–2015 cm⁻¹ assigned to on-top carbonyls on Pt⁺, a band at 1945–1955 cm⁻¹, of uncertain assignment, and a third band at 1735–1690 cm⁻¹, assigned to bridging carbonyls. In fact the experiments of CO adsorption at room or higher temperatures are affected by the reactivity of CO itself, that produces also relevant amounts of carbonate species and CO₂, and perhaps undetectable carbide species, that likely modify the state of the surface and may be also responsible for the band in the 1800–1700 cm⁻¹ region [37] previously assigned to bridging CO. Other works report that bridging carbonyls on Pt absorb in the 1950–1850 cm⁻¹ range on both low index faces [38] and on stepped surfaces [39]. In an early work [25] it has been reported that CO adsorption on 12% wt/wt K₂CO₃-Al₂O₃ catalyst does not give rise to any carbonyl formation but produces (in the absence of oxidizing agents) further carbonates, like observed here for Pt-K/Al₂O₃, confirming some kind of Boudouard-like reactivity.

Interestingly, upon outgassing at 100 °C (Fig. 11b) the bands of carbonate species even grow, likely due to the further oxidation of CO by unreduced Pt centers. The spectra of carbonate species are in similar (although not identical) positions as those observed upon adsorption of carbon dioxide over the same reduced surface (Fig. 11c).

![Fig. 11. FT-IR spectra of CO adsorbed on prereduced Pt-K/Al₂O₃ at r.t. (a) and after outgassing at 100 °C (b), and spectrum of CO₂ adsorbed on prereduced Pt-K/Al₂O₃ at r.t. (c).](image)

Low temperature adsorption experiments allow the observation of weakly acidic but very active sites like K⁺, not observed in room or higher temperature experiments, but also to avoid excessive reactivity of CO, finally giving a more precise picture of the state of the surface. However, room temperature experiments may perhaps provide evidence for some kind of “activated” adsorption phenomena, allowing several kinds
of different adsorption modes needing some energy to be allowed. The spectra observed after adsorption of CO on the Pt-K/Al₂O₃ catalyst, in analogy with those reported recently for Pt-Na/TiO₂ catalysts \(^\text{[46]}\), show the shiftdown of the absorption due to terminal carboxyls and the increased formation of bridging species caused by the addition of potassium. This could be interpreted as a further evidence of the increased electron-donating character of Pt metal centers when potassium is copresent. However, the difference among the spectra recorded at low and room temperature is indicative of more complex interactions occurring at room temperature that need some activation energy to be established. We suggest the occurrence, only upon adsorption at sufficiently high temperatures (room and higher), of complex interactions similar to those occurring on some deeply cation exchanged alkali zeolites such as Na\(^+\), K\(^+\) and Cs-ferrierite \(^\text{[41]}\). In this case, in addition of the normal C-bonding of CO to metal centers, additional interaction occurs either through the oxygen lone pairs or through the \(\pi\)-type orbitals, leading to a lowering of CO stretching frequency. We tentatively suggest that some kind of additional interaction of Pd\(^{2+}\)-carbonyls with K\(^+\) cations may be established on Pt-K/Al₂O₃ catalyst only at room or higher temperatures.

3.3. IR spectra of adsorption of CO₂ adsorption and CO/CO₂ coadsorption

In Fig. 12 the IR spectra obtained after CO₂ adsorption on Al₂O₃, on K/Al₂O₃ and on unreduced and reduced Pt-K/Al₂O₃ are compared.

![Fig. 12. FT-IR spectra of CO₂ adsorbed on Al₂O₃, K/Al₂O₃ and unreduced and prereduced Pt-K/Al₂O₃ at r.t. at saturation.](image)

The spectra obtained on K/Al₂O₃ and both reduced and unreduced Pt-K/Al₂O₃ are almost identical, being dominated by features typical of bridging or bidentate carbonates (main features at 1607, 1326 and 1076 cm\(^{-1}\) \(^\text{[42]}\)), in contrast to the bands at 3618 (not shown), 1654, 1437 and 1230 cm\(^{-1}\), due to surface bicarbonate species. These data confirm the significant basicity (or acidobasicity) induced by potassium that totally transforms at these loading levels the acidobasicity of alumina. This is also evident from the CO₂-TPD curves shown in Fig. 13. While CO₂ desorption from Pt/Al₂O₃ is complete already at 200°C, to have
an almost complete desorption from Pt-K/Al₂O₃ 350°C are needed with a small desorption of CO₂ also at 500 °C. Also the amount of CO₂ desorbed from Pt-K/Al₂O₃ is more than 5 times that desorbed from Pt/Al₂O₃.

![Fig. 13. TPD curves of CO₂ from Pt/Al₂O₃ and Pt-K/Al₂O₃.](image)

To have a further indication on the role of K-Pt interactions, we performed an experiment of sequential adsorption of CO₂ and CO over the reduced Pt-K/Al₂O₃ catalyst. In Fig. 14a, the spectrum of the reduced Pt-K/Al₂O₃ is reported. We note that the sample shows two very weak absorptions at 1562 and 1355cm⁻¹ which can be assigned to carboxylate/carbonate impurities arising from chemicals used in the preparation (e.g. acetate ions used in potassium impregnation). Additionally the spectrum shows a residual weak band at 2048cm⁻¹ (Fig. 14a), which may be attributed to CO stretching of Pt carbonyl species, that probably also origin from the conversion of chemicals used in the preparation. The frequency observed is in the same range as that observed in the experiment of CO adsorption at r.t. in Fig. 11. Adsorption of carbon dioxide causes, as said, the formation of the bands of carbonates (main maxima at 1607 and 1326cm⁻¹) and linearly adsorbed CO₂ (2345cm⁻¹). Additionally, the shift up to 2082cm⁻¹ of the band previously observed at 2048cm⁻¹ is also evident (Fig. 14b). The band resists in this position also after outgassing at r.t. (Fig. 14c), that causes the disappearance of molecularly adsorbed CO₂ but leaves bridging carbonates on the surface. This indicates that Pt species responsible for the strongest adsorption of CO is sensitive to the presence of carbonate species, thus being very likely located near the basic sites where carbonates form. Further additional contact with CO produces a new maximum now at 2066cm⁻¹. As shown by the comparison reported in Fig. 15, the spectrum observed after CO adsorption on the “carbonate precovered” reduced surface is very similar (in the 2200–1800cm⁻¹ region) to that observed after CO adsorption on the clean reduced surface, but definitely less intense. The main maximum is observed at 2066cm⁻¹ (Fig. 15c), i.e. at an intermediate position between those observed on the reduced surface at room (2056cm⁻¹, Fig. 15b) and
at low temperature (2072 cm\(^{-1}\), Fig. 15a). These data indicate that Pt centers should lie in close proximity of potassium oxides generating basicity. In fact part of Pt sites seem to be “poisoned” by carbonate species formed on K oxide centers, while part of them are perturbed electronically by the presence of such species, thus showing higher CO stretching frequencies.

![FT-IR spectra of activated prereduced Pt-K/Al\(_2\)O\(_3\) at room temperature (a), after adsorption of CO\(_2\) (b), after outgassing at r.t. (c) and after successive adsorption of CO (d).](image1)

Fig. 14. FT-IR spectra of activated prereduced Pt-K/Al\(_2\)O\(_3\) at room temperature (a), after adsorption of CO\(_2\) (b), after outgassing at r.t. (c) and after successive adsorption of CO (d).

![Comparison of the FT-IR spectra of CO adsorbed on prereduced Pt-K/Al\(_2\)O\(_3\) at −140°C (a) and at room temperature (b), and over CO\(_2\)-precovered prereduced Pt-K/Al\(_2\)O\(_3\) at room temperature (c).](image2)

Fig. 15. Comparison of the FT-IR spectra of CO adsorbed on prereduced Pt-K/Al\(_2\)O\(_3\) at −140°C (a) and at room temperature (b), and over CO\(_2\)-precovered prereduced Pt-K/Al\(_2\)O\(_3\) at room temperature (c).
4. Conclusions

The data discussed above allow us to draw the following conclusions.

1. Platinum in small amounts on alumina does not affect the number and the strength of Lewis acid sites of hydroxylated alumina. This suggests that Pt atoms tend to locate over basic sites of alumina.

2. Unreduced Pt deposited on alumina upon outgassing at 350 °C gives rise to at least three different species: i) highly oxidizing Pt cations (Pt⁴⁺ or Pt²⁺), whose carbonyls are found at 2186 cm⁻¹; ii) less oxidizing Pt cations (Pt²⁺ or Pt⁺) whose carbonyls are found at 2135–39 cm⁻¹; iii) well dispersed reduced zerovalent Pt particles whose carbonyls are found at 2085 cm⁻¹. Highly oxidizing Pt cations are so active to oxidize CO to CO₂ at 150 K.

3. Mild reduction in our condition reduced highly oxidizing Pt cations to the less active cationic species and perhaps to the zerovalent state. In any case, zerovalent Pt tends to coalesce to give rise to larger particles characterized by CO of carbonyl species at 2098 cm⁻¹. No bridging carbonyl species are found in these conditions.

4. The presence of K in Pt-K/Al₂O₃ catalysts seems to increase the reducibility of Pt, whose highly oxidizing species are not observed after outgassing at 350 °C. Additionally, the basicity of K/Al₂O₃ increases the electron density on reduced Pt, as evidenced by the slightly lower CO stretching frequency of Pt carbonyls.

5. The comparison of the data obtained upon low temperature adsorption of CO with those obtained by adsorption at room temperature show that CO acts, at room temperature, not as a completely inert probe. In fact, the formation of carbonates without any oxidant (except Pt species, in case) and the relevant modification of the spectrum of adsorbed CO suggest some reactivity of CO at r.t. On the other hand, already at −100 °C CO reduces a small part of the surface Pt ions producing CO₂. This makes low-temperature CO adsorption experiments an informative tool for the surface characterization.

6. Pt species are located near the basic oxide species of the K/Al₂O₃ “support” and their behavior is influenced by the presence of adsorbed carbonate species.

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FT-IR study of the surface redox states on platinum-potassium-alumina catalysts

References

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Paper VII

Pathways for N₂ and N₂O formation during the reduction of NOx over Pt-Ba/Al₂O₃ LNT catalysts investigated by labelling isotopic experiments

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Abstract
Mechanistic aspects involved in the formation of N$_2$ and of N$_2$O during the reduction of gas-phase NO and of NO$_x$ stored over a model PtBa/Al$_2$O$_3$ NSR catalyst are investigated using unlabelled ammonia and labelled NO. The reduction of the stored NO$_x$ species (labeled nitrites and nitrates) with NH$_3$ leads to the selective formation of N$_2$ as major product and of small amounts of nitrous oxide. Based on the nitrogen isotopic distribution, it appears that N$_2$ formation occurs primarily through the statistical coupling of N-atoms formed by dissociation of NO$_x$- and NH$_3$-related surface intermediates, although an SCR-pathway (involving the coupling of NH$_3$- and NO-derived ad-species) is also likely to occur. It appears as well that the formation of nitrous oxide involves either the coupling of two adsorbed NO molecules or the recombination of an adsorbed NO molecule with an adsorbed NH$_x$ fragment.

Keywords
Isotopic labelling experiments, PtBa/Al$_2$O$_3$ NSR catalysts, NOx Storage-reduction, reduction of nitrites, reduction of nitrates.
Pathways for N2 and N2O formation during the reduction of NOx over Pt-Ba/Al2O3 LNT catalysts

Introduction

Both diesel- and lean burn gasoline-powered vehicles are spreading in the transportation sector due to higher efficiency and lower fuel consumption if compared to the traditional stoichiometric engines. The Three Way Catalytic (TWC) converters, currently used for stoichiometric gasoline engines, are not effective in the reduction of NOx for lean burn engines, which operate in the presence of excess oxygen. Viable solutions for the control of NOx are in these cases the urea-SCR technique and the NOx Storage Reduction (NSR) or Lean NOx Trap (LNT) system. To date, the urea-SCR technology is preferred for heavy-duty vehicles and minivans, whereas LNTs are preferred for small engines. Besides, hybrid LNT/SCR systems have also been proposed.

In the NSR technology long lean phases - typically lasting 60–90 s, during which NOx are stored on the catalyst - are alternated with short rich periods – in the order of few seconds - where the exhaust is deliberately made rich. The trapped NOx are reduced to N2 although other by-products may be released (NO, N2O, NH3). NSR catalysts are composed of a high surface area support material (often γ-alumina or stabilized alumina), precious metals (usually a combination of Pt and Rh) and basic components, such as Ba or K, which act as NOx storage material.

Mechanistic aspects of the reduction of NOx stored over NSR catalytic systems have been investigated by several groups. It has been shown that the reduction of stored nitrates by hydrogen under nearly isothermal conditions (i.e. in the absence of significant thermal effects upon the lean/rich switch) does not involve the thermal decomposition of the adsorbed NOx species as a preliminary step, but instead occurs via a Pt-catalyzed route already active at low temperatures. Besides, it has been suggested that N2 is formed through a two-steps in series molecular pathway involving the fast reaction of nitrates with hydrogen to give ammonia, followed by the slower reaction of the so-formed NH3 with residual stored nitrates to give N2. Due to the high reactivity of H2 towards nitrates, and to the integral nature of the reactor, an hydrogen front develops in the reactor so that NH3 reacts with nitrates stored downstream the H2 front to give nitrogen. This has been clearly demonstrated by spaciMS measurements showing the intra-catalyst spatiotemporal species distributions during regeneration with H2 of a Pt-Ba/Al2O3 LNT trap. As also pointed out by a dedicated kinetic analysis, the development of an H2 front travelling in the reactor, along with the occurrence of the above two-steps in series pathway, is able to account for the temporal sequence of products observed at the reactor exit during the regeneration of NSR catalysts.

Based on these findings, it appears that N2 formation during the regeneration of NSR catalysts occurs via the reaction of ammonia with stored NOx. Mechanistic aspects of this reaction are still largely unclear: this has motivated the present study where the possible routes leading to the formation of N2 during the reaction of NH3 with the stored NOx have been investigated. For this purpose, isotopic labeling experiments have been carried out using unlabeled NH3 and 15NO as a source for the stored 15NOx. Since nitrites and
nitrates can be formed on the catalyst surface upon NO adsorption in the presence of O₂ at low and high temperature respectively, the reactivity of these adsorbed species with gaseous NH₃ has been investigated. The reactivity of NH₃ and ¹⁵NO in the gas phase has also been studied for comparison purposes. This allowed to better clarify mechanistic aspects involved in the formation of N₂ during regeneration of NSR catalysts, as detailed below.

Materials and Methods

Catalysts preparation and characterization – An homemade Pt-Ba/Al₂O₃ (1/20/100 w/w) catalyst has been used in this study. The catalytic system has been prepared by incipient wetness impregnation of a commercial alumina sample (Versal 250 from UOP) with aqueous solution of dinitro-diammine platinum (Strem Chemicals, 5% Pt in ammonium hydroxide) and subsequently with a solution of Ba acetate (Aldrich, 99%). The powder has been dried at 80°C and calcined in air at 500°C for 5h after each impregnation step. The impregnation order (first Pt and then Ba) has been chosen in order to ensure a good dispersion and stability of the noble metal and of the alkaline component on the alumina support, in line with recipes of Toyota patents.

The specific surface area of the sample, determined by N₂ adsorption–desorption using a Micromeritics TriStar 3000 instrument, is 160 m²/g (BET method). The Pt dispersion was also estimated by hydrogen chemisorption at 0°C (TPD/R/O 1100 Thermo Fischer Instrument); a value of 52% has been obtained.

Catalytic tests - Catalytic tests have been performed in a quartz tube micro-reactor (7 mm I.D.) loaded with 60 mg of catalyst powder (70-100 µm). A total flow of 100 cm³/min (at 1 atm and 0°C) has been used in the experiments, resulting in a GHSV of 10⁵ h⁻¹ being the density of the catalyst bed very close to 1 g/cm³. The reactor outlet was directly connected to a mass spectrometer (Thermostar 200, Pfeiffer), an UV-NOₓ analyzer (LIMAS 11HW, ABB) and a micro-gas chromatograph (Agilent 3000A) for on-line analysis of the reaction products.

Prior to the catalytic activity runs, the catalyst sample has been conditioned by performing a few storage/regeneration cycles. For this purpose NOₓ has been adsorbed at 350°C by imposing a rectangular step feed of NO (1000 ppm) in flowing He + 3% v/v O₂ until catalyst saturation. Then the NO and O₂ concentrations have been stepwise decreased to zero, followed by a He purge at the same temperature (350°C). This leads to the desorption of weakly adsorbed NOₓ species. After the He purge, catalyst regeneration (rich phase) has been carried out with H₂ (2000 ppm in He). Conditioning lasted until a reproducible behavior was obtained; this typically required 3-4 adsorption/reduction cycles. The conditioning procedure terminated with a reducing step; accordingly before the subsequent experiments the catalyst surface was free of any adsorbed NOₓ species.
After catalyst conditioning at 350°C, Temperature Programmed Reaction (TPR) of NH₃ + ¹⁵NO, and Temperature Programmed Surface Reaction (TPSR) / Isothermal Step Concentration (ISC) experiments of nitrites and nitrates with ammonia have been performed. In a typical TPR experiment, the catalyst has been exposed under temperature programming from room temperature (r.t.) to 400°C (10°C/min) to a flow of 660 ppm of NH₃ and 1000 ppm ¹⁵NO in He (i.e. according to the stoichiometry of the slow SCR reaction:

\[ 6 \text{NO} + 4 \text{NH}_3 \rightarrow 5 \text{N}_2 + 6 \text{H}_2\text{O}. \]

Before TPSR and ISC experiments, labelled nitrites and nitrates have been adsorbed on the catalyst surface. Based on previous NO₃ adsorption studies under in-situ and operando conditions nitrite and nitrate ad-species are formed on the catalyst surface upon NO/O₂ adsorption at low (150 °C) and high (350 °C) temperature, respectively \(^{25,26,27}\). Accordingly labelled nitrites and nitrates have been accumulated by contacting the catalyst with a flow of 1000 ppm ¹⁵NO in He + 3% v/v O₂ at 150°C and 350°C, respectively.

In the case of TPSR experiments, after ¹⁵NO₃ adsorption followed by a He purge at the same temperature, the catalyst has been cooled down to r.t. under He flow. Then a rectangular step feed of NH₃ (1000 ppm in He) has been admitted to the reactor at r.t. and the catalyst temperature has been linearly increased to 400°C (heating rate 10 °C/min, hold 1 hour), while monitoring the concentration of the products exiting the reactor. This procedure leads to complete removal of the stored ¹⁵NO₃, as confirmed by nitrogen balance. In the case of the Isothermal Step Concentration experiments (ISC), after ¹⁵NO₃ adsorption and He purge at 150°C or 350°C, the reduction of the stored ¹⁵NO₃ species has been carried out at the same temperature by imposing a rectangular step feed of NH₃ (1000 ppm in He).

At the end of the regeneration procedure, the catalyst was heated up to 350°C under He flow and eventually hydrogen was added to the reactor to complete the reduction of residual stored ¹⁵NO₃, if any. This procedure allowed the quantification of the residual ¹⁵NO₃ species left after reduction.

The following mass-to-charge ratios (m/e) have been used to follow the reaction products: H₂ (m/e = 2), N₂ (m/e = 28), ¹⁵NN (m/e = 29), ¹⁵N₂ (m/e = 30), NO (m/e = 30), ¹⁵NO (m/e = 31), N₂O (m/e = 44), ¹⁵NNO (m/e = 45), ¹⁵N₂O (m/e = 46), H₂O (m/e = 18), NH₃ (m/e = 15), NO₂ (m/e = 46), ¹⁵NO₂ (m/e = 47), and ¹⁵NH₃ (m/e = 16). Due to large overlapping of the cracking patterns of the reaction products, quantitative analysis has been accomplished by simultaneous mass spectrometry, gas-chromatography and UV-Vis analysis.

Calibration factors and cracking patterns of the unlabeled species have been experimentally determined from calibrated gas cylinders; those of several labeled species have been obtained from cylinders (¹⁵NO) or by dedicated experiments (e.g. lean rich cycles with ¹⁵NO leading to the formation of ¹⁵NO₂, ¹⁵N₂ and ¹⁵NH₃).

This procedure revealed that the calibration factors of ¹⁵N₂ and N₂ were almost identical; accordingly that of ¹⁵NN was assumed to be the same. Along similar lines the calibration factors of ¹⁵N₂O and ¹⁵NNO were assumed to be identical to that of N₂O. These results have also been confirmed by GC measurements.
The analytical set-up used in this work allowed to identify and quantify species which overlap each other. For example the $^{15}$N$_2$ concentration was obtained from the MS m/e = 30 signal after “cleaning” the NO and NH$_3$ contributions provided by simultaneous UV-Vis analysis; the $^{15}$NH$_3$ concentration has been estimated by subtracting from the total amount of ammonia (NH$_3$ + $^{15}$NH$_3$) obtained from the UV analyzer the concentration of $^{14}$NH$_3$ obtained from the MS signal at m/e = 15 (taking into account the overlapping of $^{15}$N). Besides, GC analysis allowed the quantification of the overall nitrogen (N$_2$ + $^{15}$NN + $^{15}$N$_2$) and nitrous oxide (N$_2$O + $^{15}$NNO + $^{15}$N$_2$O) concentrations at different instants of the runs. These total concentration values were compared to those calculated by the sum of the different isotopic species ($^{15}$N$_2$+ N$_2$+ $^{15}$NN and $^{15}$N$_2$O+N$_2$O+$^{15}$NNO) measured with the mass spectrometer to verify the accuracy of the analysis method.

N-balances, calculated from the amounts of NO$_x$ adsorbed and those of N-containing products, are generally within an experimental error of 10%.

All the experiments carried out with $^{15}$NO (TPSR and ISC) have been performed with $^{14}$NO as well to check for differences in the reactivity of the labeled and unlabeled molecules: differences have always been found to be negligible.

Results

**Adsorption of nitrites and nitrates.** Based on previous NO$_x$ adsorption studies accomplished under *in-situ* and *operando* conditions $^{15,26,27}$ nitrite and nitrate ad-species are formed on the Pt-Ba/Al$_2$O$_3$ catalyst surface upon NO/O$_2$ adsorption at low (150 °C) and high (350 °C) temperature, respectively. The results of $^{15}$NO/O$_2$ storage are shown in Figures 1A and 1B. In Figure 1A (T= 150°C) the $^{15}$NO breakthrough is immediately observed upon admission (t= 0s), along with very small amounts of $^{15}$NO$_2$ which are seen after 500 s. After steady-state conditions are attained, the $^{15}$NO inlet concentration is switched to zero; a tail is observed in the NO$_x$ outlet concentration (with a small “puff” in the NO$_2$ concentration) due to the desorption of weakly adsorbed species. At the end of the adsorption process (2750 s), nearly 0.26 mmol/g$_{cat}$ of $^{15}$NO$_x$ have been stored on the catalyst surface.

In Figure 1B (T= 350°C) the $^{15}$NO breakthrough is observed at 200 s, and the evolution of significant amounts of $^{15}$NO$_2$ are observed starting from 260 s. The outlet concentrations of both $^{15}$NO and $^{15}$NO$_2$ increase with time and tend to constant levels which are consistent with the constraints of the equilibrium of $^{15}$NO oxidation to $^{15}$NO$_2$ in the presence of 3% v/v O$_2$ ($^{15}$NO = 590 ppm vs $^{15}$NO$_{eq}$ = 445 ppm and $^{15}$NO$_2$ = 410 ppm vs $^{15}$NO$_{2eq}$ = 555 ppm, at 350°C). After roughly 2000 s, the $^{15}$NO feed is switched off and also in this case a tail is observed in the $^{15}$NO$_x$ concentration profile, due to the desorption of weakly adsorbed $^{15}$NO$_x$ species. At the end of the storage phase, nearly 0.34 mmol/g$_{cat}$ of $^{15}$NO$_x$ have been stored on the catalyst surface.
Pathways for N2 and N2O formation during the reduction of NOx over Pt-Ba/Al2O3 LNT catalysts investigated by labelling isotopic experiments

Fig.1  Adsorption of labeled NO at A) 150 and B) 350°C by imposing a rectangular step feed of $^{15}\text{NO}$ (1000 ppm) in flowing He + 3% v/v O$_2$ on Pt-Ba/Al$_2$O$_3$ catalyst

Reactivity of stored nitrites and nitrates with gas-phase NH$_3$. Figures 2 and 3 show the results of NH$_3$-TPSR and NH$_3$-ISC experiments carried out after $^{15}\text{NO}_x$ storage at 150 °C (labelled nitrites).

In the case of the TPSR experiment (Figure 2), the desorption of ammonia is observed at first; indeed ammonia is being stored on the catalyst upon admission at the beginning of the experiment, not shown in the Figure (t < 30500 s). From nearly 120°C a net consumption of ammonia is seen together with the formation of N$_2$O and N$_2$ due to the reaction of NH$_3$ with stored $^{15}\text{NO}_x$. Nitrogen is by far the most abundant product, with different isotopic composition.

Fig.2  TPSR run with NH$_3$ (1000ppm) after $^{15}\text{NO}_x$ adsorption at 150°C (1000 ppm $^{15}\text{NO} +$ O$_2$ 3% v/v in He) over Pt-Ba/Al$_2$O$_3$ catalyst
The single-labelled isotope (i.e. $^{15}\text{N}^{14}\text{N}$, m/z = 29) is initially observed in greater amounts whereas the unlabelled ($^{14}\text{N}_2$, m/z = 28) and double-labelled ($^{15}\text{N}_2$, m/z = 30) species are seen with a short delay. The single-labelled $^{15}\text{N}^{14}\text{N}$ molecule is the most abundant di-nitrogen species evolved during the experiment (49% of the total $\text{N}_2$ products), but the unlabelled ($^{14}\text{N}_2$) and double-labelled ($^{15}\text{N}_2$) di-nitrogen are also observed in significant amounts (35% and 16%, respectively). The evolution of very small amounts of single-labelled nitrous oxide ($^{15}\text{N}^{14}\text{NO}$, m/z = 47) is also observed at the onset of the reaction around 100°C (note that the concentration trace of $^{15}\text{N}^{14}\text{NO}$ is multiplied by a factor of 10).

Notably, the $\text{NH}_3$ consumption (0.3 mmol/g$_\text{cat}$, as estimated from the $\text{NH}_3$ uptake in Figure 2 in the temperature range 120-300°C) and the $\text{N}_2$ formation (0.29 mmol/g$_\text{cat}$) roughly obey the stoichiometry of reaction (1):

$$\text{Ba(NO}_2)_2 + 2 \text{NH}_3 \rightarrow 2 \text{N}_2 + \text{BaO} + 3 \text{H}_2\text{O} \quad (1)$$

Indeed nitrites are formed upon storage of NO/O$_2$ at 150°C and $\text{N}_2$ represents the major reaction product of $\text{NH}_3$-TPSR$^{25,26}$. Above 300°C, ammonia is decomposed to a small extent into $\text{N}_2$ and H$_2$ (these species can be hardly detected due to the low concentrations).

Figure 3 shows the results obtained upon reduction of the stored nitrites at 150°C ($\text{NH}_3$-ISC). Upon admission, ammonia is completely consumed and nitrogen is formed as the major reaction product along with nitrous oxide in small amounts (its concentration trace is multiplied by a factor of 10). The $\text{NH}_3$ consumption is slightly higher than that expected from the stoichiometry of reaction (1) due to ammonia adsorption onto the catalyst surface.

![Fig.3 ISC-rich phase with $\text{NH}_3$ (1000ppm) at 150°C after $^{15}\text{NO}_x$ adsorption at 150°C (1000 ppm $^{15}\text{NO}$ + O$_2$ 3% v/v in He) over Pt-Ba/Al$_2$O$_3$ catalyst](image_url)

The temporal sequence and the distribution of products resemble those seen during the TPSR run (Figure 2). The single labeled $^{15}\text{N}^{14}\text{N}$ molecule represents the main di-nitrogen isotopic product (53%) and is seen before the other isotopes; $^{14}\text{N}_2$ and $^{15}\text{N}_2$ account for 23% and 24% of total $\text{N}_2$ respectively. Concerning $\text{N}_2\text{O},$
the single-labeled molecule (\(^{15}\text{N}\)) is formed in significant amounts, along with traces (few ppm) of the double-labeled isotope (\(^{15}\text{N}_2\text{O}\)). The unlabeled molecule \(^{14}\text{N}_2\text{O}\) is not observed.

The results obtained upon reaction of ammonia with the stored nitrates are shown in Figures 4 and 5. In the case of \(\text{NH}_3\)-TPSR experiment (Figure 4), the ammonia consumption is observed from near 150°C, and is accompanied by the evolution of \(\text{N}_2\). The consumption of ammonia (0.6 mmol/g\(_{\text{cat}}\)) and the formation of \(\text{N}_2\) (0.5 mmol/g\(_{\text{cat}}\)) are in line with the stoichiometry of reaction (2):

\[
3 \text{Ba(NO}_3)_2 + 10 \text{NH}_3 \rightarrow 8 \text{N}_2 + 3 \text{BaO} + 15 \text{H}_2\text{O} \quad (2)
\]

Indeed nitrates are formed upon storage of NO/O\(_2\) at 350°C and \(\text{N}_2\) represents the only reaction product in Figure 4. \(\text{N}_2\text{O}\) is not observed in this case, at variance with the \(\text{NH}_3\)-TPSR of nitrates (Figure 2) and in line with previous literature reports showing that the reduction of nitrates with ammonia is very selective towards \(\text{N}_2\)\(^{13},^{14},^{17},^{18}\). The dynamics of the evolution of the three di-nitrogen isotopes is the same; the unlabeled \(^{14}\text{N}_2\) and the single labeled \(^{15}\text{N}^{14}\text{N}\) species are most abundant (respectively 44% and 37%), while \(^{15}\text{N}_2\) accounts for 19% of total \(\text{N}_2\).

![Figure 4 TPSR run with \(\text{NH}_3\) (1000ppm) after \(^{15}\text{NO}_x\) adsorption at 350°C (1000 ppm \(^{15}\text{NO} + \text{O}_2\) 3% v/v in He) over Pt-Ba/Al\(_2\text{O}_3\) catalyst](image)

Similar results have been obtained in the case of \(\text{NH}_3\)-ISC carried out over the stored nitrates at 350°C (Figure 5). Ammonia is completely consumed upon admission and \(\text{N}_2\) represents the only reaction product. At 350°C the adsorption of ammonia is negligible, so that the consumption of ammonia and the formation of \(\text{N}_2\) obey the stoichiometry of reaction (2), as opposite to what observed in the case of nitrites where the \(\text{NH}_3\)-ISC experiment was carried out at much lower temperature (150°C, Figure 3). Unlabeled \(^{14}\text{N}_2\) and single labeled \(^{15}\text{N}^{14}\text{N}\) species represent the main products (50% and 35% respectively), while lower amounts of \(^{15}\text{N}_2\) are observed (15%). As in the case of \(\text{NH}_3\)-TPSR of nitrates (Figure 4), \(\text{N}_2\text{O}\) is not observed and the reaction is fully selective towards nitrogen.
Pathways for N2 and N2O formation during the reduction of NOx over Pt-Ba/Al2O3 LNT catalysts investigated by labelling isotopic experiments

Reactivity of gas-phase NO and NH₃. The results of TPR of NH₃ with gas-phase ¹⁵NO are shown in Figure 6. The onset of the reaction with formation of N₂O and N₂ in comparable amounts is observed at 100°C. Up to 180°C only labelled molecules are detected, i.e. ¹⁵N₂O and ¹⁵N¹⁴NO for nitrous oxide and ¹⁵N¹⁴N for di-nitrogen. Above 180°C, where complete NO consumption is observed, the concentration of nitrous oxide species drops to zero and the formation of double labeled ¹⁵N₂ and of unlabeled ¹⁴N₂ is observed. Hence above 180°C the reaction is very selective towards N₂.

Discussion

Mechanism of N₂ formation. The results show that the NOₓ species stored onto PtBa/Al₂O₃ LNT catalyst, i.e. nitrites and nitrates, are selectively reduced by NH₃ to N₂, since no other products are observed if one neglects the formation of very small amounts of nitrous oxide in the reduction of nitrites. All di-nitrogen isotopes are formed but the abundance of single labeled ¹⁵N¹⁴N isotope is greater than those of unlabelled
$^{14}\text{N}_2$ and double labeled $^{15}\text{N}_2$ isotopes. Only in the case of nitrites the di-nitrogen isotopes show different temporal evolution; indeed the single labeled $^{15}\text{N}^{14}\text{N}$ isotope prevails at the beginning of both NH$_3$-TPSR and NH$_3$-ISC runs. Concerning nitrous oxide, only labelled species ($^{15}\text{N}^{14}\text{NO}$ and $^{15}\text{N}_2\text{O}$) are formed upon reaction of the stored NO$_x$ with ammonia. A different picture is apparent in the reaction of ammonia with gaseous $^{15}\text{NO}$. In this case comparable amounts of N$_2$O and of N$_2$ are observed at low temperature (100-180°C), but the selectivity to di-nitrogen is complete above 180-200°C where NO is completely consumed. Like during NH$_3$-TPSR and NH$_3$-ISC runs of both nitrites and nitrates, only labeled species are observed in the case of nitrous oxide ($^{15}\text{N}^{14}\text{NO}$ and $^{15}\text{N}_2\text{O}$). On the other hand all types of di-nitrogen isotopes are observed among the products, but only the single labeled $^{15}\text{N}^{14}\text{N}$ isotope is detected at 100-180°C. Mechanistic aspects involved in the formation of di-nitrogen during the reduction of NO$_x$ by NH$_3$ have been the object of long debate in the scientific literature. In the case of the NH$_3$-SCR reaction over vanadia-based catalysts and transition metal exchanged zeolites (reaction (3)):
\[
4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \tag{3}
\]
it has been shown that the reaction between unlabeled ammonia ($^{14}\text{NH}_3$) and labeled NO ($^{15}\text{NO}$) leads to the selective formation of the single labeled nitrogen molecule ($^{15}\text{N}^{14}\text{N}$)\textsuperscript{28,29,30}, indicating that one N-atom comes from ammonia and the other from NO. Accordingly the formation of N$_2$ has been suggested to occur through the intermediacy of surface species like nitrosamide or ammonium nitrite\textsuperscript{2931,32,29} formed via coupling of NH$_3$- with NO-derived species. In this pathway (SCR pathway) the self-coupling of N-species originated from ammonia and NO is ruled out due to the lack of significant amounts of $^{15}\text{N}_2$ and $^{14}\text{N}_2$ isotopes in the product mixture. The same conclusions have been reached in our labs where the reaction of stored $^{14}\text{NH}_3$ with $^{15}\text{NO}$ in the presence of excess O$_2$ has been accomplished over V$_2\text{O}_5$/TiO$_2$ and Fe-ZSM5 catalyst samples. In fact the very selective formation of $^{14}\text{N}^{15}\text{N}$ was observed (data not reported for the sake of brevity), in line with previous literature reports and with the mechanistic indications discussed above\textsuperscript{28,30}. A different picture is apparent in the reduction of NO$_x$ with ammonia in the case of the PtBa/Al$_2$O$_3$ catalyst sample investigated in this work. In the reduction of stored labeled nitrites by $^{14}\text{NH}_3$ (Figures 2 and 3) the formation of all di-nitrogen isotopes has been observed. The single labeled $^{14}\text{N}^{15}\text{N}$ species dominates (roughly 50% of total N$_2$), but relevant amounts of double labeled ($^{15}\text{N}_2$) and unlabeled ($^{14}\text{N}_2$) di-nitrogen are also observed. Worth to note that the stoichiometry of the reduction of stored nitrites with ammonia (reaction (1)) involves, like the NH$_3$-SCR reaction (3), a 1/1 molar ratio between $^{14}\text{NH}_3$ and nitrite group $^{15}\text{NO}_2$. Accordingly in this case the selective formation of only single labeled $^{14}\text{N}^{15}\text{N}$ molecule (via coupling of $^{14}\text{N}$- and $^{15}\text{N}$-containing species, as in the case of the SCR pathway) is possible. However the production
Pathways for N2 and N2O formation during the reduction of NOx over Pt-Ba/Al2O3 LNT catalysts investigated by labelling isotopic experiments

of $^{15}\text{N}_2$ and unlabeled $^{14}\text{N}_2$ has also been observed, in addition to $^{14}\text{N}^{15}\text{N}$, and this indicates that a SCR-like pathway does not represent the unique route of N$_2$ formation in the case of LNT catalysts.

Figure 7 sketches a possible pathway that can explain the formation of di-nitrogen (and of nitrous oxide, see below) during the reduction by NH$_3$ of $^{15}\text{NO}_x$ adsorbed over Pt-Ba/Al$_2$O$_3$. Stored $^{15}\text{NO}_x$ are located on Ba sites close to or far away from Pt; upon admission of ammonia the Pt sites are reduced and this drives the onset of the reduction process which involves the migration through surface diffusion of stored $^{15}\text{NO}_x$ towards reduced Pt sites, as suggested in the literature $^{33}$. The $^{15}\text{NO}_x$ species are hence decomposed at the reduced Pt sites with formation of a pool of $^{15}\text{N}$- and O- ad-atoms. These ad-species react with NH$_3$-derived species or fragments adsorbed onto the Pt sites, as suggested in the case of the NO-NH$_3$ reaction over Pt-based catalysts $^{6,12,34,35,36,37,38}$. In such a case there is a general consensus that di-nitrogen formation occurs via recombination of N-ad-atoms formed by dissociation of NO and NH$_3$ at the Pt site ($s$):

$$^{15}\text{NO}(g) + s \rightarrow ^{15}\text{NO}(a) \quad (4)$$

$$^{15}\text{NO}(a) + s \rightarrow ^{15}\text{N}(a) + O(a) \quad (5)$$

$$^{14}\text{NH}_3(g) + s \rightarrow ^{14}\text{NH}_3(a) \quad (6)$$

$$^{14}\text{NH}_3(a) + 3s \rightarrow ^{14}\text{N}(a) + 3H(a) \quad (7)$$

$$^{15}\text{N}(a) + ^{15}\text{N}(a) \rightarrow ^{15}\text{N}_2(a) + 2s \quad (8a)$$

$$^{15}\text{N}(a) + ^{14}\text{N}(a) \rightarrow ^{15}\text{N}^{14}\text{N}(g) + 2s \quad (8b)$$

$$^{14}\text{N}(a) + ^{14}\text{N}(a) \rightarrow ^{14}\text{N}_2(a) + 2s \quad (8c)$$

$$2H(a) + O(a) \rightarrow H_2O(g) + 3s \quad (9)$$

In the scheme depicted above, NO is decomposed at reduced Pt sites to form N- and O-ad-atoms (reaction (5)). Complete ammonia dehydrogenation (reaction (7)) leads to the formation of N- and H-ad-atoms, which in turn keep clean the Pt surface from O-ad-atoms via reaction (9). Eventually nitrogen formation
occurs through recombination of N-ad-atoms (reactions (8a)-(8c)), that produces all di-nitrogen isotopes with a distribution which depends on the surface concentration of $^{14}\text{N}$- and $^{15}\text{N}$-adatoms and can be derived on a statistical basis. At variance with the SCR pathway, this route does not result in the selective formation of only single labeled $^{14}\text{N}^{15}\text{N}$ species. The concentration of $^{14}\text{N}^{15}\text{N}$ is limited to a maximum of 50% of total di-nitrogen species and this occurs with equal coverage of $^{14}\text{N}$- and $^{15}\text{N}$-ad-species.

Figure 8 shows the concentration of the $^{14}\text{N}^{15}\text{N}$ isotope in % of total $\text{N}_2$ as function of time during NH$_3$-TPSR and NH$_3$-ISC experiments with nitrites and nitrates, calculated from the data of Figures 2-5. The abundance of the mixed $^{14}\text{N}^{15}\text{N}$ species is higher than 50% in the case of nitrites at the beginning of the experiments, up to 70% of total $\text{N}_2$ in the case of NH$_3$-TPSR (panel A) and up to 90% of total $\text{N}_2$ in the case of NH$_3$-ISC (panel B). This cannot be explained only with the statistical coupling of the N-ad-atoms formed upon adsorption/decomposition of stored $^{15}\text{NO}_x$ and of $^{14}\text{NH}_3$ but the occurrence of a SCR-like route involving the coupling of un-dissociated $^{15}\text{NO}_x$-derived species and of ammonia fragments (e.g. NH$_2$) must also be invoked (see Otto et al.):

$$^{14}\text{NH}_2(a) + ^{15}\text{NO}(a) \rightarrow ^{14}\text{N}^{15}\text{N}(g) + \text{H}_2\text{O}(a) + s$$ (10)

---

The occurrence of the SCR-like route is more favored in the case of nitrites possibly in view of the corresponding formal oxidation number of N in ammonia and nitrites (-3 and +3, respectively) which favors the formation of the NH$_x$-NO surface intermediate.

As pointed out by Kondratenko and Baerns, in the formation of N$_2$ over Pt the statistical coupling of N-adatoms and the SCR-like pathway may co-exist; the contribution of these routes in the formation of di-nitrogen depends on the relative coverage by adsorbed NO and NH$_3$, and on temperature. Accordingly
changes in the concentration of the $^{14}\text{N}^{15}\text{N}$ species with time in Figure 8 are likely associated to changes in the surface concentration of NH$_3$- and nitrite- or NO-derived surface species.

The results obtained in the reduction of the stored nitrates show some distinct features. First of all the selective formation of only mixed $^{14}\text{N}^{15}\text{N}$ species is not possible in NH$_3$-TPSR and NH$_3$-ISC of nitrates. In fact the formation of the double labeled $^{14}\text{N}_2$ isotope is expected in view of the molar ratio $^{14}\text{NH}_3/^{15}\text{NO}_3 = 10/6 > 1$ dictated by the stoichiometry of reaction (2). Figures 4 and 5 show that all the possible $\text{N}_2$ isotopes are formed in the reduction of nitrates with ammonia and that the phase differences of the distribution of isotopic di-nitrogen species is limited. Figure 8 (panels C and D) also shows that the abundance of the $^{14}\text{N}^{15}\text{N}$ species is still high but less that 50% of total $\text{N}_2$ so that it is not necessary to invoke a SCR-like pathway in the case of nitrates although it cannot be excluded. On the other hand the formation of di-nitrogen isotopes originating from the self-coupling of $^{15}\text{NO}_3$-derived species (i.e. $^{15}\text{N}_2$) provides evidence for the occurrence of statistical coupling of the N-ad-species.

Finally, in the reduction of gas-phase $^{15}\text{NO}$ with NH$_3$ in the absence of oxygen according to reaction (11):

$$6 \, ^{15}\text{NO} + 4 \, \text{NH}_3 \rightarrow 5 \, \text{N}_2 + 6 \, \text{H}_2\text{O} \quad (11)$$

the following statistical isotope distribution is expected for the pathway based on the statistical recombination of N-ad-atoms formed by dissociation of NO and NH$_3$ at Pt sites for the feed of Figure 6:

$$^{14}\text{N}^{15}\text{N}/\, ^{15}\text{N}_2/^{14}\text{N}_2 = 48/36/16.$$ The isotope distribution calculated from Figure 6 at $T > 200^\circ\text{C}$ where the $\text{N}_2$ selectivity is complete is $^{14}\text{N}^{15}\text{N}/\, ^{15}\text{N}_2/^{14}\text{N}_2 = 52/31/17$. This distribution compares well with that listed above and is fully consistent with the recombination pathway of N-ad-atoms formed by decomposition of gas phase NO and NH$_3$ at Pt sites. However the SCR route, that might be involved in the formation of single labeled $\text{N}_2$, cannot be excluded.

**Formation of $\text{N}_2\text{O}$** – Small and almost negligible amounts of $\text{N}_2\text{O}$ have been observed during NH$_3$-TPRS and NH$_3$-TPR of nitrites (Figures 2 and 3) and of nitrates (Figures 4 and 5) respectively, while relevant quantities of $\text{N}_2\text{O}$ have been detected during the NH$_3$ + NO reaction (Figure 6). Notably only the formation of labeled nitrous oxide (i.e. $^{15}\text{N}_2\text{O}$ and $^{14}\text{N}^{15}\text{NO}$) has been observed during these experiments.

For comparison purposes, Figure 9 shows the $\text{N}_2\text{O}$ concentration during NH$_3$-TPSR of nitrites (panel A) and during TPR of NH$_3$ and NO (panel B). The results obtained during the TPR of NH$_3$ and NO in the presence of O$_2$ (not presented previously) are also shown (panel C).

Inspection of Figure 9 shows that $\text{N}_2\text{O}$ formation is poor during the reaction of stored NOx with ammonia (TPSR of nitrites, Figure 9, panel A) but is noticeable when NO is present in the feed gas (NH$_3$ + NO reaction, Figure 9, panel B): in this last case $\text{N}_2\text{O}$ concentration is greater by one order of magnitude. A further increase in $\text{N}_2\text{O}$ concentration is seen when oxygen is present in the feed gas (Figure 9, panel C). These results and the fact that only labeled $\text{N}_2\text{O}$ species are detected (if one neglects the small amounts of unlabeled $\text{N}_2\text{O}$ observed at high temperature in Figure 9, panel C), indicate that adsorbed $^{15}\text{NO}$ takes part in
the formation of nitrous oxide. This is in line with literature proposals\(^{34,40}\) where nitrous oxide is formed either by coupling of two adsorbed NO molecules (reaction (12)), or by recombination of an adsorbed NO molecule with an adsorbed NH\(_3\) fragment (reaction (13)):
\[
2\, ^{15}\text{NO}(g) \rightarrow ^{15}\text{N}_2\text{O}(g) + ^{15}\text{O}(g) + s \\
^{14}\text{NH}_3(a) + ^{15}\text{NO}(g) \rightarrow ^{14}\text{N}^{15}\text{NO}(g) + x\, \text{H}_2(g)
\]  
(12)  
(13)
These reactions are expected to occur during TPR of \(^{15}\text{NO} + ^{14}\text{NH}_3\) (Figure 6 and Figure 9, panel B), and result in the formation of only double- and single-labeled N\(_2\)O species; the formation of unlabeled N\(_2\)O is not possible. On the other hand, during the reduction of stored nitrites \(^{15}\text{NO}_2\) (Figure 9, panel A), the rate of nitrous oxide formation is limited by the low concentration of \(^{15}\text{NO}\)-ad-species originated upon nitrite decomposition/reduction at Pt sites. Accordingly the reduction is very selective to di-nitrogen.

![Diagram showing TPSR runs with NH\(_3\) and NO and O\(_2\) in He over Pt-Ba/Al\(_2\)O\(_3\) catalyst](image)

**Fig. 9** A: TPSR run with NH\(_3\) (1000 ppm) after \(^{15}\text{NO}_2\) adsorption at 150°C (1000 ppm \(^{15}\text{NO} + \text{O}_2\) 3% v/v in He), B: TPSR run with NH\(_3\) (660 ppm) and \(^{15}\text{NO}\) (1000 ppm) in He, C: TPSR run with NH\(_3\) (660 ppm), \(^{15}\text{NO}\) (1000 ppm) and O\(_2\) (3% v/v) in He over Pt-Ba/Al\(_2\)O\(_3\) catalyst.

Notably, nitrous oxide formation is strongly affected by temperature: in fact above 180 °C the N\(_2\)O concentration is always negligible in the absence of oxygen (Figure 9, panels A and B). It is suggested that at high temperature NO dissociation is favored because Pt is kept in a reduced state by ammonia, and this prevents N\(_2\)O formation due to the lack of molecularly adsorbed NO species. Along similar lines, the nitrous oxide concentration is markedly greater in the presence of oxygen in the feed stream (compare Figure 9, panels B and C) because NO dissociation is prevented over the oxygen-covered Pt surface and this increases the concentration of NO ad-species.

However, under reducing conditions the possibility that N\(_2\)O is reduced to N\(_2\) cannot be excluded. In this light the decrease in N\(_2\)O concentration which is seen upon increasing the temperature in the absence of oxygen (Figures 9, panels A and B) might be due to the reduction of N\(_2\)O to give N\(_2\)\(^{41}\). This route may contribute only to the formation of single and double labeled N\(_2\) molecules in the experiments of Figures 9
Conclusions.

In this paper mechanistic aspects involved in the formation of N₂ and N₂O during the reduction of NOₓ stored over a model PtBa/Al₂O₃ NSR catalyst have been investigated by means of isotopic labeling experiments. The combined use of MS, UV-Vis and GC analysis has been adopted to allow a complete quantitative analysis of the reaction products.

The reduction of stored labeled NOₓ species (nitrites and nitrates) with unlabeled NH₃ leads to the selective formation of N₂, since only very small amounts of nitrous oxide have been observed in the reduction of...
nitrites only. The observed $N_2$ isotopic distribution includes all possible $N_2$ isotopes, i.e. $^{15}N_2$, $^{14}N_2$ and the mixed $^{15}N^{14}N$ species. Based on the pathway suggested for NO and NH$_3$ reaction on Pt-based catalysts, it has been found that the observed product distribution can be explained on the basis of the statistical coupling of $^{15}N$- and $^{14}N$-adatoms originated upon NH$_3$ and NO$_x$ decomposition on Pt. However the simultaneous occurrence of a SCR-like pathway, involving the formation and decomposition of a NH$_x$-NO intermediate originating from ammonia and NO$_x$, and leading to the selective formation of the mixed $^{15}N^{14}N$ species is also likely. In fact at the early stages of the reduction of stored labeled nitrites with unlabeled ammonia the reduction process is selective towards the formation of the mixed $^{15}N^{14}N$ isotope, suggesting the occurrence of a SCR-like pathway.

Isotopic labeling experiments also provide indications on the pathways involved in the formation of N$_2$O. This species is formed in very limited amounts during the reduction by ammonia of stored NOx species (nitrites and nitrates); much higher quantities have been observed during the reduction of gaseous $^{15}NO$ with NH$_3$. Since no formation of unlabeled nitrous oxide has been observed, the participation of $^{15}NO$ is necessary for the formation of nitrous oxide. In line with literature proposals, it has been suggested that nitrous oxide formation involves (on the Pt sites) either the coupling of two adsorbed NO molecules or the recombination of an adsorbed NO molecule with an adsorbed NH$_x$ fragment. Accordingly, N$_2$O formation is greatly enhanced in the presence of gas-phase NO.

Temperature also drives the selectivity to nitrous oxide. This product is favored at low temperature and is likely related to the oxidation state of Pt: at high temperatures Pt is kept in a reduced state by ammonia, and this would favor NO dissociation on the Pt sites thus preventing N$_2$O formation. Besides, N$_2$O could be reduced to N$_2$. The presence of oxygen in the feed stream favors N$_2$O formation, since it increases the concentration of molecularly adsorbed NO species and inhibits N$_2$O reduction. The route involving the coupling of NO-ad-species is however inhibited by the presence of oxygen, and hence nitrous oxide formation involves adsorbed NO and NH$_x$ fragments.
References


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Catalytic NO Oxidation Pathways and Redox Cycles on Dispersed Oxides of Rhodium and Cobalt

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Abstract
The elementary steps and site requirements of NO oxidation on Rh and Co catalysts and their respective oxidation states during catalysis were probed using isotopic tracer and chemisorption techniques combined with the measured kinetic consequences of NO, O₂, and NO₂ pressures on turnover rates. On both catalysts, NO oxidation rates were first-order in NO and O₂ and inversely proportional to NO₂ pressure, as also observed on Pt and PdO. These data suggest O₂ activation on isolated vacancies (*) on surfaces of Rh and Co oxides saturated with oxygen (O*) is the sole kinetically-relevant step.

Quasi-equilibrated NO-NO₂ interconversion steps establish oxygen chemical potentials (and O* and * coverages) on these oxides during catalysis. These chemical potentials determine the oxidation state of Rh and Co clusters and are rigorously described by the prevalent O₂ virtual pressures, which are estimated using the formalism of nonequilibrium thermodynamics. RhO₂ and Co₃O₄ are the prevalent phases present during NO oxidation catalysts at relevant conditions.

Turnover rates increased with increasing cluster size because vacancies, required for kinetically-relevant O₂ activation steps, are more abundant on large clusters, which delocalize electron density more effectively than small oxide clusters. NO oxidation turnover rates on RhO₂ and Co₃O₄ are higher than expected from the oxygen binding energy on Rh and Co metal surfaces or from the reduction potentials of Rh³⁺ and Co³⁺. NO oxidation rates fall in line with those measured on Pt and PdO when one-electron reductions processes, accessible for Rh⁴⁺ and Co³⁺ but not for Pt²⁺ and Pd²⁺, are used to describe the reactivity of RhO₂ and Co₃O₄. Such one-electron redox cycles also cause ¹⁶O₂-¹⁸O₂ exchange rates to be much larger than NO oxidation rates, in contrast with their similar values on Pt and PdO, though O₂ activation on vacancies limits both NO oxidation and O₂ exchange on all catalysts.

One-electron redox cycles allow electron sharing between metal cations and a more facile route for vacancy formation on RhO₂ and Co₃O₄, leading to high NO oxidation rates.

These data and their interpretation in terms of elementary steps, the role of vacancies in kinetically-relevant O₂ activation steps, and the consequent higher reactivity of larger clusters provide a common framework to describe NO oxidation and the active species on catalysts of practical interest.

Keywords
Lean NOx traps • NOx storage and reduction • Structure sensitivity
Introduction

Nitrogen oxides must be removed from combustion exhaust to meet environmental regulations, which is challenging for streams that contain O$_2$ and low concentrations of CO and hydrocarbons. Catalyst sites are titrated by strongly-bound chemisorbed oxygen atoms (O*) during NO decomposition in the absence of reductants. As a result, open sites on O*-saturated surfaces, required for NO dissociation, are scarce [1,2]. Such conditions cause low NO conversions to N$_2$ and favor instead NO oxidation to NO$_2$. NO$_2$, however, adsorbs on metal oxides [3-5] and reduces to N$_2$ when soot or hydrocarbons are present in exhaust streams [6-9]. These reactions provide an alternate abatement strategy for NO removal from lean-burn effluent streams, but require effective catalysts for NO oxidation to NO$_2$.

NO oxidation on Pt [10-12] and PdO [13] clusters involves kinetically-relevant O$_2$ adsorption on vacant sites (*) at O*-saturated surfaces. O* coverages during NO oxidation are set by equilibrated NO-NO$_2$ interconversions [11-13]. The kinetic relevance of O$_2$ binding was confirmed by the identical rates of $^{16}$O$_2$-$^{18}$O$_2$ isotopic exchange and NO oxidation [12,13]. These studies showed that NO oxidation rates decrease as metal or oxide cluster size decreases because small clusters bind O* more strongly than larger clusters, leading to low vacancy concentrations.

NO oxidation is also catalyzed by Rh and Co clusters [14-16]. NO oxidation rates have been correlated with the reducibility of CoOx clusters [15], suggesting that O* binding and the availability of vacancies also determines turnover rates on Co-based catalysts. The rate data in previous studies were not attributed to specific elementary steps, which we do here using kinetic and isotopic methods for both RhO$_2$ and Co$_3$O$_4$ catalysts. We show that NO oxidation on these catalysts involves similar elementary steps and site requirements as those proposed on Pt and PdO catalysts.

The turnover rates for NO oxidation and isotopic oxygen exchange are higher on Rh and Co oxides than on PdO and small Pt clusters and also than rates expected from their metaloxygen bond energies. We attribute these findings to the ability of RhO$_2$ and Co$_3$O$_4$ to undergo facile one-electron oxidation-reduction cycles during catalytic turnovers, which provides an alternate and more effective O$_2$ activation pathway than two-electron reductions on Pt and Pd catalyst systems.

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Results and Discussion

1. NO Oxidation Kinetics on Rh and Co

NO oxidation rates were measured on Rh/Al₂O₃ and Co/SiO₂ as a function of the NO, NO₂, and O₂ pressures. The measured NO consumption rates reflect the dynamics of the forward \( \dot{r}_{NO} \) and reverse \( \ddot{r}_{NO} \) directions of the stoichiometric chemical reaction:

\[
2 \text{NO} + \text{O}_2 \rightleftharpoons 2 \text{NO}_2 \tag{1}
\]

which correspond to the rates of NO oxidation and NO₂ decomposition, respectively. The values of \( \dot{r}_{NO} \) and \( \ddot{r}_{NO} \) are related by the approach-to-equilibrium factor \( \eta \) [15]:

\[
\eta = \frac{\ddot{r}_{NO}}{\dot{r}_{NO}} = \left( \frac{[\text{NO}_2]^2[\text{NO}]^2[\text{O}_2]}{\dot{r}_{NO}} \right)^{-1} \sigma \tag{2}
\]

where \( \sigma \) is a constant derived from the stoichiometric number and reaction affinity for each elementary step [15] and \( K_R \) is the equilibrium constant for Eq. 1, estimated from tabulated thermodynamic data [17]. Forward NO oxidation turnover rates are obtained from measured NO conversion rates \( \dot{r}_{NO} \) using:

\[
\dot{r}_{NO} = \dot{r}_{NO} - \ddot{r}_{NO} = \dot{r}_{NO} (1 - \eta) \tag{3}
\]

Figure 1 shows the effects of NO, NO₂ and O₂ pressures on forward NO oxidation turnover rates on Rh and Co catalysts. On all catalysts, forward NO oxidation rates increased linearly with NO and O₂ pressures and were strongly inhibited by NO₂. The dashed lines in Fig. 1 show that these data are consistent with the form of Eq. 4 and a value of \( \eta \) equal to one.

\[
\dot{r}_{NO} = 2k_{NO}[\text{O}_2][\text{NO}][\text{NO}_2]^{-1} \tag{4}
\]

as shown by the dashed curves in Figure 1.

This NO oxidation rate expression (Eq. 4) also describes all rate data on Pt and PdO catalysts and is consistent with the elementary steps proposed previously for NO oxidation on these catalysts [10-13]. These steps involve kinetically-relevant O₂ binding at unoccupied sites (*)(Scheme 1, step 1.1) on cluster surfaces nearly saturated with chemisorbed oxygen atoms (O*). Adsorbed O₂ molecules (O₂*) dissociate to form oxygen atoms (O*) in subsequent kinetically-irrelevant steps (Scheme 1, step 1.2). The surface coverages of O* and * are set by quasiequilibrated steps involving the interconversion of NO and NO₂ on cluster surfaces (Scheme 1, step 1.3). These steps, taken together with the steady-state approximation for all adsorbed species leads to the rate equation:

\[
\dot{r}_{NO} = \frac{2k_1[\text{O}_2]}{1 + K_N[\text{NO}_2][\text{NO}]} \tag{5}
\]
in which the denominator terms reflect the relative concentrations of * and O* during steady-state catalysis. This expression (Eq. 5) accurately describes all kinetic data (Eq. 4) only when O* is the most abundant surface intermediate (MASI):

$$r_{NO} = \frac{2k_1 [O_2][NO]}{K_3 [NO_2]}$$

(6)

Measured rates therefore indicate that surfaces are nearly saturated with O* and that the measured rate constant (k_NO) (Eq. 4) is proportional to the ratio of k_1 and K_3.

Figure 1. NO oxidation rates (a) on 2.4% wt. RhO_2/Al_2O_3 (573 K; 0.47 H / Rh) versus (●) NO pressure (at 0.055 kPa NO_2; 5 kPa O_2); (■) NO_2 pressure (at 0.11 kPa NO, 5 kPa O_2); and (△) O_2 pressure (at 0.11 kPa NO, 0.055 kPa NO_2) and (b) on 10% wt. Co_3O_4/SiO_2 (548 K; 0.02 H / Co) versus (●) NO pressure (at 0.060 kPa NO_2; 5 kPa O_2); (■) NO_2 pressure (at 0.12 kPa NO, 5 kPa O_2); and (△) O_2 pressure (at 0.12 kPa NO, 0.06 kPa NO_2).

Scheme 1. Proposed Elementary Steps for NO Oxidation

$$\begin{align*}
O_2 + * & \stackrel{k_1}{\rightleftharpoons} O_2^* \\
O_2^* + * & \stackrel{k_2}{\rightleftharpoons} 2O^* \\
NO + O* & \stackrel{K_3}{\rightleftharpoons} NO_2 + *
\end{align*}$$

(1)  (2)  (3)

O* coverages, as well as the driving force for the formation of Rh and Co oxides, depend on the oxygen chemical potentials at cluster surfaces. This oxygen chemical potential is rigorously given by a virtual oxygen pressure (O_2^*) during NO oxidation catalysis [12, 13]. O_2^* values are established by NO-NO_2 adsorption
equilibria, and its value is obtained by non-equilibrium thermodynamic treatments of chemical kinetics as \(^{12,13}\):

\[
[O_2^*] = [NO_2]^2 [NO]^2 K_R^{-1}
\]  

(7)

in which \(K_R\) is the equilibrium constant for Eq. 1 as written, which can be calculated from tabulated thermodynamic data. \(O_2^v\) equals the value of the \(O_2\) pressure that gives the same \(O^*\) coverage at equilibrium as the \(O^*\) coverage during steady-state NO oxidation catalysis at a given \(NO_2/NO\) ratio.

The equilibrium constant for \(NO_2\) dissociation (\(K_3\), Scheme 1, Step 1.3) is related to the equilibrium constant for \(O_2\) dissociation (\(K_O\); Eq. 9) by \(^{12,13}\):

\[
K_3 = K_O^{1/2} / K_R^{1/2}
\]  

(8)

because the stoichiometry of step 1.3 corresponds to the difference between Eqs. 1 and 9:

\[
2^* + O_2 \rightleftharpoons 2O^*
\]  

(9)

Eqs. 5, 7, and 8 can be combined to show that NO oxidation rates depend only on the \(O_2(g)\) pressure and on the prevailing oxygen chemical potential, rigorously given by \(O_2^v\):

\[
r_{NO} = 2k_1[O_2][^*] = \frac{2k_1[O_2]}{1 + (K_O[O_2^v])^{1/2}}
\]  

(10)

The assumption that \(O^*\) is present at near saturation coverages leads to a simpler version of Eq. 10:

\[
\frac{r_{NO}}{[O_2]} = \frac{k_1[^*]}{[O_2]} = \frac{k_i}{(K_O[O_2^v])^{1/2}}
\]  

(11)

Thus, NO oxidation rates depend only on the \(O_2\) pressure and on the chemical potential of oxygen at working catalytic surfaces. Eq. 11 is used in the sections that follow to probe any residual dependence of NO oxidation rate constants on \(O_2^v\), indicative of structural or composition changes associated with phase transitions, and to compare NO oxidation rates with \(^{16}O_2-{^{18}}O_2\) exchange rates at similar \(O^*\) coverages.

2. Oxidation State of Rh and Co during NO Oxidation

The oxygen chemical potentials set by NO/NO\(_2\) reactions on catalyst surfaces (Eq. 7) represent the rigorous thermodynamic driving force not only for the prevalent \(O^*\) coverages but also for oxide-metal phase transitions during steady-state NO oxidation catalysis. Any changes in measured NO oxidation rate constants with \(O_2^v\) (Eq. 7) could reflect the occurrence of a phase transition consequential to catalysis, while rate constants that do not depend on \(O_2^v\) preclude phase transitions consequential for catalysis within the experimental range of conditions. The rearrangement of Eq. 11 given by:

\[
\left( \frac{[O_2]}{r_{NO}} \right)^2 = \frac{K_O}{k_i^2} [O_2^v]
\]  

(12)
describes all rate data, as shown by the linear dependence in Fig. 2. The consequent constant slope shows that NO oxidation rate constants on Rh and Co catalysts represent true constants unaffected by oxygen chemical potentials (0.01-0.4 and 0.001-0.15 kPa O_2 for Rh and Co, respectively) or by any metal-oxide transitions. We conclude that the oxidation state of Rh and Co clusters remains unchanged throughout the conditions of this study and corresponds to the bulk phase dictated by these oxygen chemical potentials.

The phase diagram for bulk Rh oxides, \[^{15}\] taken together with thermodynamic data for bulk Rh, Rh_2O_3 (\(\Delta H^\theta = -135\) kJ (mol O)^\(-1\)), and RhO_2 (\(\Delta H^\theta = -122\) kJ mol\(^{-1}\)) \[^{20}\] and Co, CoO (\(\Delta H^\theta = -237\) kJ (mol O)^\(-1\)), and Co_3O_4 (\(\Delta H^\theta = -223\) kJ (mol O)^\(-1\)) \[^{17}\] indicate that Rh and Co clusters exist as RhO_2 and Co_3O_4, respectively, at all conditions used in this study (573-673 K, 0.2-3.0 NO_2/NO, and 0.001-2 kPa O_2 for Rh; 548-623 K, 0.25-2 NO_2/NO, and 0.0001-2 kPa O_2 for Co). Rh and Co can form structures with lower oxidation states (Rh_2O_3 and CoO), but these oxides are stable only at significantly lower oxygen chemical potentials or higher temperatures than used here. For example, RhO_2/Rh_2O_3 and the Co_3O_4/CoO phase transitions occur at 10-6 and 10-14 kPa O_2, respectively, at 573 K. We conclude that the predominant phases of each catalyst are Co_3O_4 or RhO_2 during steady-state catalytic NO oxidation for clusters of all sizes.

The oxidation state of Co during catalysis was confirmed by O_2 uptakes in the temperature range of NO oxidation catalysis. The O_2 uptake at 548 K on Co/SiO_2 (0.02 H/Cor) was 0.57 mol O_2 (mol Co)^\(-1\) (O/Co = 1.14) after the sample was treated in H_2 at 673 K for 1 h and remained unchanged between 5 and 60 kPa O_2 (Fig. 3). These data indicate that most Co atoms (85%) are present as Co3O4 upon contact with
O₂ and therefore with NO/NO₂ mixtures that provide equivalent oxygen chemical potentials during catalysis. The remaining Co atoms (15%) are present as Co silicates, which do not reduce during treatment in H₂ at 673 K [17] and therefore cannot uptake O₂. The constant uptakes with O₂ pressure (548 K, 5-60 kPa; Fig. 3) show that clusters do not change their oxidation state within this pressure range, as expected from thermodynamic data [17] and from measured rate constants that did not vary with O₂ pressure (Fig. 2b). Co³⁺ in Co₃O₄ and Rh⁴⁺ in RhO₂ can reduce to Co²⁺ in CoO and Rh³⁺ in RhO₂, respectively, via one-electron reductions. We infer in the next section that the availability of these one-electron oxidation-reduction cycles influence the pathways and dynamics of O₂ activation on RhO₂ and Co₃O₄ during both catalytic NO oxidation and O₁₆O₁₈O₂ isotopic exchange.

Figure 3. O₂ uptake at 548 K on 10% wt. Co/SiO₂ (0.02 dispersion) previously treated at 673 K with flowing 100 kPa H₂ for 1 h (0.1 cm³ g⁻¹ s⁻¹) and then under vacuum for 1 h.

3. O₁₆O₁₈O₂ Exchange and NO Oxidation Rates

¹⁶O₂-¹⁸O₂ isotopic exchange and NO oxidation (Scheme 1, step 1) share a common kinetically-relevant step (O₂ adsorption on vacant sites) on Pt and PdO clusters [12, 13]. On Pt and PdO, these two reactions occur at identical rates, irrespective of temperature or oxygen chemical potential, consistent with their common limiting elementary step. Similar experiments are used here to probe the kinetic relevance of O₂ activation during NO oxidation on RhO₂ and Co₃O₄ catalysts.

O₂ activation rates (r⁰₂(ex)) were determined from measured O₁₆O₁₈O₂ isotopic exchange rates (rₑx) at 2 kPa O₂(g) in the absence of NOx using the equation:

\[
r_{ex} = r_{O_2(ex)} \left( \frac{[^{16}O_2][^{18}O_2]}{[O_2]^2} \right) \left( 1 - \frac{[^{16}O^{18}O]^2}{4[^{16}O_2][^{18}O_2]} \right)
\]

(13)
which describes measured steady-state exchange rates, irrespective of the mechanism of exchange \[^{[22]}\]. In this equation, the terms in parenthesis account for the approach to isotopic equilibrium and the [O2] term denotes the sum of the pressures of all oxygen isotopologues ([\(^{16}\)O\(_2\)], [\(^{18}\)O\(_2\)], and [\(^{16}\)O\(^{18}\)O]). The \(r_{O_2(ex)}\) term is the O\(_2\) activation rate, which depends on the total O\(_2\) pressure and on the coverage of vacancies (*) \[^{[22]}\]. Previous rate data on Co\(_3\)O\(_4\) and other Group VIII metal oxides indicate that O\(_2\) exchange rates obey the equation \[^{[22]}\] :

\[
\frac{r_{O_2(ex)}}{[O_2]} = k_{ex}[*] = \frac{k_{ex}}{(K_O[O_2])^{1/2}}
\]

in which \(k_{ex}\) is the rate constant for O\(_2\) activation. Eq. 14 is consistent with a rate-determining step for exchange requiring isolated vacancies on surfaces nearly saturated with O*, as is also the case in NO oxidation reactions (Eq. 11). The density of vacancies (*) during exchange is given by the chemical equilibrium of Eq. 9 with KO as the equilibrium constant. Both Eq. 14, describing O\(_2\) exchange rates, and Eq. 11, describing NO oxidation rates, probe O\(_2\) activation rates on cluster, which depend only on the rate constant for O\(_2\) activation and the availability of vacancies (*).

The rate constants of O\(_2\) activation during exchange and during NO oxidation are shown in Fig. 4. NO oxidation rate constants were measured at NO/NO\(_2\)/O\(_2\) pressures corresponding to O\(_2\)\(^y\) values of 2 kPa (Eq. 7) and compared with O\(_2\) exchange rates measured at an actual total pressure of 2 kPa O\(_2\)(g).

**Figure 4.** O\(_2\) activation rates \(r_{O_2}\) divided by the prevalent O\(_2\) pressure during (■) NO oxidation at 2 kPa O\(_2\)\(^y\) and during (●) O\(_2\) exchange at 2 kPa O\(_2\) on (a) 2.4% wt. Rh\(_3\)O\(_4\)/Al\(_2\)O\(_3\) (0.47 dispersion) and (b) 10% wt. Co\(_3\)O\(_4\)/SiO\(_2\) (0.01 dispersion).
Figure 4 shows that $k_{ex}$ (Eq. 13) is larger than $k_1$ (Eq. 11), by a factor of ~10 on $\text{Co}_3\text{O}_4$ and ~100 on $\text{RhO}_2$. Exchange rates depended more weakly on temperature than NO oxidation rates, suggesting that oxygen exchange has a lower activation energy than NO oxidation. These results contrast those reported previously on Pt and PdO clusters [12, 13], on which NO oxidation rate constants were the same within experimental accuracy.

The larger rate constants for exchange ($k_{ex}$) compared with those for NO oxidation ($k_1$) on $\text{RhO}_2$ and $\text{Co}_3\text{O}_4$ catalysts (Fig. 4) indicate that $O_2$ activation during $^{16}O_2$-$^{18}O_2$ exchange occurs via different kinetically-relevant steps than those required for $O_2$ activation in NO-O$_2$ reactions. $^{18}O_2$ exchange with lattice $^{16}O^{(16}O^*)$ on some oxides [23] can occur via concerted three-atom transition states that mediate the $O_2$ activation and exchange elementary steps (Scheme 2). This step does not lead to $O_2$ dissociation and therefore it cannot contribute to NO oxidation turnovers, which require the ultimate dissociation of $O_2^*$ to form active $O^*$ species. The contributions of these three-atom transition states, in addition to those that can lead to both $O_2$ exchange and dissociation, is likely to contribute to $O_2$ exchange rates much larger than for $O_2$ activation during NO oxidation catalysis, even though both reactions are limited by elementary events that require the activation of $O_2$ via interactions with vacant sites on surfaces of clusters nearly saturated with oxygen.

Scheme 2. Proposed mechanism of $^{16}O_2$-$^{18}O_2$ exchange on $\text{Co}_3\text{O}_4$ and $\text{RhO}_2$

NO oxidation and $O_2$ exchange rates differ from each other on $\text{RhO}_2$ or $\text{Co}_3\text{O}_4$, but these two processes occur at similar rates on Pt [12] or PdO [13]. This different behavior of $\text{RhO}_2$ and $\text{Co}_3\text{O}_4$ compared with Pt and PdO may reflect the ability of each of these catalysts to transfer electrons into adsorbed dioxygen molecules, as previously proposed for $O_2$ exchange [24]. Both Pd$^{2+}$ [17] and Pt$^{2+}$ [17] form Pd$^0$ or Pt$^0$ via direct two-electron reduction processes in aqueous electrochemical systems, but Co$^{3+}$ [17] and Rh$^{4+}$ [25, 26] reduce sequentially via one-electron processes to Co$^{2+}$ and Rh$^{3+}$, respectively, as is also the case for such cations in their respective bulk oxides. Co$^{3+}$ in Co$^3\text{O}_4$ and Rh$^{4+}$ in $\text{RhO}_2$ undergo one-electron reductions to form Co$^{2+}$ centers in CoO and Rh$^{3+}$ in $\text{Rh}_2\text{O}_3$, while Pd$^{2+}$ in PdO and Pt$^{2+}$ in PtO and Pt$_3\text{O}_4$ reduce directly to the respective metals. We infer from these differences between Pt$^{2+}$/Pd$^{2+}$ and Co$^{3+}$/Rh$^{4+}$ reduction paths that $O_2$ exchange may proceed via concerted reactions of $O_2$ with $O^*$ when metal centers at vacant sites can undergo a one-electron reduction processes. NO oxidation on $\text{Co}_3\text{O}_4$ and $\text{RhO}_2$ is slower than $^{16}O_2$-$^{18}O_2$ exchange apparently because more than one electron must be transferred to $O_2$ during the catalytic cycle for NO oxidation, but not during isotopic exchange.
In spite of these differences in \( O_2 \) activation modes on \( \text{Co}_3\text{O}_4 \), \( \text{RhO}_2 \), Pt and PdO, the kinetically-relevant step for NO oxidation on all catalytic systems is the activation of \( O_2 \) on scarce vacancies at surfaces nearly saturated with oxygen species, bound on Pt metal cluster surfaces and part of exposed planes in a bulk oxide for the others. This suggests that NO oxidation turnover rates on all materials depend on strength of surface metal-oxygen bonds, which determine the density of vacancies for any given oxygen chemical potential in the reacting mixture.

### 4. Site Requirements for NO Oxidation on Rh and Co Oxides

NO oxidation rates on Rh and Co oxides clusters were normalized by the \( H_2 \) uptake on the reduced catalyst to account for the fraction of sites on cluster surfaces. NO oxidation rates on dispersed \( \text{RhO}_2 \) clusters increased with increasing cluster size (Fig. 5), consistent with the trends reported on Pt \([10,12]\) and PdO \([13]\) (Fig. 5). Oxide clusters become more difficult to reduce with decreasing size, as their valence electrons become confined within smaller domains and their HOMO-LUMO gaps become larger \([27,28]\). Consequently, vacancies become scarcer as oxide domains become less reducible with decreasing size, causing NO oxidation turnover rates to decrease with decreasing size because vacancies are required for kinetically-relevant elementary steps in NO oxidation catalytic sequences.

**Figure 5.** NO oxidation rates on (▲) \( \text{RhO}_2/\text{Al}_2\text{O}_3 \), (◆) \( \text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3 \), (■) Pt/\( \text{Al}_2\text{O}_3 \) [12], and (●) PdO/\( \text{Al}_2\text{O}_3 \) [13] at 603 K, 5 kPa \( O_2 \), 120 Pa NO, 56 Pa NO\(_2\).

NO oxidation turnover rates on large \( \text{Co}_3\text{O}_4 \) clusters (40-100 nm) were much higher than rates on all other catalysts examined (Fig. 5). NO oxidation rates on \( \text{RhO}_2 \) were higher than those on PdO and similar in magnitude to those on Pt clusters similar in size (Fig. 4). The NO oxidation rate constant on each catalyst depends on the rate constant for \( O_2 \) activation (\( k_1 \)) and the \( O^* \) binding energy (via \( K_3 \) or \( K_0 \)) (Eq. 6 or 11). \( O^* \) binding energies account for these cluster size effects observed in NO oxidation (Fig. 5); as a result, they must also account for the trends in NO oxidation rates among these different catalytic elements.
Indeed, Pd(111) binds O* more strongly than Pt(111) by ~30 kJ mol⁻¹ [29]. This difference in O* binding energies apparently persists on working catalysts (PdO and Pt surfaces saturated with O*), consistent with the lower NO oxidation rates on PdO catalysts (Fig. 5). In their metallic states, Rh(111) and Co(111), however, bind O* much more strongly than Pt(111) or Pd(111) by 100-200 kJ mol⁻¹ [30]. Yet, NO oxidation turnover rates on Rh and Co oxides are much higher than on Pt or Pd and than expected from these high O* binding energies on Rh and Co metal (Fig. 5).

Clearly, O* binding energies on Rh and Co metal surfaces are not accurate descriptors of reactivity, because they are not inherently relevant to the stability and concentration of vacancies on catalysts that exist as oxides during NO oxidation catalysis.

Vacancy formation on clusters nearly saturated with oxygen occurs via the formal reduction of cations bound to chemisorbed or lattice oxygen atoms. The thermodynamics of such events should parallel those of electrochemical redox cycles. The standard reduction potential for Co³⁺/Co²⁺ cycles (1.8 V) is significantly larger than for Pt²⁺/Pt⁰ cycles (1.3 V), which is larger, in turn, than for Pd²⁺/Pd⁰ cycles (0.9 V) [17] (Fig. 6). These reduction potentials indicate that Co³⁺ reduction to Co²⁺ is more facile than reduction of either Pt³⁺ or Pd⁴⁺ to the corresponding zero-valent state. For these systems, NO oxidation turnover rates and electrochemical reduction potentials appear to share common features that cause the correlation evident from the data in Fig. 6 for Co₃O₄, Pt, and PdO. The correlation in Fig. 6 suggest that the thermodynamics of electrochemical redox cycles parallels those relevant for vacancy formation on catalyst surfaces, which affect, in turn, O₂ adsorption rates for any given oxygen chemical potential during NO oxidation. The wide range of reduction potentials reported for Rh⁴⁺/Rh³⁺ reduction cycles (0.8-1.7 V, for different coordinating ligands [25,26]) make any attempts at relating it to NO oxidation reactivity less precise than for the other metal systems. NO oxidation rate data suggest that the reduction tendency (and vacancy density) of RhO₂ clusters lies between that for Pt and PdO and is much greater than indicated by the reduction potential for Rh³⁺/Rh⁰ cycles (Fig. 6).

The correlation between NO oxidation rates and redox potentials (Fig. 6) suggests that high NO oxidation turnover rates on RhO₂ and Co₃O₄ reflect the ability of Rh⁴⁺ and Co³⁺ to undergo one-electron reductions, which are more facile than reductions requiring the transfer of two electrons from a single cationic center. Such facile one-electron transitions in RhO₂ and Co₃O₄ lead to higher vacancy concentrations on these substrates than expected from the redox potentials for Rh³⁺/Rh⁰ and Co²⁺/Co⁰ transitions (Fig. 6) and from the strong binding of O* on Rh and Co metal. Moreover, the higher rates of O₂-O₂ exchange on RhO₂ and Co₃O₄ than NO oxidation appear to also reflect the ability of these substrates to undergo one-electron redox cycles.

These effects of one-electron cycles on NO oxidation rates (Fig. 6) and the much higher rates for O₂-O₂ exchange than for NO oxidation on RhO₂ and Co₃O₄ (but not on Pt or PdO) (Fig. 4) indicate that O₂
dissociation to form O* atoms involves multiple Co$^{3+}$ or Rh$^{4+}$ centers, whereas $^{16}$O$_2$-$^{18}$O$_2$ exchange occurs on only one Co$^{3+}$ or Rh$^{4+}$ center.

We note that Co oxides have been reported to exhibit high reactivity for electrochemical H$_2$O oxidation to O$_2$, a reaction that shares elementary steps with NO oxidation $^{[31,32]}$ in their common requirement for oxygen vacancies in their respective kinetically-relevant steps. In H$_2$O oxidation, vacancies form via reduction of Co$^{4+}$ to Co$^{3+}$, apparently by similar one-electron transitions that occur on Co$^{3+}$ during NO oxidation.

These mechanistic connections between electrochemical reduction thermodynamics and NO oxidation turnover rates (Fig. 6) indicate a fundamental resemblance between electron transfer processes in solvated coordination complexes and inorganic oxides. For both, reduction tendencies reflect the energy levels of the frontier orbitals that accept electrons, which are set by metal-ligand and electron-electron interactions. Theoretical estimates of such energies remain uncertain, because DFT methods do not accurately describe the critical electron-electron interactions that influence the thermodynamics of electron transfer processes in inorganic solid oxides [33]. The connections inferred here between the reduction tendencies of aqueous metal complexes and solid oxides (and their consequences for reduction-oxidation catalysis) provide significant impetus for parallel efforts in the development and use of more exact theoretical approaches to describe the redox properties of solids, if so required by the use of coordination complexes as model systems more amenable to rigorous theoretical treatments to assess the accuracy of these theoretical methods.

**Conclusion**

The effects of NO, NO$_2$, and O$_2$ pressures on NO oxidation rates on RhO$_2$ and Co$_3$O$_4$ were consistent with a mechanism in which O$_2$ binding on oxygen atom vacancies is the kinetically-relevant step for NO oxidation, as also observed on Pt and PdO. Equilibrated reactions involving NO and NO2 establish vacancy concentrations and oxygen chemical potentials at catalyst surfaces. The oxygen chemical potentials prevalent during NO oxidation caused Rh and Co clusters to exist as RhO$_2$ and Co$_3$O$_4$ during catalysis. NO oxidation rates increased with increasing cluster size on RhO$_2$, as also observed for rates on Pt and PdO clusters because small oxide and metal clusters bind oxygen more strongly, resulting in lower concentrations of vacant sites that bind O$_2$ in kinetically-relevant steps. Both RhO$_2$ and Co$_3$O$_4$ have cations (Rh$^{4+}$ and Co$^{3+}$) that reduce via one-electron redox cycles to form vacancies. This leads to $^{16}$O$_2$-$^{18}$O$_2$ exchange rates on RhO$_2$ and Co$_3$O$_4$ that are much larger than NO oxidation rates because exchange occurs by an O$_2$ activation pathway that requires only a one-electron transfer. NO oxidation, in contrast, requires that O$_2$ dissociates to oxygen atoms by two consecutive one-electron reductions of multiple Co$^{3+}$ or Rh$^{4+}$ centers in Co$_3$O$_4$ or RhO$_2$. NO oxidation rates on all catalysts correlated strongly
to the electrochemical redox potential when the one-electron transitions involving Co\(^{3+}/Co^{2+}\) and Rh\(^{4+}/Rh^{3+}\) were used to describe the reducibility of Co\(_2\)O\(_4\) and RhO\(_2\) catalysts. The presence of the one-electron pathways on Co\(_2\)O\(_4\) and RhO\(_2\) leads to NO oxidation rates that are higher than expected from the large O\(^*\) binding energy on Rh and Co metal, causing both to be effective NO oxidation catalysts.

Experimental Section

Catalyst Synthesis and Characterization. \(\gamma\)-Al\(_2\)O\(_3\) (Sasol, SBA-200, 180 m\(^2\) g\(^{-1}\)) and SiO\(_2\) (Davisil, Grade 646, 300 m\(^2\) g\(^{-1}\)) supports were heated to 1023 K at 0.07 K s\(^{-1}\) in flowing dry air (Praxair, Extra Dry, 1 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) and held for 4 h. Rh(NO\(_3\))\(_3\)•H\(_2\)O (Sigma Aldrich) or Co(NO\(_3\))\(_2\)•(H\(_2\)O)\(_6\) (Sigma-Aldrich) were added to de-ionized distilled water (Barnstead, Nanopure) and the solution was added dropwise to \(\gamma\)-Al\(_2\)O\(_3\) or SiO\(_2\) to the incipient wetness point (0.45 g solution (\(\gamma\)-Al\(_2\)O\(_3\))-1, 0.9 g solution (g SiO\(_2\))\(^{-1}\)) to prepare samples with 0.8% and 2.4% wt. Rh and 10% wt. Co. Impregnated supports were heated in ambient air at 393 K for 4 h and then in flowing dry air (Praxair, extra dry, 1 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) for 4 h by heating at 0.07 K s\(^{-1}\) to a temperature between 673-1148 K. Rh- or Co-containing samples were then heated to 873 K or 673 K, respectively, at 0.07 K s\(^{-1}\) and held in 9% H\(_2\)/He (Praxair, 99.999% purity, 1 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) for 5 h. Materials were treated with 0.5% O\(_2\)/He (Praxair, 99.999% purity, 1 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) at 295 K for 1 h before exposure to ambient air.

H\(_2\) and O\(_2\) uptakes were measured volumetrically (Autosorb-1; Quantachrome) to determine the number of Rh and Co atoms exposed at cluster surfaces (Rhs and Cos) and the number of reducible Co atoms (Cor). Samples (0.5-1.0 g) were heated to 673 K at 0.08 K s\(^{-1}\) and held at 673 K for 2 h in flowing H\(_2\) (1 bar) and then evacuated for 1 h at 673 K before H\(_2\) or O\(_2\) uptake measurements at 313 K and 673 K, respectively, and 5-50 kPa titrant pressure. Uptake isotherms were extrapolated to zero pressure to exclude contributions from weakly-bound species. Mean cluster diameters were estimated from measured uptakes using the assumptions of one chemisorbed H atom per surface Rh or Co atom (denoted Rhs or Cos), 1.33 O atoms per reducible Cobalt atom, and hemispherical clusters with densities of bulk Rh or Co (12.4 g Rh cm\(^{-3}\); 72 Rh nm\(^3\); 8.9 g Co cm\(^{-3}\); 91 Co nm\(^{-3}\)\(^{[17]}\)).

NO Oxidation Rate Measurements. NO oxidation rates were measured on 0.12-0.18 mm Rh/Al\(_2\)O\(_3\) and Co/SiO\(_2\) aggregates. Samples were held on a porous quartz frit within a tubular quartz reactor (10 mm). Reactants (15% O\(_2\)/He, 2% NO/He, 1% NO\(_2\)/He, and 5% CO\(_2\)/He) and He carrier (Praxair, 99.999% purity) were metered using electronic controllers (Porter Instruments) to achieve a broad range of reactant pressures (1-12 kPa O\(_2\), 0.04-0.25 kPa NO, 0.02-0.25 kPa NO\(_2\), 0-2 kPa CO\(_2\)). A resistively-heated furnace with a controller (Watlow, 96 series) and a K-type thermocouple were used to maintain constant temperatures (548-673 K). Inlet and outlet concentrations were measured using an infrared analyzer (MKS 2030; 2 cm\(^3\) cell; 2 cm pathlength; 338 K). NO oxidation rates are reported as turnover
Isotopic Oxygen Exchange Measurements. $^{16}$O$_2$-$^{18}$O$_2$ exchange rates were measured using a gradientless batch reactor (498 cm$^3$ volume), in which reactants were circulated by a graphite gear pump (Micropump; 2 cm$^3$ s$^{-1}$). Gases (99.999% chemical purity) were obtained from Praxair (90% O$_2$/Ar, He) and Ikon Isotopes ($^{18}$O$_2$, 96% isotopic $^{18}$O purity). Catalysts were heated to 573-653 K at 0.07 K s$^{-1}$ and held for 1 h in flowing 2 kPa $^{16}$O$_2$/Ar/He (30 cm$^3$ s$^{-1}$ g$^{-1}$) before the reactor was evacuated and filled with an equimolar $^{16}$O$_2$-$^{18}$O$_2$ mixture and He as balance. Isotopomer concentrations were measured by pulses injected periodically into a mass spectrometer (MKS Mini-Lab).

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Reference
Paper VIII
Catalytic NO Oxidation Pathways and Redox Cycles on Dispersed Oxides of Rhodium and Cobalt
