

EFFECT OF THE PRESENCE OF SOOT ON THE REMOVAL OF NO_x UNDER LEAN CONDITIONS

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The NO_x storage activity of a Pt-Ba/Al₂O₃ catalyst, in presence and absence of soot, has been investigated in this work. It was found that the presence of soot reduces the NO_x storage capacity of the catalyst in the range 200 - 350°C and with different values of the NO inlet concentration. The observed decrease of the storage activity has been ascribed to the lower gas-phase NO₂ concentration which is involved in soot oxidation. Besides the presence of soot favors the decomposition and the reduction of the stored nitrates, while soot is being oxidized. In parallel to the NO₂-soot oxidation, a direct reaction between the stored nitrates and soot has also been suggested, that has been explained on the basis of the surface mobility of the adsorbed nitrates.

1. INTRODUCTION

The reduction of pollutant emissions from mobile sources, and in particular from the exhausts of Diesel engines, is nowadays a relevant problem on which the scientific community tries to give effective solutions. In this context, the use of exhaust after-treatment technologies able to reduce both particulate matter and NO_x (Johnson, 2008) is mandatory to cope with the next coming emission standards for diesel-equipped vehicles (Euro 6). In particular, the severity of Euro 6 regulations requires new solutions based on more integrated systems for reducing both NO_x and particulate matter. The integrated systems currently proposed combine filter devices for particulate removal (the so-called Diesel Particulate Filters, DPF) and catalytic De-NO_x systems such as Selective Catalytic Reduction (SCR) with NH₃ and/or LNT (Lean NO_x Trap). Among these, the DPNR (Diesel Particulate NO_x Reduction) technology, which involves the use of LNT catalysts, working under lean-rich cycling conditions, is the first commercialized example of such a technology (Nakatani et al., 2002).

In previous works of our group the capability of model DPNR catalysts (e.g. Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃) to simultaneously remove soot and NO_x has been investigated. It has been shown that during the lean phase, while NO_x are being stored on the catalyst surface, soot oxidation occurs involving primarily NO₂, formed upon NO oxidation (Castoldi et al., 2006; Matarrese et al., 2007). However, other studies carried out in our labs have shown that NO_x species, stored onto the trapping component of the catalyst, may 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 (Matarrese et al., 2008; Castoldi et al., 2010). According to these results, Kustov et al. (2009) 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.

In the present work we wanted to analyze more in details the effects of the presence of soot on the behavior of a model Pt-Ba/Al₂O₃ LNT catalyst. For this purpose, NO_x 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. The interaction between soot and the stored NO_x species has also been investigated by Temperature Programmed Methods under inert flow (TPD) in 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 Pt-Ba/Al₂O₃ (1/20/100 w/w) sample used in this study has been prepared by incipient wetness impregnation with barium acetate (Sigma Aldrich, 99%) of a Pt/Al₂O₃ (1/100 w/w) sample, which in turn was prepared by impregnating the commercial γ -alumina (Versal 250 from UOP) with dinitro-diammine platinum (Strem Chemicals, 5% Pt in ammonium hydroxide). After impregnation the sample was dried at 80°C and then calcined at 500°C for 5h. Printex-U (Degussa) was used as model soot, whose properties were well addressed (Setiabudi et al., 2004). Catalyst-soot mixtures were prepared by gently mixing in a vial the catalyst powder (74-105 μ m) with the soot, thus realizing a loose contact; a soot loading near 10 % w/w has been typically employed. The 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) and a micro GC (Agilent 3000A) for the on-line analysis of the outlet gases. The outlet NO, NO₂, NH₃ concentrations were also detected by an UV analyzer (Limas 11HW, ABB). In each run 66 mg of soot-catalyst mixture have been used and the total flow rate was set at 100 cm³/min (at 0 °C and 1 atm). The catalytic De-NO_x and De-soot activity was investigated by performing lean-rich cycles at constant temperature alternating rectangular step feeds of NO (1000 ppm v/v) and 3% v/v of O₂ in He (lean phase) with feeds of H₂ (4000 ppm v/v in He, rich phase). The abrupt switches between the adsorption and the regeneration phase has been realized simultaneously with the use of four-port valves. Soot is progressively consumed during each test; accordingly several catalyst/soot batches have been used. All the experiments refer to a soot loading close to 7-8 % w/w, i.e. near the initial loading. 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 (250, 500, 1000 ppm).

In order to analyze the interaction between soot and the stored NO_x, TPD experiments were also performed. Accordingly NO_x have been stored onto the catalytic surface in the absence or presence of soot at 350°C with NO (1000 ppm v/v) in He + O₂ (3% v/v) + H₂O (1% v/v) + CO₂ (0.1% v/v); then the sample was cooled in He and finally heated (10 °C/min) up to 500°C in He + H₂O (1% v/v) + CO₂ (0.1% v/v).

Further details on the experimental setup, procedures and catalyst characterization are reported elsewhere (Castoldi et al., 2006; Matarrese et al., 2007; Matarrese et al., 2008).

3. RESULTS

3.1 Lean-rich cycles at different temperatures

Lean-rich cycles have been performed at different temperatures in the absence and in the presence of soot in order to study the effect of soot on the catalyst activity both in the adsorption and in the reduction phase. The operative conditions adopted in this study differ from those used before (Castoldi et al., 2006; Matarrese et al., 2007; Matarrese et al., 2008; Castoldi et al., 2010) where the lean and rich phases were 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. At variance, in this study the absorption and reduction of the NO_x has been investigated by alternating short lean and rich phases with no inert purge in between, thus providing results more close to the transient conditions adopted under real applications.

3.1.1 Lean-rich cycles in the absence of soot

In Fig. 1 are reported lean-rich cycles performed at 200 °C (A and B) and at 350 °C (C and D) in the absence (A and C) and in the presence of soot (B and D), respectively. The outlet NO, NO₂ and CO₂ concentration curves are displayed as a function of time, along with that of the N₂, NH₃ and H₂.

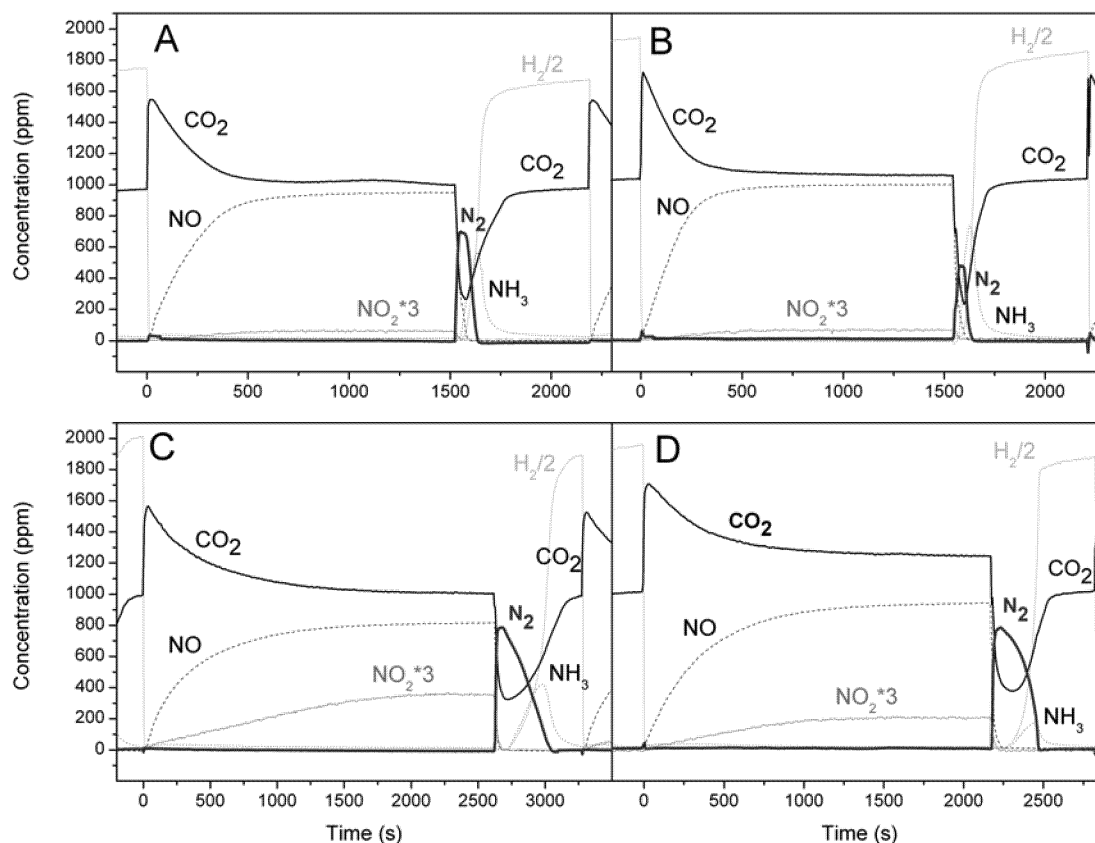


Fig. 1: Lean-rich cycles performed over Pt-Ba/Al₂O₃ in the absence of soot (panels A-C) and in the presence of soot (panels B-D). Panels A-B: $T = 200\text{ }^{\circ}\text{C}$; panels C-D: $T = 350\text{ }^{\circ}\text{C}$

Considering the adsorption phase of the cycle carried out at 200°C in absence of soot (Fig 1A), it can be observed that upon NO and O₂ admission the NO outlet concentration starts to increase without a significant time delay. The NO concentration increases with time, approaching the asymptotic values corresponding to the NO inlet concentration at about 750 s. NO₂ is also observed, due to the oxidation of NO on Pt sites, but its production at this temperature is very limited, being near 15 ppm.

The amount of NO_x that has been stored on the catalyst surface during the lean phase has been calculated by difference between the amount of NO_x fed to the reactor and the amount of NO_x detected at the reactor outlet. As apparent from Fig. 2, which shows the amounts of NO_x stored as function of time-on-stream, at $200\text{ }^{\circ}\text{C}$ in absence of soot 0.26 mmol/g_{cat} of NO_x has been stored during the lean phase.

Notably, upon NO admission the evolution of CO₂ is also observed; its concentration increases rapidly from its background level (1000 ppm) showing a maximum and then decreases to the inlet value at the end of the pulse. The evolution of CO₂ at this temperature is due to the replacement of the Ba-carbonates upon NO_x adsorption onto the catalytic surface, according to stoichiometry of reaction (1):



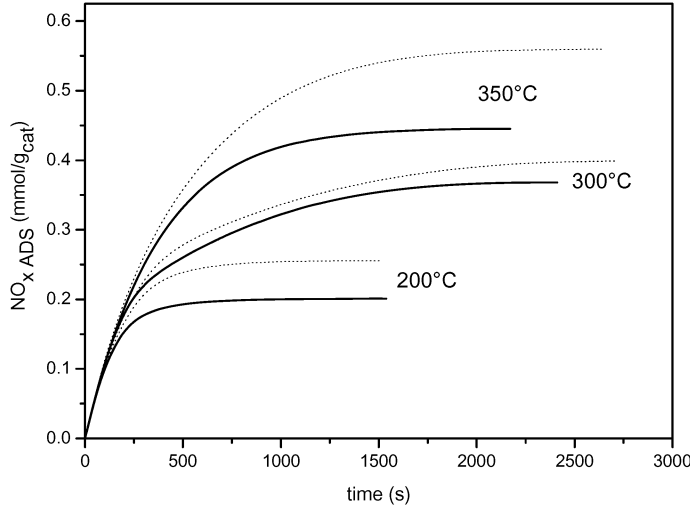
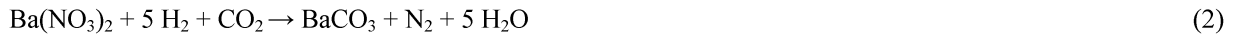


Fig. 2: Amounts of adsorbed NO_x versus time over $\text{Pt-Ba/Al}_2\text{O}_3$ (dotted lines) and over $\text{Pt-Ba/Al}_2\text{O}_3/\text{soot}$ mixture (solid lines) at different temperatures.

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 (1), a net CO_2 concentration trace is obtained (not shown in the Figure) that closely resembles the inlet CO_2 concentration value.

At the end of the NO_x adsorption, the reduction phase takes place in order to regenerate the catalyst surface. Accordingly upon NO and oxygen shutoff, 4000 ppm of H_2 have been fed to the reactor. H_2 is completely consumed upon admission and N_2 (at first) and NH_3 (later on) are produced according to the overall stoichiometry of reactions (2) and (3):



Slightly after NH_3 breakthrough, the H_2 concentration trace slowly increases up to the inlet concentration value. As detailed in previous studies (Lietti et al., 2008; Nova et al., 2008; Forzatti et al., 2008), the observed sequence of reaction products (with NH_3 following N_2) has been explained on the basis of a two-step pathway involving at first the fast formation of ammonia upon reaction of nitrates with H_2 (reaction (3)), followed by the slower reaction of the so formed ammonia with the stored nitrates leading to the selective formation of N_2 according to the stoichiometry of reaction (4):



Notably, the observed temporal evolution of products during the reduction is due to the development of an H_2 front which travels along the reactor: accordingly NH_3 formed at the H_2 front reacts with NO_x stored downstream the front, leading to N_2 formation; NH_3 evolution is observed among the reduction products only when the nitrates are completely reduced and the H_2 front reaches the end of the catalyst bed.

Finally, N_2O production is also detected at the beginning of the H_2 admission. The amounts of N_2O , estimated by discontinuous GC analysis, are near 200 ppm. N_2O formation is likely due an unselective reduction of the stored nitrates possibly over oxidized Pt sites catalyst, which are present at the beginning of the rich pulse after the lean

phase. As a matter of fact, negligible formation of N_2O has been observed during lean-rich cycles with a He purge in between, i.e. when oxygen was completely removed before the rich phase (Castoldi et al., 2010).

The storage and reduction of NO_x over the Pt-Ba/ Al_2O_3 sample has been investigated in a wide temperature range, and the results obtained at 350 °C are shown in Fig. 1C. At all the investigated temperatures, the evolution of the signals during the adsorption phase is qualitatively similar to that previously reported at 200 °C (Fig. 1A). However, the amounts of NO_x stored up to steady-state increase with temperature, from 0.26 mmol/gcat at 200 °C to 0.40 mmol/gcat at 300 °C and 0.56 mmol/gcat at 350 °C (Fig. 2). The maximum NO_x adsorption capacity is observed near 350 °C, in line with several literature reports (Lietti et al., 2001; Matarrese et al., 2009). Moreover, the temperature affects also the adsorption rate; in fact the slope of the adsorption curves in Fig. 2 increases with temperature.

Also the NO_2 concentration at the reactor outlet, measured at the end of the lean phase (steady-state), increases with temperature. As matter of fact near 15 and 120 ppm of NO_2 have been detected at 200 and 350 °C, respectively. Consequently, the NO/NO_2 ratio decreases from 60 at 200 °C down to 7 at 350 °C.

These results, i.e. the observation that the amounts of the stored NO_x and the NO_2 concentration increase with temperature, suggest that at steady-state the amounts of NO_x adsorbed are governed by thermodynamic equilibrium with the gas-phase NO_2 concentration, whose formation in our experimental conditions is kinetically controlled and hence increases with temperature. This is 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, as previously suggested (Nova et al., 2004)), which is predominant in the presence of CO_2 (Frola et al., 2007).

The effect of temperature on the reduction phase has been also investigated. From a qualitative point of view, similar results have been obtained at all the investigated temperatures (with nearly complete nitrogen selectivity at the beginning of the rich phase followed by ammonia formation). As expected, the amount of reduction products increases with temperature. Obviously, this is related to the higher adsorption capacity of the catalyst at high temperatures, as previously discussed. Moreover the overall nitrogen selectivity of the reduction process increases with temperature, from roughly 57 % at 200 °C up to 80% at 350 °C. This is in line with the occurrence of the two-steps pathway previously suggested for N_2 formation: 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.

3.1.2 Lean-rich cycles in the presence of soot

The capability of the Pt-Ba/ Al_2O_3 catalyst to accomplish the removal of NO_x was investigated also in the presence of soot at the same temperatures. The results of lean-rich cycles performed at 200 and 350 °C are shown in Fig. 1B and 1D, respectively.

At 200 °C in the presence of soot (Fig. 1B) the evolution of NO and NO_2 during the lean phase is qualitatively similar to those observed for the soot-free catalyst (Fig. 1A). Upon NO admission, the outlet NO concentration increases with time reaching a steady-state level after 500 s. In this case the amount of adsorbed NO_x at the end of the lean phase is near to 0.20 mmol NO_x/g_{cat} (see Fig. 2), if compared to 0.26 mmol/ g_{cat} in the absence of soot. In line with several studies, this indicates the detrimental effect of soot on the storage capacity of the catalyst (Sullivan et al., 2007; Castoldi et al., 2010).

The storage of NO_x is accompanied by evolution of CO_2 . In the presence of soot, CO_2 evolution might be related to the soot combustion; however calculation showed that at this temperature (200 °C) the CO_2 evolution is almost entirely due to the decomposition of surface carbonates upon NO_x adsorption on the catalytic surface according to reaction (1). This indicates that at 200 °C the oxidation of soot is quite negligible.

Upon increasing the temperature, as in the case of soot-free catalyst, the amounts of NO_x stored up to steady-state increases (from 0.20 mmol/ g_{cat} at 200 °C up to 0.45 mmol/gcat at 350 °C); however, the amounts of NO_x stored in the presence of soot are always lower than those measured in its absence. Accordingly the detrimental effect of soot on the storage of NO_x is observed at all the investigated temperatures.

Also the NO_2 concentration, measured at steady state, increases with temperature and it is always lower than that observed in the absence of soot (e.g. 65 ppm vs. 120 ppm at 350 °C in the presence and in the absence of soot, respectively). As previously suggested, the decrease in the NO_x storage capacity of the catalyst at steady state in the presence of soot can be likely correlated to the decrease in the NO_2 concentration.

Concerning the soot oxidation activity, it becomes appreciable above 300 °C. As matter of fact, at 350 °C (Fig. 1D), a net CO_2 production near 225 ppm was calculated. As discussed in our previous work (Castoldi et al., 2010) and in line with several literature reports (Krishna et al., 2006; Sullivan et al., 2007) soot oxidation is most likely accomplished by NO_2 formed upon oxidation of NO over Pt-sites according to the reactions (5) and (6):



As well known in the literature (Stanmore et al., 2001; van Setten et al., 2001), upon soot oxidation by NO_2 , CO may also form. However, in our conditions this species is readily oxidized into CO_2 on Pt-sites; in fact no CO formation has been observed during these experiments. The involvement of NO_2 in the oxidation of soot is also pointed out by the fact that when the NO_x storage is carried out in the presence of soot, a higher NO/ NO_2 molar ratio is observed (i.e. 14 vs. 7 at the end of the NO pulse, with and without soot respectively). This points out that soot removal occurs by oxidation with NO_2 , although a specific role of the stored nitrates cannot be ruled out, as will be discussed below.

Finally, considering the reduction phase, in the presence of soot no significant differences were observed with respect to the soot-free catalyst, with the only exception of the minor amount of reduction products which is related to the reduced NO_x storage capacity of the catalyst in presence of soot, as discussed above.

3.2 Lean-rich cycles at different NO inlet concentrations

The effect of the NO inlet concentration on the simultaneous NO_x and soot removal over the Pt-Ba/ Al_2O_3 catalyst were addressed by performing lean-rich cycles at 350 °C in the 250-1000 ppm NO inlet concentration range. Figure 3 shows the results obtained in terms of NO_x adsorbed during the lean phase as function of time in the case of the different NO inlet concentrations both in the presence (solid lines) and in the absence (dotted lines) of soot.

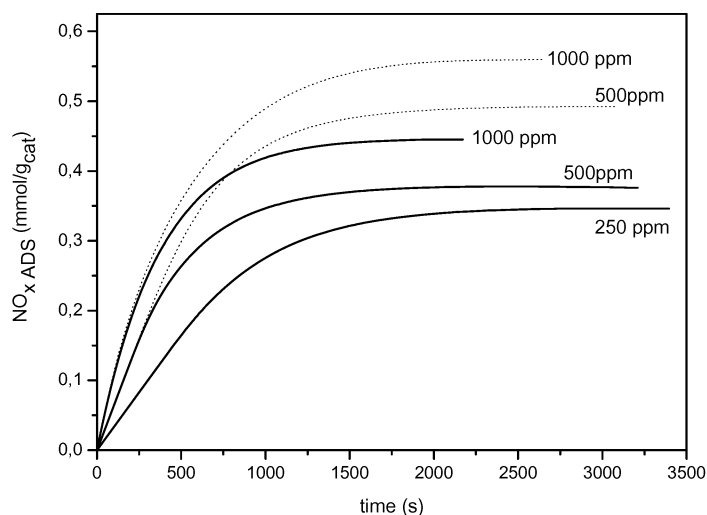


Fig. 3: Amounts of adsorbed NO_x versus time over PtBa/ Al_2O_3 (dotted lines) and over PtBa/ Al_2O_3 /soot mixture (solid lines) at different NO inlet concentrations.

From figure 3 it clearly appears that in all cases the amounts of stored NO_x increase during the lean phase reaching an asymptotic value corresponding to the steady-state conditions. The amounts of stored NO_x increase with the NO inlet concentration both in the absence and in the presence of soot; moreover the NO_2 outlet concentration at steady-state (not shown) increases upon increasing the inlet NO concentration. Hence, as discussed above in the case of the effect of temperature, the higher NO_x storage capacity which is observed upon increasing the NO inlet concentration is likely related to higher concentration of produced NO_2 . Again, this is in line with the previous hypothesis of a thermodynamic control on the amounts of NO_x stored at steady state by the NO_2 concentration. Nevertheless, factors other than thermodynamics involving gas phase NO_2 , e.g. direct NO uptake on the catalyst surface, governing the amounts of NO_x stored at steady state cannot be excluded.

The increase of the NO inlet concentration (and of NO_2 concentration as well) increases also the rate of the NO_x adsorption, as revealed by the slopes of the adsorption curves of Figure 3 in the region where the storage is not limited by the supply of NO .

Finally, from Figure 3 it appears that the presence of soot negatively affects the storage of NO_x , as revealed by the comparison of the adsorption curves obtained in the absence and in the presence of soot (dotted lines vs. solid lines). In fact in the presence of soot the amounts of adsorbed NO_x 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). As matter of fact, higher NO/NO_2 ratios are calculated at any investigated NO inlet concentration value in the presence of soot rather than in its absence. As previously discussed, this is related to the involvement of NO_2 in soot combustion according to reaction (6). Accordingly, the lower NO_2 concentrations obtained in these cases might explain the decrease in the NO_x storage capacity of the catalyst in the presence of soot.

Finally, it can be observed that the rate of NO_x adsorption decreases with the addition of soot. Again, this is likely related to the effect of the NO_2 concentration on the rate of NO_x adsorption.

3.3 Interaction of soot with the stored NO_x

The bulk of the data discussed above clearly indicates the negative effect of soot on the storage activity of Pt-Ba/ Al_2O_3 system. In order to analyze more in details the effect of soot on the adsorbed NO_x species and in particular on their stability/reactivity, dedicated TPD experiments have been carried out. For this purpose NO_x have been stored by contacting the catalyst with NO (1000ppm)/ O_2 (3%) in He at 350 °C in the absence or presence of soot; the samples were cooled in He at 250 °C and finally heated (10 °C/min) up to 500 °C (in He + H_2O (1%) + CO_2 (0.1% v/v)). The results of the TPD runs are shown in Figure 4 in the absence (A) and in the presence of soot (B).

In the absence of soot (i.e. in the case of the soot-free Pt-Ba/ γ - Al_2O_3 catalyst) the decomposition of nitrates occurs above the temperature of adsorption (350 °C) and results in the initial evolution of NO_2 , accompanied by that of NO and O_2 in similar amounts, in accordance with the following reactions (7) and (8):



Notably, the process was not complete at temperatures as high as 500 °C, corresponding to the maximum heating temperature. Concerning the CO_2 concentration, in correspondence with the nitrate decomposition, a decrease of the CO_2 signal is observed. This is due to the re-adsorption of CO_2 on Ba sites forming Ba carbonates upon decomposition of Ba nitrates.

In the presence of soot (Pt-Ba/ γ - Al_2O_3 /soot mixture) the decomposition onset of the stored NO_x is observed about at the same temperature of adsorption (350 °C). Of note, 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 NO_x adsorbed onto the catalytic surface in the presence of soot, as already discussed in the above section.

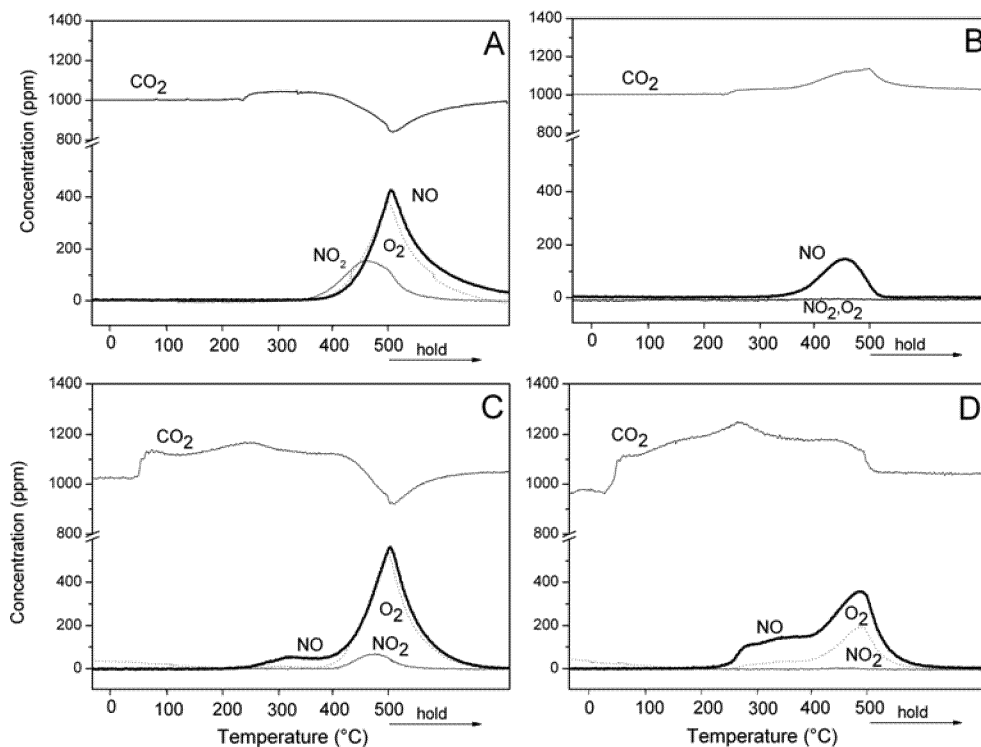


Fig. 4: TPD experiments: runs after NO_x adsorption at 350 °C over Pt-Ba/Al₂O₃ catalyst (A); Pt-Ba/Al₂O₃ catalyst-soot mixture (B); runs after NO_x adsorption over one batch of Pt-Ba/Al₂O₃ catalyst, then divided in two portions: one heated without soot (C), the second mixed with soot (D).

Moreover, it is worth noticing that the distribution of desorbed products is different in the presence and in the absence of soot (compare Fig. 4A and AB). In particular, negligible amounts of NO₂ and O₂ are observed in the presence of soot, being NO the major decomposition product. In line with some literature reports (Kustov et al., 2009) this suggests that NO₂ and O₂ produced from the nitrates decomposition can be readily consumed in the soot combustion although their direct reaction with soot cannot be excluded.

Finally, Figure 4B shows that the nitrates decomposition is concluded at lower temperature (near 500 °C) than in the absence of soot. This clearly indicates a lower thermal stability of the NO_x adsorbed species in the presence of soot. However, also the different nature of the NO_x stored in the absence and presence of soot, could be invoked to justify their different stability.

For this reason, to further address the interaction between soot and the adsorbed NO_x species, a new set of experiments have been performed in which: i) NO_x have been stored at 350 °C onto the catalytic surface in one batch, in the absence of soot; then ii) the sample has been cooled and divided into two portions, one gently mixed in a vial with soot prior the TPD experiment, while the second (not mixed with soot) used as a reference; finally iii) the samples were heated (10 °C/min) from 50 °C up to 500 °C.

The results of the TPD runs performed in the absence and in the presence of soot are shown in Figure 4C and 4D, respectively.

In the case of the soot-free catalyst, results very similar to those previously discussed in Figure 4A were obtained. Most of the nitrate decomposition is observed above 350 °C (the adsorption temperature) with the

evolution of NO and O₂ and minor amounts of NO₂. Of note, a very small NO evolution is observed also near 260°C, i.e. below the temperature of NO_x adsorption: this is likely related to the different procedure used in this case, that involves the exposure of the nitrated catalyst to air for several hours before the TPD run, and that can affect the thermal stability of the NO_x adsorbed species.

The NO_x decomposition process is not complete at temperatures as high as 500°C, corresponding to the maximum heating temperature. In correspondence of NO_x and oxygen evolution an uptake of CO₂ is observed due to the formation of barium carbonates.

Worth to note that the overall amounts of evolved NO, O₂ and NO₂, estimated by integration of the TPD peaks, are well in line with the stoichiometry of the nitrates decomposition in accordance with reactions (7) and (8). As matter of fact the measured O/N atomic ratio in the evolved products is 2.6, hence very close to the theoretical value of 2.5.

The presence of soot leads to significant changes in the TPD spectra (see Figure 4D). In this case the decomposition of nitrates is clearly observed at lower temperatures. As matter of fact a significant release of NO and O₂ is observed in the temperature range 260 – 350°C. The decomposition of nitrates is then completed above 350°C, with a NO peak maximum near 485°C. As already discussed in the previous TPD run in presence of soot (Fig. 4B), no NO₂ along with minor amounts of O₂ are detected at the reactor outlet due to their involvement in the soot oxidation. As a matter of fact, no CO₂ uptake is observed in this case. Besides, the calculated oxygen/nitrogen atomic ratio of the gaseous products evolved during the entire TPD in the presence of soot was found near 1.7, which is lower than the stoichiometric O/N value of 2.5 of the nitrate decomposition.

Notably, below 350°C (i.e. before the onset of nitrate thermal decomposition) the concentration of the evolved products obeys the stoichiometry of nitrate reduction by soot, according to reaction (9):



These results suggest the presence of a direct interaction between NO_x ad-species and soot which can be explained on the basis of the surface mobility of the adsorbed nitrates. The driving force for this process may be the presence of carbon reducible sites, in analogy with the pathway proposed for nitrate reduction during lean/rich operation of LNT catalysts (Clayton et al., 2009; Bhatia et al., 2010).

4. CONCLUSIONS

The influence of soot on the NO_x storage properties of a model Pt-Ba/Al₂O₃ catalyst was investigated in this work. It was found that soot leads to an appreciable decrease both of the NO_x storage capacity and of the rate of NO_x adsorption. This effect has been observed at different temperatures and with different NO inlet concentration. During NO_x storage, soot oxidation also occurs above 300°C, thanks to the presence of NO₂ formed upon NO oxidation over Pt sites. As matter of 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, Ba and soot can compete for reaction with NO₂, 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, being in both cases N₂ the major reaction product.

As pointed out by TPD experiments, the adsorbed NO_x participate in the soot oxidation upon release of NO₂ and O₂ which actively oxidize soot. Besides, it has been found that the presence of soot favors the decomposition and the reduction of the stored NO_x, 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.

5. REFERENCES

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