



Effect of soot on the storage–reduction performances of PtBa/Al₂O₃ LNT 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 NO_x 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.

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1. Introduction

Diesel-equipped vehicles are considered as one of the primary sources of NO_x and particulate (soot) emissions in industrialized countries. Accordingly regulations to limit their emissions are becoming very strict. In Europe, the current Euro 5 rules limit NO_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_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_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 continuously regenerating trap (CRT) 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 NO₂, which then oxidizes at low temperature the particulate matter trapped and is back-reduced to NO:



Thanks to the high combustion activity of NO₂ 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 NO₂ oxidation, and on the NO concentration as well. In fact, the NO_x content of the exhaust may be not high enough to ensure the complete filter regeneration.

Integrated De-NO_x and De-soot after-treatment technologies have also been proposed. One example is the diesel particulate-NO_x reduction (DPNR) 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_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 alkaline-earth metal oxides which present a high NO_x-storage capacity. These catalytic systems work under cyclic conditions, alternating long lean periods with short regeneration periods under rich conditions. During the lean phase the NO_x produced by the engine are oxidized and adsorbed on the alkaline or alkaline-earth 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 NO_x

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storage–reduction mechanism in the DPNR system is similar to that already proposed by Toyota for NSR systems [6–9]. Soot oxidation occurs under lean conditions thanks to the presence of NO_x and the excess of oxygen in the exhaust gas; soot removal is also claimed to occur during the rich phase as well.

Whereas the behavior of NSR catalysts is well investigated [10–15], 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 NO_x 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 PtBa/Al₂O₃ sample is able to simultaneously remove soot and NO_x. It has also been shown that NO_x species stored onto the trapping component of the catalyst participate in the combustion of soot via the release of NO_x 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 NO_x trapping component like BaO in Pt/SiO₂ system does not promote *per se* the particulate combustion, but favors soot combustion due to the increase in the NO₂ gas phase concentration upon nitrate decomposition. Accordingly there is a general consensus on the fact that the NO_x storage function of the NSR catalysts affects the combustion of soot.

Besides, soot may have a role on the NO_x storage capacity of the catalysts as well. In a recent work we have shown that the presence of soot negatively influences the NO_x 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 NO_x adsorbed species, thus suggesting an interaction between soot and the stored NO_x.

Aim of the present work is to provide new insights on the pathways involved in the NO_x 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 behavior of the selected catalyst sample in which the reactivity in the NO_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/Al₂O₃ (1/20/100, w/w/w) sample used in this study has been prepared by incipient wetness impregnation of a γ-Al₂O₃ calcined at 700 °C (Versal 250 from UOP) with a solution of Pt(NH₃)₂(NO₂)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/Al₂O₃ sample was then impregnated with an aqueous solution of Ba(CH₃COO)₂ (Sigma Aldrich, 99%), dried at 80 °C and further calcined at 500 °C for 5 h to prepare the ternary PtBa/Al₂O₃ 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 [24]. The obtained catalytic powder was grinded and sieved at 70–100 μm before use.

The catalyst was characterized by XRD analysis (Bruker D8 Advanced Instrument equipped with graphite monochromator on

the diffracted beam), surface area and pore size distribution by N₂ adsorption–desorption at 77 K (Micromeritics TriStar 3000 instrument) and Pt dispersion by hydrogen pulse chemisorption at 0 °C (TPD/R/O 1100 Thermo Fischer Instrument).

The PtBa/Al₂O₃ sample presents a surface area near 160 m²/g_{cat} and pore volume of 0.8 cm³/g_{cat}, while the Pt dispersion is close to 60%. In the XRD patterns of the freshly calcined PtBa/Al₂O₃ catalyst both the monoclinic (JCPDS 78-2057) and orthorhombic (Whiterite, JCPDS 5-378) polymorphic forms of BaCO₃ were detected in addition to microcrystalline γ-Al₂O₃ (JCPDS 10-425); no other crystalline phases were observed. Further details of catalyst preparation and characterization are reported elsewhere [12,15,20,25,26].

Printex-U (Degussa) was used as model soot [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 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 (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 stabilization 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 NO_x storage proceeded up to nearly steady state, then the inlet NO concentration was stepwise decreased to zero. After 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 behavior (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 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 $\text{He} + \text{O}_2$ (3%, v/v), H_2O (1%, v/v) and CO_2 (0.1%, v/v) until a steady-state behavior 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 out by heating the prepared catalyst–soot mixture at a rate of $10^\circ\text{C}/\text{min}$ in $\text{He} + \text{H}_2\text{O}$ (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 [18–20].

3. Results and discussion

3.1. Effect of temperature

The NO_x storage-reduction over $\text{PtBa}/\text{Al}_2\text{O}_3$ has been investigated in the temperature range $200\text{--}350^\circ\text{C}$ in the absence and in the presence of soot, and the results are shown in Figs. 1 and 2, respectively.

3.1.1. 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 ($t=0\text{ s}$) 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 signifi-

cant NO_2 evolution is observed at this temperature. At $t=2200\text{ s}$ 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 $0.29\text{ mmol}/\text{g}_{\text{cat}}$, as apparent from Fig. 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 Fig. 1A (the lag time of the apparatus has been found to be negligible, see Section 2).

Upon NO admission, an increase in the CO_2 concentration is also observed, from the background level of 1000 ppm (Fig. 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):



As a matter of fact, by subtracting from the CO_2 concentration trace the concentration of CO_2 estimated from the NO_x uptake according to the stoichiometry of reaction (3), a net CO_2 concentration trace is obtained (see Fig. 1A) that closely resembles the inlet CO_2 concentration value (1000 ppm). This indicates that the evolution of CO_2 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 CO_2 uptake is observed, due to the occurrence of the reverse of reaction (3).

The NO_x storage behavior of the catalyst is affected by the temperature. The NO_x breakthrough increases from few seconds at 200°C (Fig. 1A) to 25 s at 300°C and 40 s at 350°C (Fig. 1C and E). Besides the amounts of NO_x stored up to steady-state increase with temperature, from $0.28\text{ mol}/\text{g}_{\text{cat}}$ at 200°C to $0.34\text{ mol}/\text{g}_{\text{cat}}$ at 300°C and $0.59\text{ mol}/\text{g}_{\text{cat}}$ at 350°C (Fig. 3 and Table 1). The NO_2 concen-

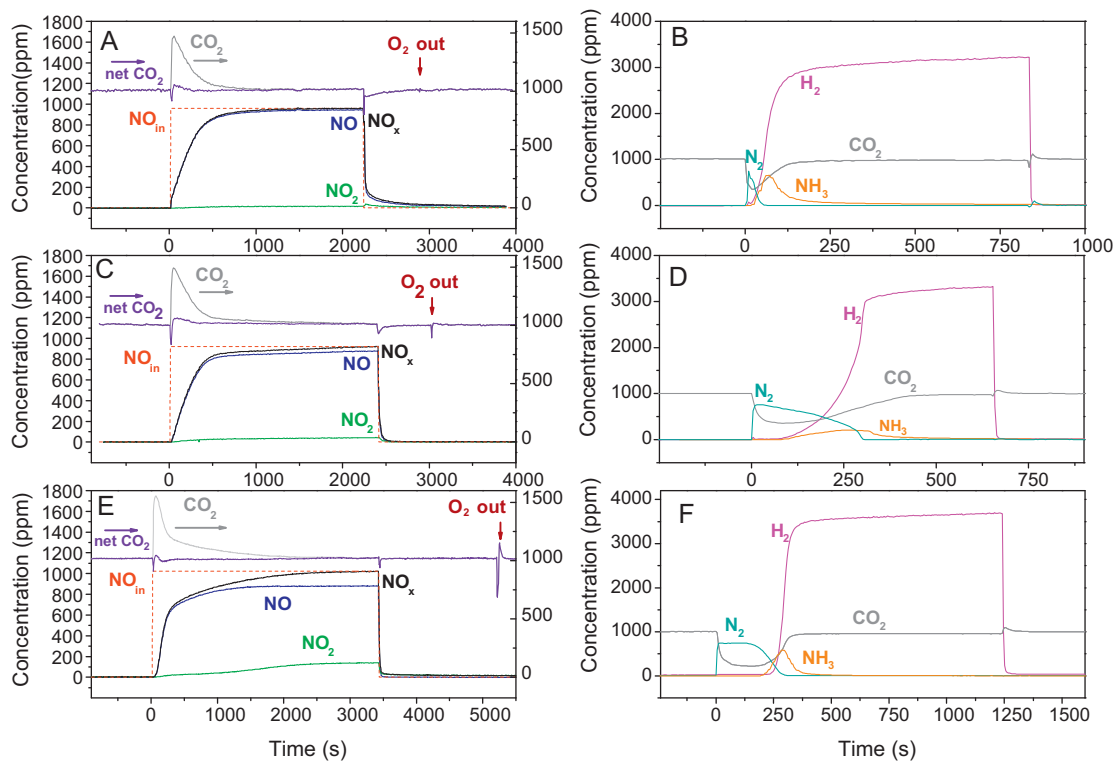


Fig. 1. Lean-rich cycles performed over $\text{PtBa}/\text{Al}_2\text{O}_3$ in the absence of soot at different temperatures in the presence of H_2O (1%, v/v) and CO_2 (0.1%, v/v). Lean phase (A, C and E): 1000 ppm $\text{NO} + \text{O}_2$ (3%, v/v) in He ; rich phase (B, D and F): 4000 ppm H_2 in He . Other experimental conditions: catalyst weight 60 mg, total flow rate 100 cc/min at 0°C and 1 atm. Panels A and B: $T=200^\circ\text{C}$; panels C and D: $T=300^\circ\text{C}$; panels E and F: $T=350^\circ\text{C}$.

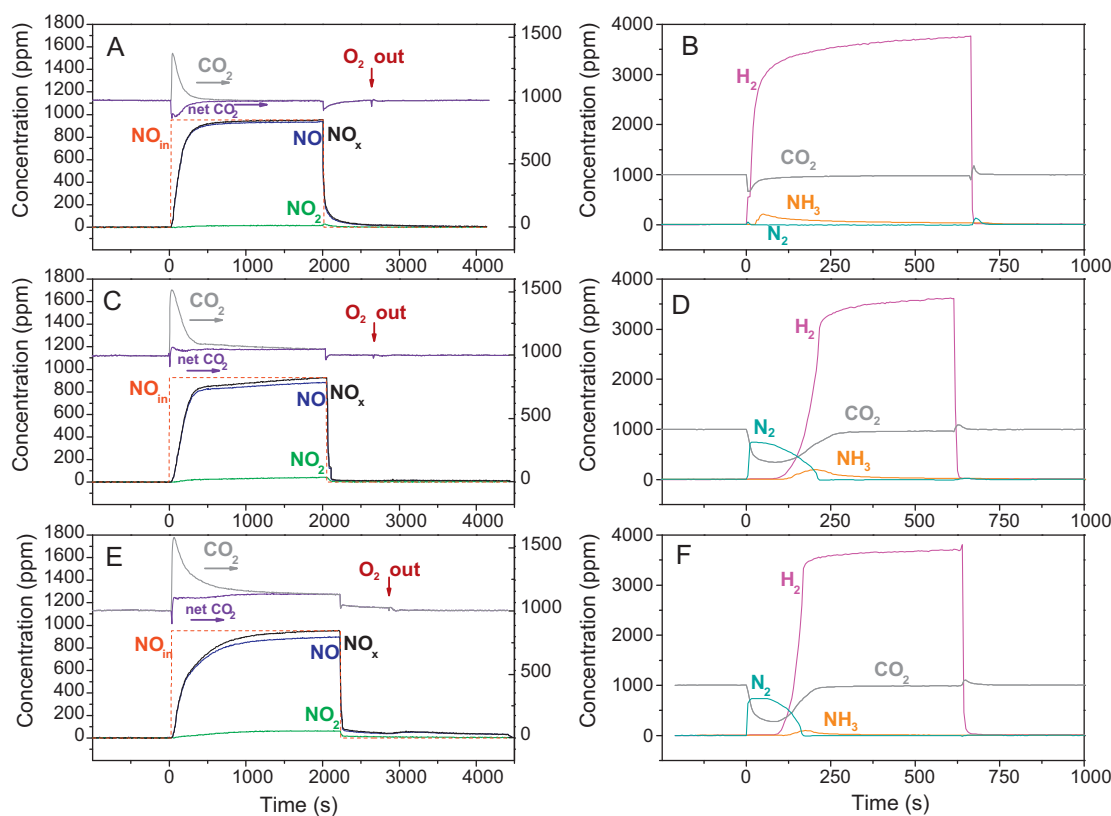


Fig. 2. Lean-rich cycles performed over PtBa/Al₂O₃/soot mixture at different temperatures in the presence of H₂O (1%, v/v) and CO₂ (0.1%, v/v). Lean phase (A, C and E): 1000 ppm NO + O₂ (3%, v/v) in He; rich phase (B, D and F): 4000 ppm H₂ in He. Other experimental conditions: 60 mg of catalyst + 6 mg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

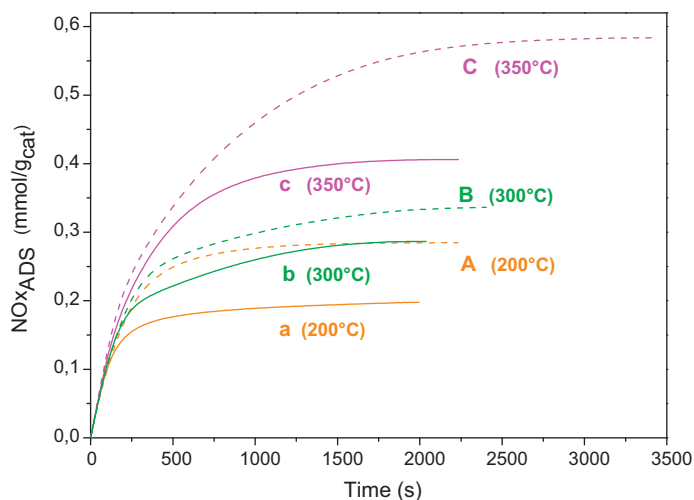


Fig. 3. Amounts of adsorbed NO_x versus time over PtBa/Al₂O₃ (dotted lines) and over PtBa/Al₂O₃/soot mixture (solid lines) at different temperatures.

Table 1

Stored NO_x, desorbed NO_x (1300 s after NO_x shutoff) and percentage of desorbed NO_x/stored NO_x ratio at different temperatures, in the absence and in the presence of soot (NO 1000 ppm, H₂O 1% v/v, CO₂ 0.1% v/v).

Temperature (°C)	Without soot			With soot		
	Stored NO _x (mmol/g _{cat})	Desorbed NO _x after NO shutoff (mmol/g _{cat})	Desorbed NO _x /stored NO _x (%)	Stored NO _x (mmol/g _{cat})	Desorbed NO _x after NO shutoff (mmol/g _{cat})	Desorbed NO _x /stored NO _x (%)
200	0.28	0.09	34.0	0.20	0.09	43.8
300	0.34	0.02	7.2	0.29	0.06	19.6
350	0.59	0.06	10.0	0.39	0.10	27.2

tration at the reactor outlet measured at the end of the NO_x dose (steady-state) also increases with temperature. It has been suggested that NO₂ is precursor in the storage of NO_x, in line with the occurrence of a “nitrate” pathway for the storage of NO_x (i.e. NO oxidation to NO₂ followed by NO₂ adsorption in the form of nitrates via a disproportionation reaction) [13]. Accordingly it is speculated that in the investigated temperature range the amounts of NO_x 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 NO_x 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 NO_x 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 NO_x stored at steady state are related with the NO₂ concentration. On the other hand,

since other routes may be involved in the NO_x adsorption process, e.g. direct NO uptake on the catalyst surface, etc., factors other than thermodynamics involving gas phase NO₂ may govern the amounts of NO_x 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 molar 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 index of the average NO_x adsorption rate can be derived from the slope of the adsorption curves in Fig. 3. Notably, in the initial part the curves are almost superimposed since the rate of NO_x 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 NO_x, increases with temperature.

The results obtained when the same experiments have been carried out in the presence of soot are shown in Fig. 2A, C and E. Also in the presence of soot the NO_x outlet concentration shows a dead time and then increases approaching the asymptotic values corresponding to the NO inlet concentration. The NO_x breakthrough increases with temperature but it is always lower than in the absence of soot. Along similar lines the amounts of NO_x stored up to steady-state (see Fig. 3, solid lines) increase with temperature (from 0.20 mmol/g_{cat} at 200 °C, up to 0.40 mmol/g_{cat} at 350 °C), but the amounts of NO_x 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 indicate that soot reduces the NO_x 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 NO_x storage capacity of the catalyst at steady state is primarily related to the decrease in the NO₂ concentration.

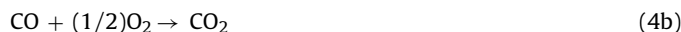
Finally, the presence of soot also decreases the rate of NO_x adsorption, as apparent from the comparison of the slopes of the adsorption curves collected at the same temperature in the presence and in the absence of soot at fixed amounts of stored NO_x (Fig. 3). This is likely associated to the decrease in the NO₂ 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 Figs. 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 CO₂ is also observed (Fig. 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, CO₂ may also be formed due to soot combustion according to the stoichiometry of reactions (4a) and (4b):



where NO₂ is formed upon NO oxidation and CO₂ is formed upon CO oxidation at Pt sites. As a matter of fact, soot oxidation experiments by NO₂ 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 CO₂ by O₂ at Pt sites.

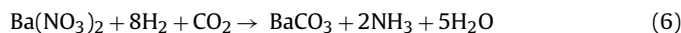
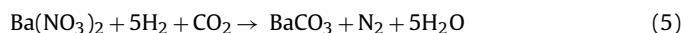
Accordingly reactions (4a) and (4b) imply the consumption of NO₂ and a decrease of its concentration at the reactor outlet. In order to determine the amounts of CO₂ produced upon soot oxidation, the “net” CO₂ production has been calculated as previously indicated, and the results are shown in Fig. 2. In the presence of soot a net CO₂ production is observed, which is negligible at 200 °C (Fig. 2A), but it is appreciable at 300 °C and 350 °C where the trace of the net CO₂ 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 CO₂ formation is observed. Hence NO₂, formed upon NO oxidation, is suggested to be the actual oxidizing agent of soot, accordingly to reactions (4a) and (4b), 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.

3.1.2. 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 H₂ in He in the presence of CO₂ and H₂O. 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 Figs. 1 and 2, respectively.

On the soot-free catalyst, upon the step addition of H₂ (at $t = 0$ s) at 200 °C (Fig. 1B), the H₂ outlet concentration profile shows a dead time during which it is completely consumed and then it increases with time. During H₂ consumption, the evolution at first of N₂ and then of NH₃ is seen at the reactor outlet, together with a consumption of CO₂. No formation of other products (e.g. N₂O) has been detected in appreciable amounts. The evolution of N₂ and NH₃, and the consumption of CO₂ as well, are in line with the overall stoichiometry of the following reactions (5) and (6):



which consider the re-adsorption of CO₂ onto the Ba sites once NO_x has been reduced.

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 NO_x by H₂ already proposed in previous studies of our group [32–34]. The suggested pathway involves a first fast step during which the stored NO_x react with H₂ to give NH₃, followed by the

slower reaction of ammonia with residual nitrates to form nitrogen. The observed products evolution with time is due to an H_2 front which develops and travels along the reactor. Accordingly, NH_3 is formed at the H_2 front and reacts with the NO_x stored downstream the front, leading to 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 NO_x stored downstream and this leads to the evolution of ammonia, which accordingly follows that of N_2 .

Similar results have been obtained (in the absence of soot) at the other temperatures, i.e. $300^\circ C$ and $350^\circ C$ (Fig. 1D 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 NO_x with temperature (Fig. 3); and (ii) the overall nitrogen selectivity of the reduction process increases with temperature, from roughly 35% at $200^\circ C$ up to 85% at $350^\circ C$. This is in line with the occurrence of the two-steps pathway previously suggested for N_2 formation [32–34]: 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 NO_x at the same temperatures in the presence of soot are shown in Fig. 2B, D and F. A comparison with the results obtained in the absence of soot (Fig. 1B, D and F) indicates that the presence of soot does not influence significantly the reduction of the stored NO_x .

3.2. Effect of NO inlet concentration on the NO_x storage/reduction and soot oxidation

3.2.1. Lean phase

The effect of the NO inlet concentration on the simultaneous NO_x and soot removal over the model PtBa/Al₂O₃ catalyst has been addressed by performing lean-rich cycles at $350^\circ C$ in the presence of CO₂ (0.1%, v/v) and H₂O (1%, v/v) with 250, 500 and 1000 ppm of NO in the feed (NO_{in}) 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 Figs. 1E and 2E, respectively, and have been previously discussed. Fig. 4 shows the results obtained at $350^\circ C$ in terms of 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 Fig. 3, these amounts are calculated from the NO_x concentration curves of Figs. 1 and 2.

As shown in Fig. 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 $0.59 \text{ mmol/g}_{cat}$ has been measured at steady state when 1000 ppm of NO are fed to the reactor (trace A), which decreases to $0.37 \text{ mmol/g}_{cat}$ for a NO inlet concentration value of 250 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 primarily related to the 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 Fig. 4 (dotted lines) in the region where the storage is not limited by the supply of NO.

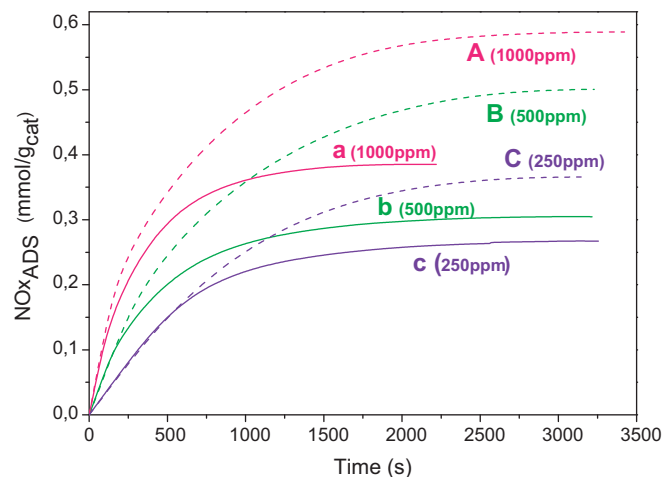


Fig. 4. Amounts of adsorbed NO_x versus time over PtBa/Al₂O₃ (dotted lines) and over PtBa/Al₂O₃/soot mixture (solid lines) at different NO inlet concentrations.

Finally, upon NO and O₂ 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 concentration (0.06 and 0.03 mmol/g_{cat} for NO = 1000 and 250 ppm, respectively), but are very similar if normalized to the amounts of NO_x initially stored (near 8–10%).

The presence of soot influences the storage of NO_x , as revealed by the comparison of the adsorption curves obtained in the absence and in the presence of soot (Fig. 4, dotted lines vs. solid lines). In the presence of soot the amounts of adsorbed NO_x decrease upon decreasing the NO inlet concentration, from 0.39 down to $0.27 \text{ mmol } NO_x/g_{cat}$, and these amounts are always lower than those observed with the soot-free catalyst. The presence of soot also decreases the NO_2 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/ NO_2 ratios are calculated at any investigated NO inlet concentration value. As previously discussed, this is related to the involvement of NO_2 in the soot combustion according to reactions (4a) and (4b). Along to the lines previously discussed, the decrease in the NO_x storage capacity of the catalyst at steady state in the presence of soot is primarily explained by the lower NO_2 concentrations obtained in these cases.

The rate of NO_x 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 NO_x , respectively). Again, this is likely associated to the effect of the NO_2 concentration on the rate of NO_x adsorption.

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

3.2.2. Regeneration phase

The reduction of the NO_x stored at $350^\circ C$ 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 Fig. 1B (adsorption with NO = 1000 ppm at $350^\circ C$, absence of soot) and Fig. 2B (adsorption with NO = 1000 ppm at $350^\circ C$, presence of soot). The results obtained in the absence and in the presence of soot point out that

Table 2
Stored NO_x, desorbed NO_x (1300 s after NO_x shutoff) and percentage of desorbed NO_x/stored NO_x ratio at different NO inlet concentration, in the absence and in the presence of soot (Temperature 350 °C, H₂O 1% v/v, CO₂ 0.1% v/v).

NO inlet concentration (ppm)	Without soot			With soot		
	Stored NO _x (mmol/g _{cat})	Desorbed NO _x after NO shutoff (mmol/g _{cat})	Desorbed NO _x /stored NO _x (%)	Stored NO _x (mmol/g _{cat})	Desorbed NO _x after NO shutoff (mmol/g _{cat})	Desorbed NO _x /Stored NO _x (%)
250	0.37	0.03	8.32	0.27	0.08	30.1
500	0.50	0.04	8.14	0.31	0.07	24.1
1000	0.59	0.06	10.0	0.39	0.10	27.2

the presence of soot does not influence significantly the reduction of the stored NO_x.

3.3. Interaction of the stored NO_x with soot

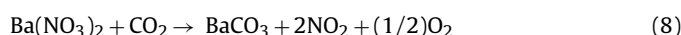
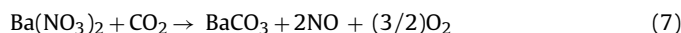
The results reported above pointed out that the presence of soot influences the storage of NO_x over PtBa/Al₂O₃. In fact soot (i) decreases the NO_x storage capacity of the catalyst, and (ii) favors the decomposition of the stored NO_x species. These conclusions apply when NO_x are stored at different temperatures and when different values of the NO inlet concentration are used. On the other hand, the reduction of the stored NO_x (i.e. catalyst regeneration) is not significantly influenced by the presence of soot, if one neglect a small increase in the N₂ selectivity. During NO_x 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 NO₂, formed upon NO oxidation, that is well recognized in the literature [16,22,31]. However, the participation of adsorbed NO_x 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 NO_x adsorbed on the catalyst surface is investigated. For this purpose TPD experiments have been carried out in which the thermal stability and reactivity of NO_x 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 NO_x 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 NO_x, the NO_x 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 Section 2). NO_x 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 Fig. 5A (absence of soot) and B (presence of soot). In the case of the soot-free PtBa/Al₂O₃ catalyst (Fig. 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.

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 indi-

cating 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:



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 affect 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 NO_x towards adsorption onto the Ba sites.

The results of the TPD experiment of Fig. 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 NO_x adsorption. This is likely related to the different procedure used in this case, which involves

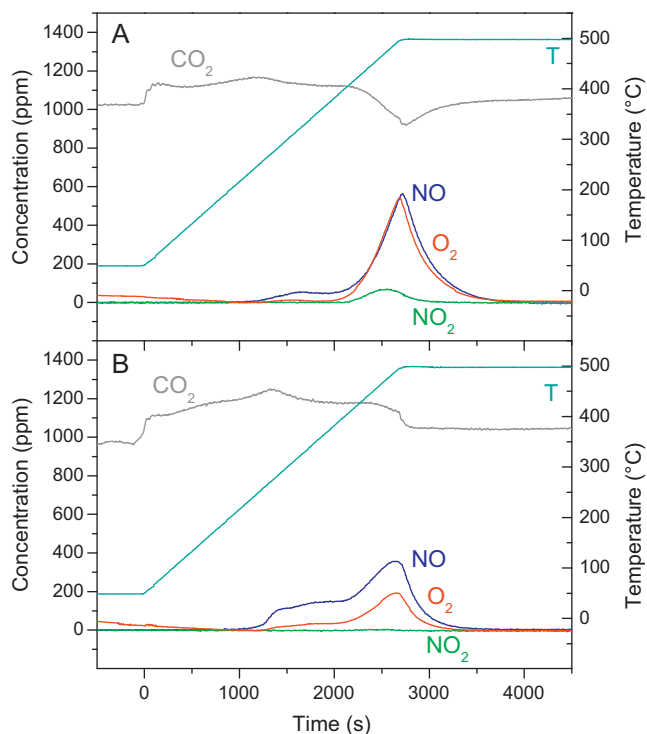


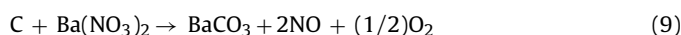
Fig. 5. TPD run after NO_x adsorption at 350 °C (1000 ppm NO + O₂ (3%, v/v) in He + H₂O (1%, v/v) + CO₂ (0.1%, v/v)) over (A) PtBa/Al₂O₃ catalyst; (B) PtBa/Al₂O₃/soot mixture.

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 NO_x 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 NO_x are affected by surface hydration already at room temperature [36].

Fig. 5B shows the results of the TPD experiments carried out after mixing the catalyst with soot. A comparison with Fig. 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 260–350 °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 Fig. 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 (Fig. 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)).

The effect of soot on the stability of the stored nitrates has also been pointed out by the ISC experiments discussed above (Figs. 1 and 2) showing that the amounts of NO_x 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 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 [16,37]. 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:



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 Fig. 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 satisfied. In

fact above 350 °C the O/N ratio in the products (considering both NO_x and O₂) is higher than 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 (Fig. 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 (Fig. 5A, O/N = 2.6).

Accordingly TPD data indicate 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 NO₂ that occurs in the presence of gas-phase NO₂, i.e. upon the NO_x storage during lean/rich operation of the NSR catalyst.

The suggested mechanism implying the direct interaction between nitrate ad-species 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_x storage properties of the investigated PtBa/Al₂O₃ catalyst, when estimated in the presence of water and CO₂. In fact soot leads to an appreciable decrease of both the NO_x storage capacity and the rate of NO_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_x storage, soot oxidation also occurs at 300 °C and above, 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 in the absence of 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 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 NO₂ followed by NO₂ adsorption in the form of nitrates via a disproportionation reaction), Ba and soot compete for reaction with NO₂, as suggested by Sullivan et al. [22], leading to the observed decrease in the NO_x storage properties. On the other hand, the reduction of the stored NO_x 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. These aspects deserve however further investigation.

Finally, it is worth of note that the adsorbed NO_x oxidize soot at temperature well below those corresponding to their thermal decomposition originating NO₂ 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 NO_x, 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.

Acknowledgement

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