On the activity and stability of Pt-K/Al_2O_3 LNT catalysts for diesel soot and NO_x abatement

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1. Introduction

The main pollutants emitted by diesel engines are nitrogen oxides and soot particles (particulate matter, PM) whose adverse effects on the environment and human health are widely recognized. For this reason, the abatement of NO_x and particulate from diesel exhausts is a major issue nowadays, forced by the application of the upcoming legislative emissions standards. In fact, diesel particulate filters (DPF) are typically used to cope with the PM emission standards required by the current legislation. Concerning NO_x reduction, the existing technical solutions are primarily based on the technological improvement of the diesel engines (e.g. by means of advanced fuel injection technologies, exhaust gas recirculation (EGR) control, etc.). However it is widely accepted that in order to meet the upcoming legislative emissions standards (e.g. Euro VI (2014) regulations, in Europe), the adoption of after-treatment systems will be required [1,2].

The three-way technology, currently used on the traditional stoichiometric gasoline-powered engines, is unable to reduce NO_x under the typical lean conditions of diesel engines. Accordingly innovative NO_x abatement technologies have been developed. Among them the NH_3/urea selective catalytic reduction (SCR) and the NO_x storage–reduction (NSR), also quoted as lean NO_x trap (LNT), are widely accepted as the most promising NO_x control strategies. The former has been essentially developed for heavy-duty vehicles while for the light vehicles a competition between SCR and NSR, still exists [3]. In this complex technological context, the development of integrated De-NO_x and De-soot after-treatment technologies have also been proposed. One example is the diesel clean advanced technology (D-CAT) emission control system proposed by the Toyota group and recently equipped on its Avensis model [4]. The heart of the D-CAT system is the DPNR (diesel PM and NO_x reduction) system which has the unique capacity to remove simultaneously both soot and NO_x via the combination of a ceramic wall-flow filter coated with a new catalytic layer [5,6]. The DPNR catalyst is very similar to that already proposed by Toyota for its lean NO_x traps (LNT catalysts), initially designed for use with Toyota's lean-burn gasoline engines [7] and is composed of a high surface area support material (often γ-alumina), precious metals (usually a combination of Pt and Rh) and a basic component, such as Ba or K phases, which acts as NO_x storage material. As the LNTs, DPNR systems work under cyclic conditions alternating long lean periods with short regeneration periods under rich conditions [5,6]. During the lean phase the NO_x produced by the engine are oxidized and adsorbed on the alkaline or alkaline-earth metal oxide component; during the rich phase the stored NO_x species are reduced to molecular nitrogen by CO, H_2 and UHCs. In addition, under lean conditions the DPNR system works as a catalyzed soot filter (CSF) in which soot combustion is primarily ascribed to NO_2 formed upon NO oxidation over noble metals, followed by NO recycle to NO_2

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as suggested by Krishna et al. [8]. Moreover, also the NO_x storage function of the LNT catalysts is claimed to assist the combustion of soot by means of the NO_x adsorbed species [6]. Of note, Toyota researchers proposed that active oxygen species, which are formed during NO_x adsorption, are effective in soot oxidation under rich conditions as well [5,6].

In spite of the fact that many studies are available in the literature concerning the behaviour of LNT systems in the removal of NO_x (e.g. the reviews by Epling et al. [9] or Roy and Baiker [10] and references therein), investigations on the DPNR system are very scarce. Besides, most of them are focused on the effect of soot on the NO_x storage efficiency of LNT systems or on the interaction between the NO_x storage function and soot oxidation capacity [8,11–14] rather than on the combined soot-NO_x reduction activity under lean-rich cycling conditions, typical of the DPNR technology [15].

In a previous work from our group [16] the capability of a model PtBa/Al_2O_3 LNT catalyst to remove simultaneously soot and NO_x according to DPNR concept has been addressed. It has been shown that during the lean phase NO_x are stored on the catalyst surface, while soot oxidation simultaneously occurs involving NO_2 formed upon NO oxidation over Pt sites. However a role of the NO_x adsorbed species in the soot oxidation has also been invoked [17,18]. The reactivity of a model Pt-K/Al_2O_3 catalyst has been recently investigated and compared with an analogous Pt-Ba/Al_2O_3 sample [19,20]. It has been found that the two samples have similar De-NO_x activity but the K-containing system shows significantly higher activity for soot combustion. According to the literature [21–23] it has been suggested that potassium may favour soot oxidation through the formation of low melting point compounds, thus improving the mobility of the active surface species and consequently improving activity according to a higher contact between catalysts and soot. However, because of alkali mobility, K-based catalysts are blamed for low thermal stability which is associated to several technological problems such as interactions with the monolith support or loss of active phase (i.e. with consequent catalysts deactivation) due to volatilization and/or dissolution by condensed water.

On these bases, in this work the reactivity of a model Pt-K/Al_2O_3 catalyst has been investigated in the simultaneous removal of NO_x and soot under more realistic conditions (i.e. in the presence of CO_2 and H_2O and in the temperature range 250–350 °C) by performing isothermal concentration step change (ICSC) experiments. The same experiments have been performed in the absence of soot in order to analyze the influence of soot on the behaviour of the LNT catalyst in terms of NO_x storage–reduction. Also a comparison with a model Pt-Ba/Al_2O_3 catalyst is provided to obtain information on the interaction between De-NO_x and De-soot performances and on the role of the storage component (i.e. K vs. Ba). Moreover, the activity and stability of the Pt-K/Al_2O_3 catalysts during repeated lean-rich cycles in the presence of soot have been also investigated. FT-IR spectroscopy has also been used to compare the peculiarities of the fresh and aged Pt-K/Al_2O_3 sample.

2. Experimental

2.1. Catalysts preparation and characterization

A homemade Pt-K/Al_2O_3 (nominal loadings 1/5.4/100 w/w) catalyst has been prepared by incipient wetness impregnation of a commercial alumina sample (Versal 250 from UOP) with an aqueous solution 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 alkali component on the alumina support, in line with recipes of Toyota patents [7]. This sample has molar amount of K comparable to that contained in the Pt-Ba/Al_2O_3 (1/20/100 w/w) model catalyst previously used for similar studies (0.146 mol K or Ba/100 g of Al_2O_3) and reported here for comparisons [17,18]. 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_2 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 Pt-K/Al_2O_3 sample presents a surface area near 167 m^2/g_{cat} and pore volume of 0.90 cm^3/g_{cat}, while the Pt dispersion is close to 30%.

Both fresh and aged Pt-K/Al_2O_3 catalysts were analyzed by SEM-EDS technique to evaluate the potassium content; loadings of 6.2% and 5.7% have been estimated in the fresh and in the aged samples, respectively. Printex U (Evonik-Degussa) was used as model soot, which is widely used as a model substance for diesel particulate [8,15,24] and whose properties are well described in the literature [25,26].

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 [27,28].

2.2. Catalytic tests

All reactivity tests were performed in a micro flow-reactor apparatus consisting of a quartz tube reactor (7 mm 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, NO_2, N_2, H_2, O_2, CO, CO_2, N_2O and NH_3). 66 mg of the soot-catalyst mixture (corresponding to 59.4 mg of the bare catalyst and 6.6 mg of soot) 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 concentration step change (ICSC) experiments have been performed at 350 °C by imposing a rectangular step feed of NO (1000 ppm) + 3% v/v O_2 in flowing He + 1% H_2O + 0.1% CO_2 (lean phase) until catalyst saturation. Then the NO and O_2 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 NO_x species. After the He purge, catalyst regeneration (rich phase) has been carried out with H_2 (3500 ppm) in flowing He + 1% H_2O + 0.1% CO_2. Conditioning lasted until a reproducible behaviour was obtained; this typically required 3–4 adsorption–reduction cycles.

After catalyst conditioning at 350 °C, the catalytic activity of Pt-K/Al_2O_3 has been tested with typical ICSC runs in the temperature range 250–350 °C. Part of the conditioned catalyst has been also mixed with soot (9:1 w/w ratio) and ICSC run have been performed on catalyst/soot mixture at the same temperatures.

Finally, the stability of the Pt-K/Al_2O_3 catalyst has also been studied. The pre-conditioned catalyst has been mixed with soot (9:1 w/w ratio) and ICSC experiment has been performed at 350 °C. During this first run (Run 1), soot has been progressively consumed. After the complete consumption of soot, the clean sample has been mixed again with soot (in the same ratio) (Run 2) and further lean-rich cycles 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).

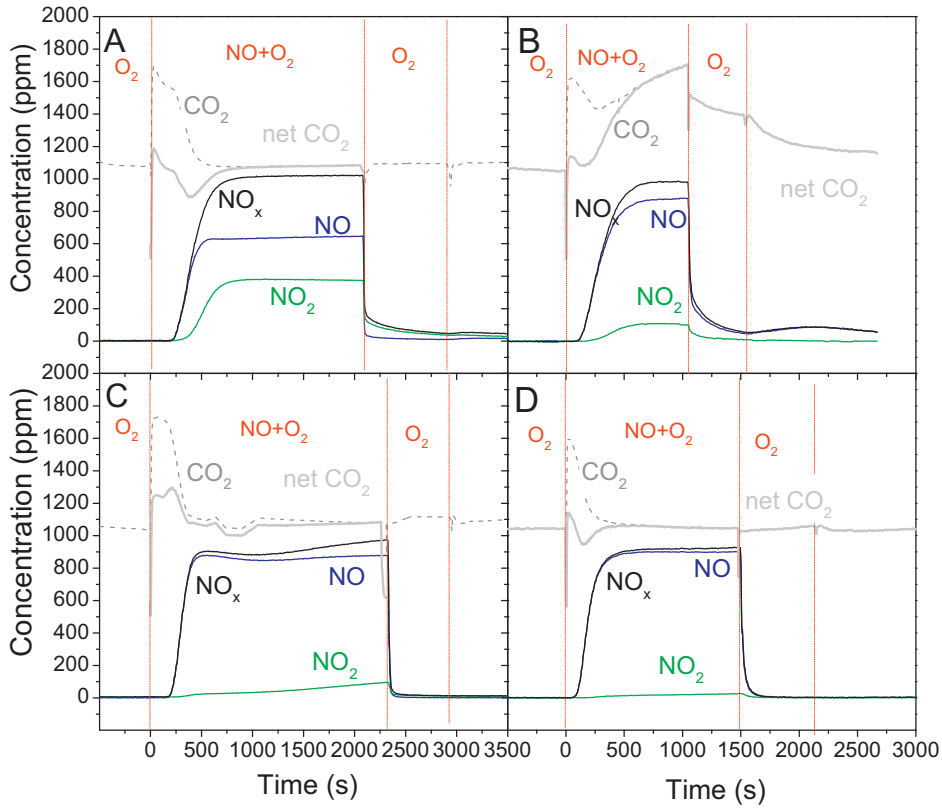

Fig. 1. Adsorption phase over Pt-K/Al_2O_3 in the absence of soot (A: 350 °C; C: 250 °C) and in the presence of soot at different temperatures (B: 350 °C; D: 250 °C). 1000 ppm NO and 3% O_2 in the presence of H_2O (1% v/v) and CO_2 (0.1% v/v).

2.3. FT-IR analysis

The catalyst has been characterized by FT-IR spectroscopy upon CO and CO_2 adsorption. FT-IR analysis have been carried out by means of a Nicolet Nexus Fourier Transform instrument over both the fresh and aged Pt-K/Al_2O_3 catalyst pressed in self supporting disks of average weight 30 mg. Catalysts have been outgassed at 350 °C before any adsorption experiment. After the activation step, CO adsorption has been carried out at liquid nitrogen temperature and the evolution of surface species has been studied after outgassing upon warming. CO_2 adsorption has been carried out at room temperature.

3. Results and discussion

3.1. Effect of temperature on the NO_x storage–reduction activity

3.1.1. NO_x storage

The NO_x storage–reduction activity over Pt-K/Al_2O_3 catalyst in the absence of soot has been investigated in the 250–350 °C temperature range. The NO, NO_2, NO_x (i.e. NO + NO_2) and CO_2 concentration profiles measured during the lean phase when 1000 ppm NO are fed to the reactor in the presence of O_2, H_2O and CO_2 are shown in Fig. 1. For the sake of brevity, only the data obtained at 250 °C and 350 °C are shown.

At 350 °C (Fig. 1A), upon NO admission to the reactor (t = 0 s) a delay near 200 s is observed in the NO outlet concentration. Then, the NO concentration increases with time and reaches a steady state value near 645 ppm. NO_2 breakthrough is observed with a delay of 50 s with respect to NO and increases until its asymptotic level of 375 ppm. As well known, the NO_2 production is related to the NO oxidation on Pt sites (reaction (1)):

$$NO + 1/2O_2 \rightarrow NO_2 \quad (1)$$

The overall amount of NO_x stored at this temperature at the end of adsorption is near 0.56 mmol/g_{cat}, corresponding to the involvement of 40.5% of the overall K loading by assuming the formation of KNO_3 species. As shown in other works [27,28], both bidentate and ionic nitrates are present at this temperature at the end of the storage phase.

When the NO inlet concentration is switched off (t = 2000 s), weakly adsorbed NO_x species desorb [28], causing a decrement of roughly 25% in the amount of stored NO_x.

Upon NO admission, an increase in the CO_2 concentration is also observed; this is due to the decomposition of surface carbonates upon NO_x uptake according to the stoichiometry of the following reaction:

$$K_2CO_3 + 2NO + 3/2O_2 \rightarrow 2KNO_3 + CO_2 \quad (2)$$

In fact by subtracting from the CO_2 concentration trace the amounts of CO_2 evolved due to carbonate decomposition estimated according to the stoichiometry of reaction (2), we obtain a curve (net CO_2 concentration trace reported in Fig. 1A) that roughly resembles the inlet CO_2 concentration. In the experiments carried out in the presence of soot (see below), the net production of CO_2 will be determined and this will be used to estimate the amounts of soot combusted.

The results of the NO_x adsorption carried out at the lowest investigated temperature are shown in Fig. 1C for comparison purpose. As apparent from Fig. 1A and C the NO_x storage behaviour of the catalyst is affected by the temperature: (i) the NO_x breakthrough

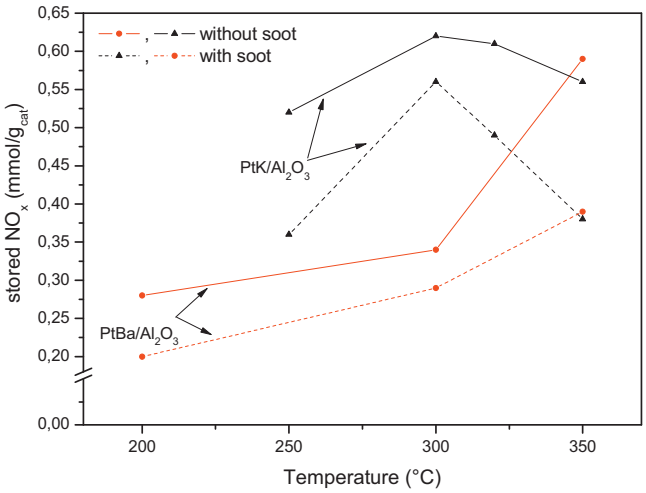

Fig. 2. Amounts of stored NO_x vs. temperature over Pt-K/Al_2O_3 and Pt-Ba/Al_2O_3 catalysts in the absence of soot (solid lines) and in the presence of soot (dotted lines).

increases from 90 s at 250 °C (Fig. 1C) to 200 s at 350 °C (Fig. 1A); (ii) the NO_2 concentration measured at the reactor outlet at the end of the NO_x dose (i.e. at steady-state) increases with temperature as expected being the reaction kinetically controlled under our experimental conditions. Accordingly, the NO/NO_2 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.

The quantitative analysis of the NO_x adsorption carried out at the various investigated temperatures is reported in Fig. 2 and Table 1. The amounts of NO_x stored up to steady state show a maximum near 0.6 mmol/g_{cat} at 300 °C, corresponding to the involvement of 45% of the overall K loading. These data have been compared with those collected over a Pt-Ba/Al_2O_3 catalyst [17], as shown in Fig. 2 and Table 1. Over the Pt-Ba/Al_2O_3 sample the storage capacity shows a distinct temperature dependence [29] with respect to Pt-K/Al_2O_3, in that it increases with temperature in the investigated *T*-range. However at 350 °C the storage capacity of the two catalysts is very similar. Worth to note that the fraction of K sites involved in the storage of NO_x (i.e. the K utilization) is higher than that of Ba at any temperature (i.e. 40.5% vs. 20.3%, respectively, at 350 °C).

In Table 1 the amounts of NO_x desorbed after NO shut-off (calculated in all cases 430 s after NO_x shut-off) are also reported. Over the Pt-K/Al_2O_3 catalyst sample the amounts of desorbed NO_x increase with temperatures and are always higher than over Pt-Ba/Al_2O_3 (12% vs. 8% at 350 °C).

3.1.2. NO_x reduction

The stored NO_x are then reduced under isothermal conditions by admitting H_2 in the presence of H_2O and CO_2 and results are shown in Fig. 3A (350 °C) and 3 C (250 °C).

At 350 °C (Fig. 3A), upon the addition of H_2 (at $t = 0$ s) N_2 is immediately observed at the reactor outlet along with a CO_2 consumption. This uptake of CO_2 is in line with the occurrence of the overall reaction (3) which considers the re-adsorption of CO_2 onto the K sites once NO_x have been reduced:

$$2KNO_3 + 5H_2 + CO_2 \rightarrow K_2CO_3 + N_2 + 5H_2O \quad (3)$$

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. No production of ammonia or other byproducts like N_2O is observed. Only a small amount of NO is detected along with nitrogen and this leads to a N_2 selectivity of ca. 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.

Similar results have been obtained at the other investigated temperatures, i.e. 320, 300, 250 °C (see Fig. 3C at 250 °C): the main reduction product is nitrogen and only small amounts of NO are detected as byproduct. The overall nitrogen selectivity is in all cases higher than 95%. 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 activity in the presence of soot

NO_x adsorption–reduction experiments have been carried out also in the presence of soot in the temperature range 250–350 °C. The results obtained at 350 °C and 250 °C are shown in Fig. 1B and D (NO_x storage) and Fig. 2B and D (NO_x reduction).

3.2.1. NO_x storage

At 350 °C (Fig. 1B) the NO outlet concentration shows a dead time lower than in the absence of soot (Fig. 1A) (i.e. 90 s vs. 210 s); then, it increases approaching an asymptotic value of 880 ppm. NO is also oxidized to NO_2 whose concentration measured at steady state is near 100 ppm.

The amounts of NO_x stored at steady-state in the presence of soot are near 0.38 mmol/g_{cat}, i.e. lower if compared to those measured in the absence of soot (0.56 mmol/g_{cat}), corresponding to the involvement of 27.5% of K (vs. 40.5% for the soot-free case). Similar effects have been observed at 250 °C (compare Fig. 1D with B) and at the other investigated temperatures (see Fig. 2 and Table 1).

The effect of soot on the NO_x storage capacity has also been investigated on Ba-based systems [17,30], and similar effects have been pointed out. In fact also for the Ba containing system the presence of soot reduces the NO_x storage capacity of the catalyst, in line with the results of Pieta et al. [15] and Sullivan et al. [11,12]. According to these authors soot may compete with Ba sites for reaction with NO_2 by offering another reaction route to the desired formation of surface nitrates. 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 Fig. 1B and A) possibly due to the participation of NO_2 in the combustion of soot according to the following reaction:

$$2NO_2 + C \rightarrow CO_2 + 2NO \quad (4)$$

Accordingly, in the presence of soot the NO/NO_2 molar ratio is higher than that measured in the case of the soot-free catalyst (near 8.8 vs. 1.72). Note that reaction (4) is a global reaction possibly involving the following two steps:

$$NO_2 + C \rightarrow CO + NO \quad (5)$$

$$CO + 1/2O_2 \rightarrow CO_2 \quad (6)$$

During our experiments CO formation is not observed, likely because CO is oxidized to CO_2 by O_2 on Pt sites [17].

Notably, by comparing Fig. 1A and B, a more pronounced tail in the NO concentration is observed upon NO shutoff in the presence of soot, indicating that the presence of soot influences the stability of the adsorbed NO_x species. A significant NO_x release is apparent also upon oxygen shut off, which on the other hand is negligible over the soot-free catalyst.

In Fig. 1B the trace of the outlet CO_2 concentration is also reported. In the presence of soot, the CO_2 evolution results from two different contributions: (i) the decomposition of surface carbonates upon nitrates formation (reaction (2)); (ii) soot combustion according to the reaction (4). The amounts of CO_2 produced due to soot oxidation (net CO_2 production) have been calculated as previously indicated, and shown in the figure. The soot combustion is

Table 1
Stored NO_x up to steady state (NO 1000 ppm, O_2 3% v/v, H_2O 1% v/v, CO_2 0.1% v/v), desorbed NO_x after NO_x shutoff (430 s) and desorbed NO_x/stored NO_x ratio (%) at different temperatures in the absence and in the presence of soot over Pt-K/Al_2O_3 and Pt-Ba/Al_2O_3 catalysts.

	Without soot			With soot		
	Stored NO_x up to steady state (mmol/g_{cat})	Desorbed NO_x upon NO shutoff (mmol/g_{cat})	Desorbed NO_x/stored NO_x (%)	Stored NO_x up to steady state (mmol/g_{cat})	Desorbed NO_x upon NO shutoff (mmol/g_{cat})	Desorbed NO_x/stored NO_x (%)
Pt-K/Al_2O_3 catalyst						
250 °C	0.52	0.03	7	0.36	0.04	11
300 °C	0.62	0.05	8	0.55	0.07	13
320 °C	0.61	0.04	7	0.46	0.08	17
350 °C	0.56	0.07	12	0.38	0.10	26
Pt-Ba/Al_2O_3 catalyst						
200 °C	0.28	0.07	25	0.20	0.05	26
300 °C	0.34	0.03	8	0.29	0.04	14
350 °C	0.59	0.05	8	0.39	0.05	12

apparent only after NO admission to the reactor, i.e. in the presence of O_2 only, no CO_2 production is observed. This is in line with several literature reports indicating the beneficial effect of NO on soot combustion specifically over noble metal-containing samples [8,16,31,32]. The suggested mechanism is based on the oxidation of NO to NO_2 promoted by Pt; NO_2 rapidly oxidizes soot with formation of CO_2 and NO; NO is then oxidized again by O_2 over Pt and hence it is "recycled". This points out that NO_2 is involved in soot removal. However, a specific role of the stored nitrates is also likely, as pointed out by the observation that the NO_x release occurring upon NO and O_2 shut-off is higher in the presence than in the absence of soot. This calls for the existence of direct interaction between soot and the stored nitrates which results in the soot combustion as evidenced by the production of CO_2 and NO after NO shutoff according to the following overall stoichiometry (7):

$$3C + 4KNO_3 \rightarrow CO_2 + 4NO + 2K_2CO_3 \quad (7)$$

Several authors reported that the presence of NO_x species adsorbed onto the storage material of the LNT catalyst promotes the combustion of soot [6,11,24]. It is suggested that these species decompose increasing the NO_2 concentration in the gas phase, thus favouring the soot oxidation. However recent studies of our group [17,18,33] indicated the direct participation of the surface nitrates in soot oxidation, without their preliminary thermal decomposition, as also pointed out in [13,14,34–36], hence suggesting the involvement of a redox mechanism occurring between nitrates and soot particles.

ICSC experiments in the presence of soot have been performed at other temperatures; the results obtained at 250 °C (taken as example) are shown in Fig. 1D while the quantitative analysis of the results for all the investigated temperatures is reported in Fig. 2 and Table 1. The NO_x breakthrough increases with temperature but it is always lower than in the absence of soot (i.e. 50 s vs. 90 s at 250 °C). The amounts of NO_x stored up to steady-state shows a maximum

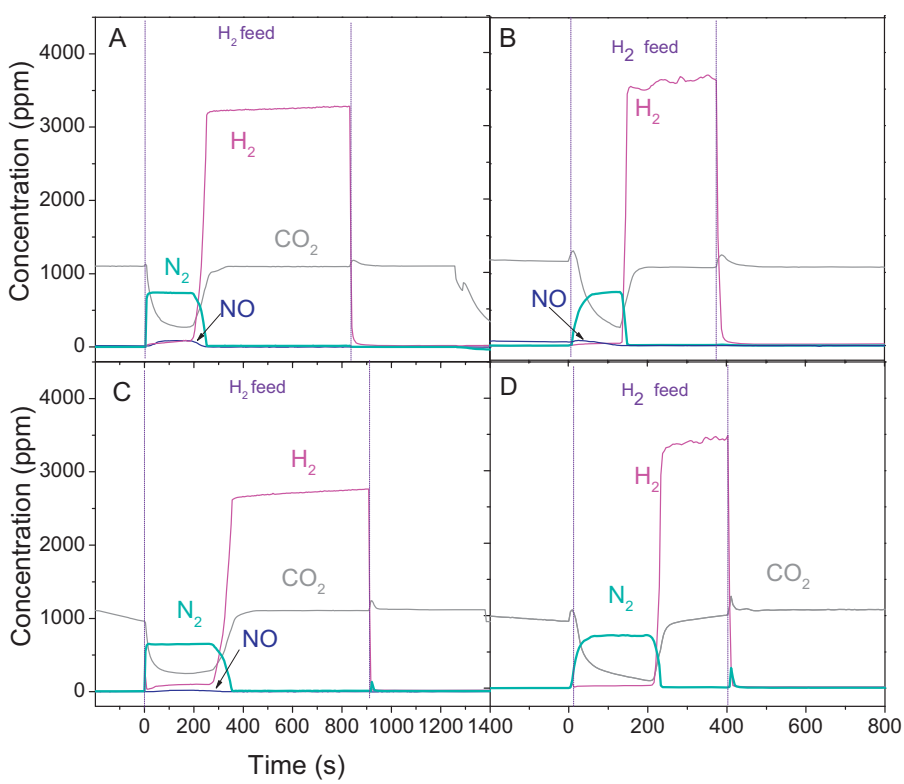

Fig. 3. Reduction phase over Pt-K/Al_2O_3 in the absence of soot (A: 350 °C; C: 250 °C) and in the presence of soot at different temperatures (B: 350 °C; D: 250 °C). 3500 ppm H_2 in the presence of H_2O (1% v/v) and CO_2 (0.1% v/v).

at 300 °C and also in this case are always lower than in the absence of soot (Fig. 2 and Table 1).

Also the amounts of desorbed NO_x after NO shutoff increase with temperature (Table 1) and are always higher than in the absence of soot. This confirms the destabilizing effect of soot on the stored species that is more evident at high temperatures.

Finally, higher NO/NO_2 ratios are measured at steady state in the presence of soot as a result of the participation of NO_2 in soot oxidation, that becomes significant at temperature higher than 250 °C (a net CO_2 formation is observed during the NO adsorption only above 250 °C). Note that by increasing the temperature the participation of the adsorbed NO_x species in the soot combustion increases as well, as pointed out by the net CO_2 formation which is observed after NO shut-off.

The data herein presented well parallel those obtained over Pt-Ba/Al_2O_3 catalyst [17]. However the performances of the Pt-K/Al_2O_3 sample in terms of NO_x storage activity keep higher than those of Ba-based catalyst also in the presence of soot (see Fig. 2 and Table 1). Inspection of Table 1 also shows that, at temperature higher than 300 °C, larger amounts of NO_x are desorbed over Pt-K/Al_2O_3 than Pt-Ba/Al_2O_3. This is accompanied by a higher production of CO_2 after NO shutoff over Pt-K/Al_2O_3 than that observed in [17] for Pt-Ba/Al_2O_3, indicating a greater contribution of reaction (7) to soot combustion when potassium is present in catalyst formulation instead of barium. In line with the mechanistic proposals suggested above, the greater reactivity of NO_x stored over K-containing samples can be likely explained on the basis of the higher mobility of nitrates stored on potassium [21,22,37], likely enhancing the soot-catalyst contact [23,38] and hence favouring the soot combustion. As matter of fact, when Ba and K are in tight contact with soot, they exhibit a similar reactivity [32,39], thus confirming that the higher activity of K-based systems even under loose conditions is likely due to the high mobility of the K surface species.

3.2.2. NO_x reduction

Fig. 3B and D shows the data collected during the rich phase of cycling in the presence of soot at 350 °C and 250 °C respectively. The products evolution is similar to that previously described for the regeneration phase in the absence of soot (Fig. 3A and C), 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_x at any temperature.

3.3. Effect of soot loading on De-NO_x activity and stability of the Pt-K/Al_2O_3 catalyst

The results herein presented point out that the presence of soot affects the catalytic performance of the Pt-K/Al_2O_3 catalyst by lowering not only the amount but also the stability of the NO_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_2O_3 upon repeated soot oxidation cycles, 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_2O_3 at 350 °C until the complete consumption of soot. The amounts of NO_x stored during the various lean phases are plotted as a function of the soot loading in Fig. 4 (Run 1, line A–B). After this sequence, the clean catalyst has been mixed again with soot and it has been again cycled under the same experimental conditions until complete soot oxidation for other two times (Run 2, line C–D; Run 3, line E–F of Fig. 4). The storage capacity of the fresh catalyst is also reported for comparison purpose (dashed line). During the first run (line A–B in Fig. 4) with the initial soot loading (near 11% w/w) roughly 0.31 mmol/g_{cat} of

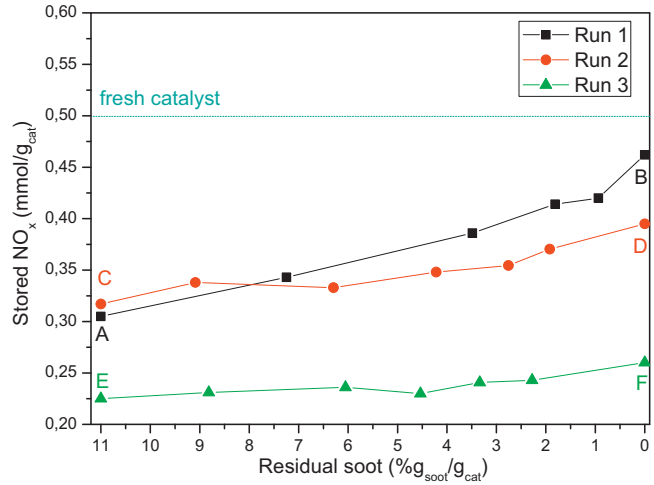

Fig. 4. Stored NO_x (mmol/g_{cat}) as an function of residual soot over Pt-K/Al_2O_3 in three subsequent runs.

NO_x have been loaded on the catalyst (point A in Fig. 4). Then, the amounts of NO_x stored on the catalyst increase upon decreasing the soot loading; roughly 0.46 mmol/g_{cat} of NO_x are stored when all the soot has been consumed (point B in Fig. 4). Such amount is very close to that calculated over the fresh catalyst (0.50 mmol/g_{cat}, dashed line in Fig. 4).

During the second run, the catalyst does not recover the initial NO_x storage capacity (Run 2, line C–D in Fig. 4) even after complete oxidation of the particulate. The storage capacity remains poor during the third sequence of lean-rich cycles (Run 3, line E–F in Fig. 4).

These data clearly point out that NO_x storage capacity of LNT Pt-K/Al_2O_3 catalysts decreases on ageing upon repeated lean-rich cycles. This is in line with the studies of Krishna et al. [8] reporting the decrease of NO_x storage capacity of Pt/K–Al_2O_3 catalyst upon ageing under soot oxidation conditions.

The soot oxidation activity of the Pt-K/Al_2O_3 catalyst has also been evaluated during these runs by calculating the soot conversion during the lean phases and results are shown in Fig. 5A. A reduced soot oxidation activity of the aged Pt-K/Al_2O_3 catalyst is observed during the second and the third run if compared to the first run. Concerning the NO/NO_2 molar ratio (Fig. 5B), it strictly depends on the soot loading; as expected, the ratio decreases by lowering the amount of soot, since NO_2 is not more involved in the soot combustion. However, the NO/NO_2 molar ratio calculated over the clean catalysts after the complete removal soot (points in correspondence of residual soot 0%), during all the three runs, is always quite similar to the value calculated for fresh catalyst (near 2.1 vs. 1.72). This indicates that the ageing process seems not to affect the NO oxidizing capacity of the system, occurring at the Pt-sites. Accordingly, the observed decrease in the soot oxidation activity over the aged catalyst could be ascribed to changes in the alkali component and/or losses of the active phase [22,40,41].

Notably, after the first run the catalyst seems to be stabilized in its oxidation activity. This effect is in line with our previous results obtained with a Pt-free K/Al_2O_3 catalyst which has been used for repeated soot oxidation cycles at 400 °C [32]. Also in that case, a significant decrease in the combustion activity was noticed passing from the first to the second isothermal cycle but then the catalyst activity becomes stable and reproducible. The reason of such behaviour is still unclear even if modification in surface morphology and composition should be considered as responsible. These aspects were considered by Gross et al. [42] who investigated the stability of potassium/ceria catalysts during successive TPO

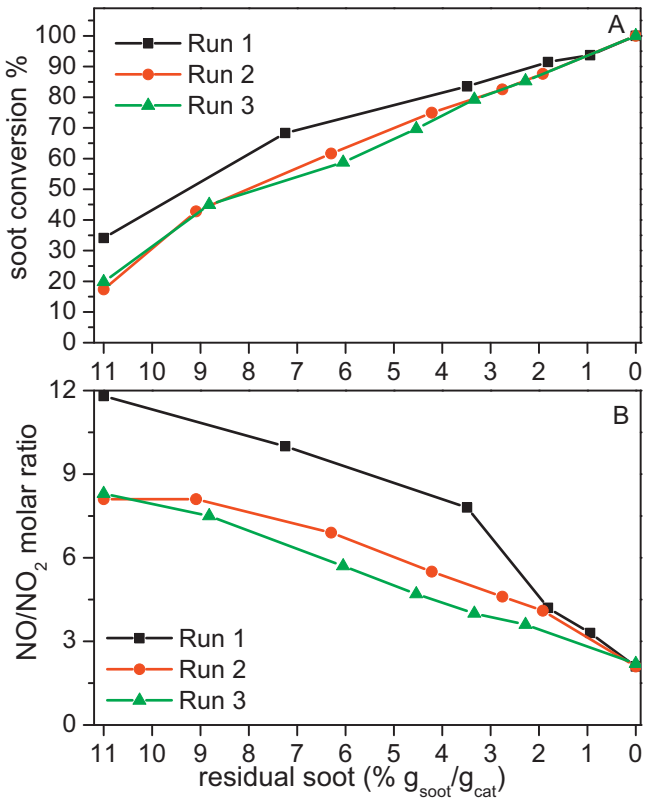

Fig. 5. Soot conversion (%) (A) and NO/NO_2 molar ratio at NO shutoff (B) as a function of residual soot over Pt-K/Al_2O_3 during three different runs (1000 ppm NO and 3% O_2 in the presence of H_2O (1% v/v) and CO_2 (0.1% v/v) at 350 °C).

experiments. Based on the FT-IR characterization of both fresh and aged catalysts they observed that, during the ageing, the catalyst reached a steady-state concerning the most relevant species (e.g. carbonates or carbonate-like compounds). These authors considered the sequential formation and decomposition of these compounds during soot combustion, as a prerequisite for a long term catalytic activity. Moreover, they suggested that if these compounds would not decompose, the catalytic surface would be enriched in carbonates composition leading to the catalyst deactivation.

In order to better understand the reason for the observed catalyst loss of activity, the Pt-K/Al_2O_3 aged sample has been characterized by FT-IR spectroscopy and results compared with the

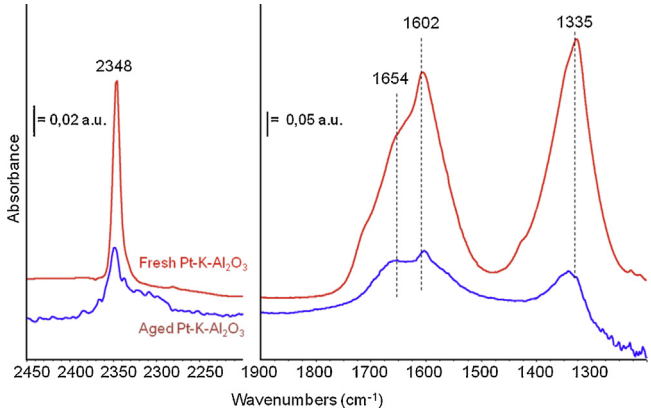

Fig. 6. FT-IR subtraction spectra of fresh and aged Pt-K/Al_2O_3 catalyst after outgassing at 350 °C and adsorption of CO_2 at room temperature. The activated surface spectrum has been subtracted.

fresh system. In Fig. 6 the IR spectra obtained after CO_2 adsorption on the fresh and aged Pt-K/Al_2O_3 samples are compared in common scale. The fresh sample spectrum is dominated by a sharp band ay 2348 cm^{-1} (molecularly adsorbed CO_2) and by two strong bands at 1602 and 1335 cm^{-1} due to bridging or bidentate surface carbonate species, resulting from CO_2 reactive adsorption. As shown previously [43,44], these bands are associated to the presence of potassium on the surface and are unaffected by the presence of Pt. The slight complexity of the higher frequency band is likely due to the presence of more slightly different configurations of surface potassium carbonates.

CO_2 adsorption over the spent aged catalyst gives rise to quite similar, but definitely weaker, features, i.e. bands at 1602 and 1335 cm^{-1}, while the component at 1654 cm^{-1} (due to another carbonate species) is very pronounced here. The spectrum observed after CO_2 adsorption on the fresh catalyst is indeed the same observed previously for CO_2 adsorbed on the same catalyst [43] and also on the Pt-free sample [44] while that of the aged sample closely resembles that observed over a sample with a lower K content (3% K/Al_2O_3 sample, see [44]). This may indicate that the aged sample suffered a partial potassium loss, as pointed out by SEM–EDS analysis showing a small decrease in the K content (6.2% in the fresh sample, 5.7% in the aged catalyst). However the observed effects (loss of the NO_x storage and soot oxidation capacity) may also be explained by considering that the availability of K is decreased, e.g. due to interactions with the support and/or with the noble metal whose characteristics are in fact changed on the aged sample (see below). This is in line with the documented intrinsic high activity of K in the soot combustion [39].

To gain further information on the effect of ageing in modifying the behaviour of Pt-K/Al_2O_3 catalysts, low temperature CO adsorption has been also performed over the aged catalyst. Fig. 7 shows the spectra of surface species arising after outgassing, upon warming. The band at 2151 cm^{-1} is due to CO interacting with hydroxyl groups of the alumina support. In agreement with this assignment, the corresponding OH stretching bands are shifted towards lower frequencies and a negative band can be detected at 3715 cm^{-1} in the subtraction spectra (Fig. 7, inset A). The shoulder at 2180 cm^{-1} is due to CO linearly coordinated over Al^{3+} ions, whereas a weak absorption in the range 2140–2130 cm^{-1}, has been previously assigned to CO coordinated over exposed K^+ over the same fresh catalyst [43]. The low frequency of carbonyl stretching vibrational modes points out that these sites act as very weak Lewis sites.

Spectra reported in Fig. 7 are consistent with those reported by Montanari et al. [43] recorded in the same conditions following adsorption of CO over the fresh Pt-K/Al_2O_3 catalyst although some differences can be highlighted. In spite of the heavy K-doping, spectra of CO adsorbed over the aged catalyst show residual Lewis sites (exposed Al ions) characterized by the band at 2180 cm^{-1}, whereas the frequency of the band due to CO interacting with OHs, close to the frequency of CO adsorbed on pure alumina (2151 vs. 2153 cm^{-1}), seems to indicate that the residual OHs at the surface show some acidity consistent with the exposed support. Moreover, the deconvolution of the CO main band (Fig. 7, inset B), following outgassing at −140 °C, clearly evidences three components, at 2156, 2148, and 2140 cm^{-1}, the former due to CO H-bound to alumina hydroxyl groups, still detectable after a brief outgassing, and the latter two due to CO coordinated over K^+ sites behaving as Lewis sites. The quality of such K^+ sites is not affected by the conditioning (i.e. the frequency reported here are the same discussed in Ref. [43]), but it is clear that these are not anymore the only components in the carbonyl spectra. This effect could be explained again on the basis of a partial loss of available potassium in the aged catalyst, thus exposing support ions and hydroxyl groups, in agreement

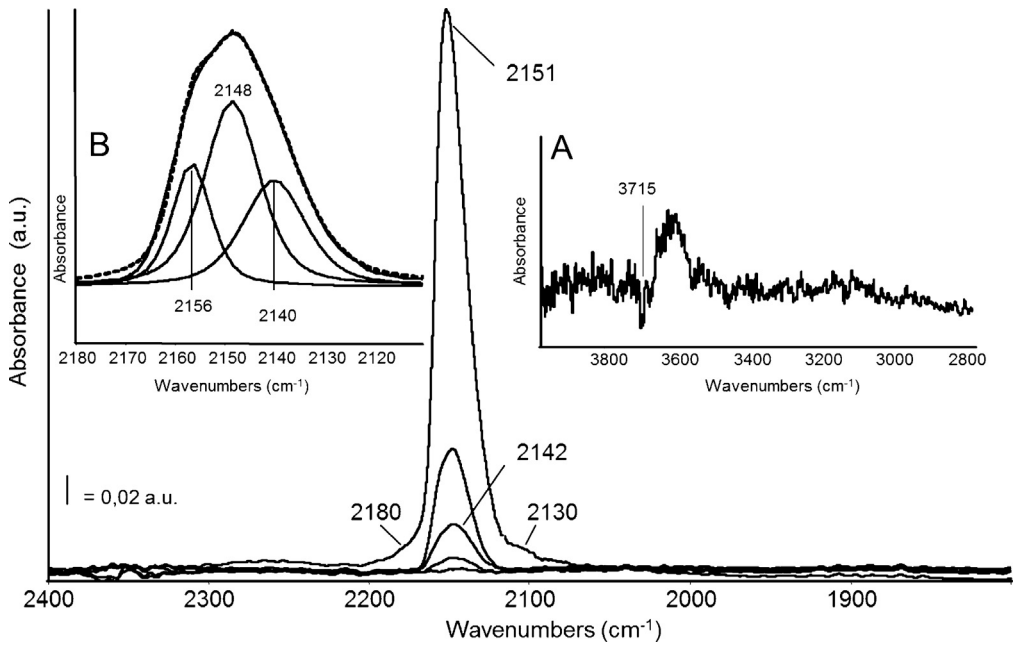

Fig. 7. FT-IR subtraction spectra of the species arising from low temperature CO adsorption over the aged catalyst, outgassed at 350 °C (−140/−80 °C). The activated surface spectrum has been subtracted. Inset A: OH stretching region. Inset B: deconvolution of the spectrum of the species arising from CO adsorption and outgassing at −140 °C over the aged catalyst.

with the activity results from ageing tests and from CO_2 reactive adsorption experiments.

Finally, the comparison of aged and fresh Pt-K/Al_2O_3 catalysts (see Fig. 7 and Ref. [43] respectively) points out some differences concerning also the platinum species. CO adsorption over the fresh catalyst led to the detection of a band at 2075 cm^{-1}, due to carbonyls linearly coordinated over Pt metal particles. Moreover, the fresh catalyst showed a quite high oxidizing capability due to residual Pt ions which are able to oxidize CO even at such low temperatures: as a result CO_2 was detected. On the spent catalyst (Fig. 7) the spectral features due to CO adsorbed on Pt metal (2100–2000 cm^{-1}) are extremely weak, if any, and CO_2 was not detected during CO adsorption over the aged catalyst and this effect can be an evidence of modifications of the metal species. On this regard, it may be argued that Pt ions are at least partially covered, or their CO adsorption capacity inhibited, by stronger interaction with K species, as consequence of the above discussed alkali mobility. This however does not lead to appreciable changes in the NO oxidation activity. It is speculated that the Pt sites are more active in the NO oxidation than those present in the fresh catalyst and this may be related to the changes in the K phase resulting in a different interaction with Pt. This point is however not completely understood and deserves further investigations.

4. Conclusions

The data herein presented highlight the catalytic behaviour of DPNR Pt-K/Al_2O_3 catalyst in the simultaneous removal of soot and NO_x. It has been found that the presence of soot decreases the storage capacity of the catalytic system at any temperature in the range 250–350 °C. The decrease in the NO_x storage capacity has been related to the competition between soot and K sites towards NO_2 that could be involved both in the combustion of soot and/or in the storage process.

Moreover, soot decreases the stability of the NO_x stored species. In fact, when soot is present, a pronounced tail in the NO_x concentration is observed upon NO shutoff indicating the decomposition of the adsorbed NO_x. Besides, a simultaneous production of CO_2 is observed. This can be taken as an indication of a direct interaction between soot and stored nitrates leading to soot oxidation, favoured by the high mobility of K-species.

The investigated Pt-K/Al_2O_3 catalyst suffers deactivation upon ageing with repeated NO_x storage–reduction cycles and soot combustion. In fact the aged catalyst shows a decreased NO_x storage capacity and also a lower soot oxidation activity. This behaviour has been attributed to a decrease of the availability of the K active species, due to partial loss of K and/or to involvement of the K active species in interactions with alumina and/or Pt.

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