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Synthetic gas bench study of a 4-way catalytic converter: Catalytic oxidation, NOx storage/reduction and impact of soot loading and regeneration

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ABSTRACT

The so-called 4-way catalytic converter (4WCC) has the ability to simultaneously convert CO, HC, NOx and particulate matter on a single support. It allows diesel vehicles to obey to increasingly stringent emission regulations while at the same time decreasing the space needed by the exhaust aftertreatment system. It is combined with fine engine control strategies so as to ensure conversion of all pollutants. It is hence associated with a large number of catalytic reactions which interact with each other and compete for active sites. The behavior of a commercial 4WCC was characterized on a synthetic gas bench. Gas composition, temperatures and gas hourly space velocity were chosen close to real engine operating conditions. Samples were loaded with soot on an engine bench test. Oxidation reactions were dominant in a lean environment: CO oxidation by NO_2 at low temperature followed by H_2, CO, NO and HC oxidation by O_2. NOx were stored on barium storage sites. In rich conditions H_2, CO and HC were used to reduce NOx. NH_3 production from H_2 was also observed. It could be used to further reduce NOx in lean conditions if stored on a downstream SCR system like in the Honda system [1]. A further conversion of HC was obtained at high temperature due to steam reforming. Interactions and inhibitions were also found. NOx storage appeared to be inhibited by CO oxidation with NO_2 at low temperatures and also by HC, maybe through competition for storage sites with CO_2 produced during HC oxidation. Catalytic reactions were affected by the soot deposit. Continuous oxidation of soot by NO_2 also induced a slower NOx storage rate.

1. Introduction

Environmental, ecological and health concern result in increasingly stringent emissions regulations of pollutant emissions from vehicle engines. Lean-burn engines are one way to reduce CO_2 emissions and at the same time improve fuel economy. The drawback is the difficulty to selectively reduce NOx in an oxygen-rich environment. Two approaches are being developed to answer to this challenge. A first technology deals with the continuous selective catalytic reduction (SCR) of NOx. It takes advantage of the ability of some catalysts to allow the selective reaction of a limited amount of reductant with NOx rather than O_2. An alternative technology is based on a cycle of NOx storage and reduction. The overall principle of catalyst operation during this cycle can be described by five reaction stages as summarized by Epling et al. [2]:

1. NO oxidation to NO_2
2. NO or NO_2 sorption on the surface in the form of nitrites or nitrates
3. reductant evolution when the exhaust is switched to the rich condition
4. NOx release from the nitrite or nitrate sites
5. and NOx reduction to N_2.

Each of these catalytically activated stages is critical for an efficient operation of the lean NOx trap (LNT).

Particulate matter (PM) emissions are also severely regulated for lean-burn engines. It is currently not possible to simultaneously meet NOx and PM requirements by improving the diesel engine combustion alone. Again, specific aftertreatment devices must be developed and used. A considerable amount of research has hence been conducted about diesel particulate filters (DPF) for several years. PSA Peugeot Citroen launched the first passenger vehicle equipped with a fuel additive DPF in 2000 [3]. This emission control strategy uses a fuel-borne, ceria-based catalyst in combination with precise engine and exhaust gas temperature control. PM trapped into the DPF is periodically oxidized. Johnson Matthey developed the continuously regenerating trap (CRT) [4]. In this approach an oxidation catalyst turns NO into NO_2 upstream

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from the DPF. The DPF collects the PM, and the NO_2 generated over the catalyst combusts this PM at temperatures much lower than is the case for combustion with oxygen (250 °C instead of 550 °C). A number of car manufacturers now use DPFs on their vehicles.

A few developers have been working on a catalyzed filter able to reduce both NOx and PM emissions [5]. The objective is to couple PM treatment and deNOx functions on a single support. As CO and HC catalytic oxidation functions are also present on the deNOx system, the catalyst can be named a "4-way catalytic converter" (4WCC). Its main advantage is that it decreases the space needed along the exhaust line for the set of catalysts. Such a system was first put into serial production in 2003 by Toyota [6,7]: The so-called "DPNR" (for diesel particulate NOx reduction) is a particulate filter coated with NOx storage reduction catalyst and combined with engine control strategies as described by Suzuki and Matsumoto [8].

The reaction mechanism is expected to be quite complex in such a system mainly due to the number of possible reactions and the range of different reducing agents used in real driving conditions. The objective of this work was to study this reaction mechanism, to highlight the reactions that occur during catalyst light-off and operation and the way these reactions interact. The impact of soot was also emphasized. Studies available in the literature about this subject usually consider simple conditions rather far away from real driving conditions. This study used a commercially available monolithic catalyst sample and synthetic gas feeds close to those found downstream from an engine. Simpler feeds were also used when it appeared necessary to better emphasize some reactions or interactions.

2. Experimental

2.1. Catalyst

The commercial 4-way catalytic converter that was investigated in this study is a porous monolithic honeycomb structure, 1.44 L in volume and 300 cells/in.^{2} (cpsi) in cell density. Filter channels are alternatively plugged so as to ensure particle filtration. The fine porous ceramic is coated with NOx storage reduction catalyst. The catalyst formulation and coating were characterized by X-ray fluorescence analysis (XRF), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

Samples prepared for our study were 25 mm in diameter and 50 mm in length. Channels were alternatively plugged. Their catalytic activity was first stabilized by a 5 h conditioning at 800 °C under a 300 L/h synthetic air flow.

2.2. Synthetic gas bench

Three different types of experiments were performed:

- Catalyst light-off during a temperature ramp of 10 °C min^{-1}
- Isothermal NOx storage experiments with different gas compositions
- And storage/reduction cycles: rich pulses close to real conditions

Experiments were carried out in a flow reactor under atmospheric pressure and realistic flow conditions with synthetic diesel exhaust gas. The catalyst sample was placed in a quartz tube. A thermocouple in front of the catalyst was used to control the temperature and another one was inserted downstream from the catalyst. The fact that no thermocouple was introduced inside the monolith added some uncertainty to the temperature assignments of reaction light offs, although the downstream temperature was assumed to be quite close. The quartz tube was placed in an electrically heated oven. Valves allowed to rapidly switch from one gas composition to another are likely to generate alternating rich and lean pulses. Different gas compositions were chosen close to a lean diesel environment (equivalence ratios ER = 0.3 and 0.6) and to a rich pulse environment (ER = 1.1) as detailed in Table 1. Other compositions were also tested when considered useful to better understand the catalyst behavior. No SO_2 was used. Propylene was used to represent unburned hydrocarbons emitted by engine combustion.

The gas hourly space velocity was 30 000 h^{-1}. All gases were fed to the reactor via mass flow controllers, while water vapor was injected through a vaporizer in an N_2 flow. Analyzed gases were CO_2, O_2, CO, HC, NOx, NO and NO_2, and H_2 and NH_3 for some of the tests.

Tests were conducted in absence and in presence of soot. In the latter case samples were previously loaded with soot on an engine test bench. A PSA DW12 2.2 L engine was used to generate soot on the following stabilized operating point: engine speed 3000 rpm and BMEP 2.8 bar. A revolver cylinder like device was built so as to load 18 samples at once (see Fig. 1). Soot mass was around 140 mg per sample, i.e. 5.7 g/L^{-1} of catalyst.

2.2.1. Catalyst light-off runs

For this experiment the temperature was increased from 50 to 400 °C at a 10 °C/min rate. The catalyst activity in terms of CO, HC and NOx conversion efficiencies were determined as a function of the temperature measured upstream from the catalyst.

2.2.2. Isothermal NOx storage

The gas temperature was increased up to the desired value under an N_2 flow. The experiment then switched to a lean feed and NOx, NO and NO_2 were monitored downstream from the catalyst. Once the 4-way catalyst was saturated the gas mixture switched back to N_2 and the temperature was increased so as to thermally release the complete amount of stored NOx (N_2-TPD: temperature programmed desorption). The NOx storage capacity (NSC) and the NO oxidation efficiency of the catalyst were determined at different temperatures and storage times.

2.2.3. Rich pulses

The gas temperature was increased up to the desired value under an N_2 flow. The gas flow then switched between 40 s lean feed periods (ER = 0.3) and 2 s rich pulses (ER = 1.1, see Table 1).

3. Results and discussion

3.1. Catalyst composition

Main components of the support material are Al_2O_3 and ZrO_2, with some TiO_2 and ceria. Trapping materials are mainly barium and a small amount of potassium. Active species are Pt and Rh. A combination of these two noble metals is required to achieve good NOx storage and reduction performance, together with good sulfur regeneration ability [9].

Scanning electron microscopy revealed that the wash-coat was deposited into the pores and hence intimately bound to the cordierite. EPMA showed that all wash-coat elements were mixed together before being wash-coated in one stage.

Table 1
Gas compositions used for the tests. Gas composition also included H_2 = CO/3, H_2O = 4% and N_2 = balance.

Eq. ratio	HC (ppmC)	CO	NOx (ppm)	CO_2 (%)	O_2 (%)
0.3	900	700 ppm	300–700	4	15
0.6	3000	2400 ppm	300–700	9	8
1.1	6500	3%	350	12	1.2

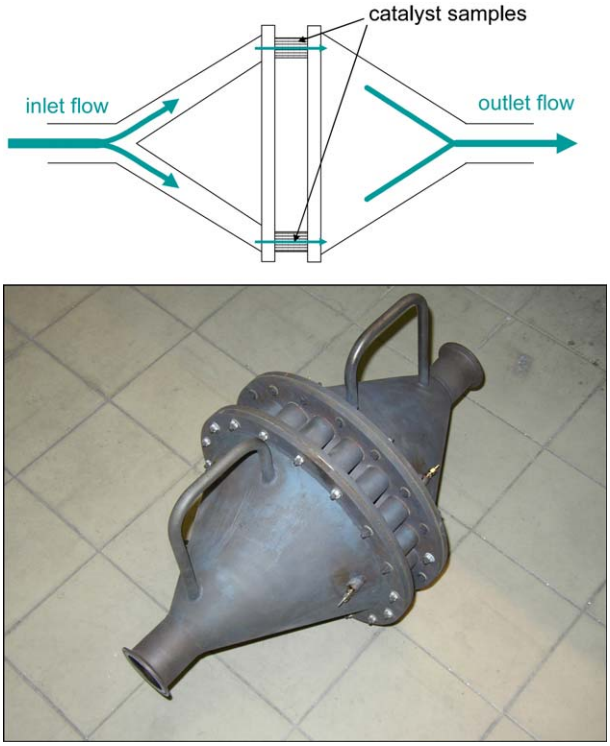

Fig. 1. Sketch and picture of the soot loading device used in an engine test bench.

3.2. Lean operating conditions without soot

3.2.1. Catalyst light-off runs

An illustration of light-off test results is given on Fig. 2. Pollutant emissions measured downstream from the catalyst are given as a function of the inlet gas temperature for a 0.3 equivalence ratio. CO and HC light-off temperatures (i.e. temperature at 50% conversion) are respectively 175 and 180 °C for this test.

The main NOx emission variations observed in this lean feed were due to

- partial non-selective NOx reduction yielding N_2O between 170 and 350 °C. Isothermal NOx storage tests (described later in this section) proved that no selective NOx reduction to N_2 occurred.
- and NOx storage above 180 °C and release above 320 °C.

NO_2 formation correlated with NOx storage. It reached a maximum at 360 °C and then dropped because of the NO/NO_2 thermodynamic equilibrium limitation. This is consistent with the fact that the most effective pathway for NOx storage from NO/O_2 mixtures is a "nitrite" route, which implies the stepwise oxidation of NO leading to the formation of nitrite ad-species [10].

NO_2 was not detected at low temperature until CO was oxidized. Schmeisser et al. [11] found that reductants in the lean feed such as CO and C_3H_6 hindered NO_2 formation as long as they were present. Our results agree with these observations as shown in Fig. 3: NO_2 was monitored during a light-off test for both a complete lean feed, i.e., including reductants, and for a simple gas mixture with only NO, O_2 and N_2. NO_2 formation activated at 125 °C without reductants instead of 180 °C with reductants. This difference is due to the competition among reduction of NO_2 with CO, oxidation of NO by O_2 and oxidation of CO by O_2, the latter being favored at higher temperatures.

A specific test was performed to illustrate the CO/NO_2 reaction proceeding by replacing NO with NO_2 in the feed so as to suppress the NO oxidation phase which is a limiting stage at low temperatures. The outlet NOx concentration was lower than the inlet one below 100 °C because NO_2 was stored on the trapping material. Between 100 and 180 °C, CO clearly appeared to reduce NO_2, yielding CO_2 (not displayed) and NO and thus preventing NOx storage. Erkfeldt et al. [12] obtained similar results in a study of low temperature NOx storage (at 100 and 140 °C). After catalyst light-off (above 180 °C), results displayed in Fig. 4 were about the same as those shown earlier in Fig. 2 with NO in the feed.

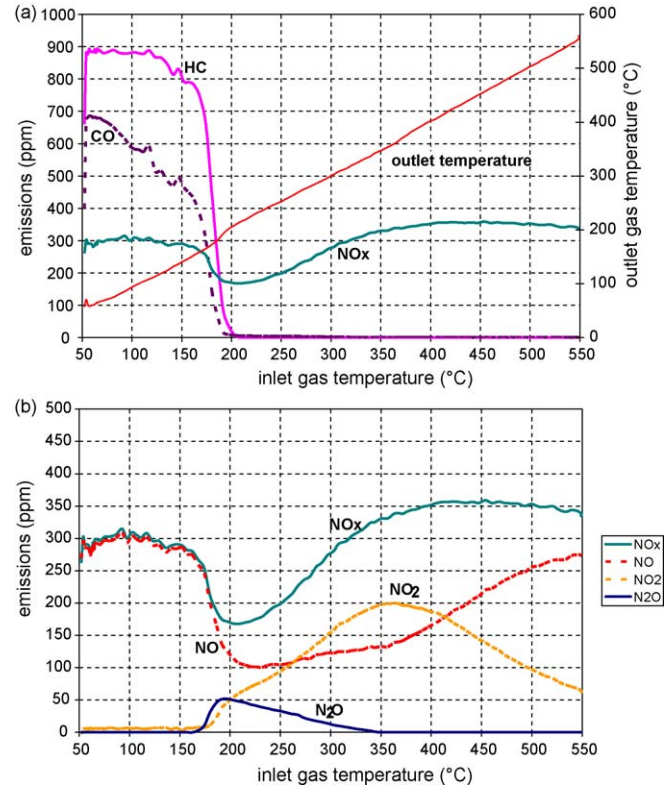

Fig. 2. Pollutant emissions measured downstream from the 4WCC during a light-off test – ER = 0.3.

Last but not the least, significant amounts of NO were detected at low temperatures although the NO_2/NOx rate for a NO_2 feed with 15% O_2 should remain above 95% below 250 °C according to thermodynamic equilibrium calculations. This NO formation could be explained with the disproportionation mechanism [2,10]:

$$BaO + 3NO_2 = Ba(NO_3)_2 + NO \quad (1)$$

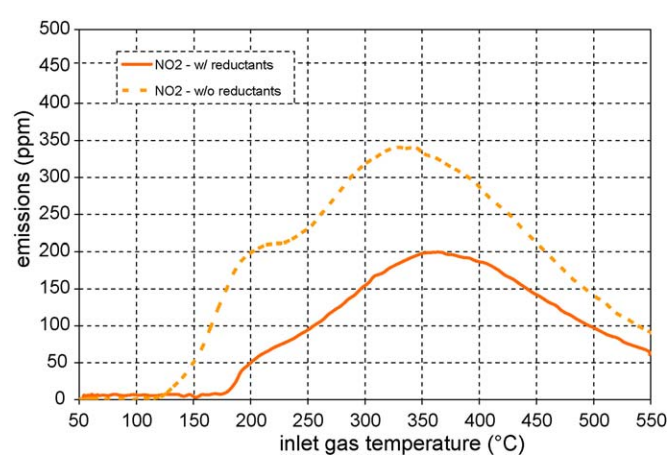

Fig. 3. NO_2 measured downstream from the catalyst with reductants (complete lean mixture, 350 ppm NO, ER = 0.3, see Table 1) and without reductants in the feed (simple gas mixture: 350 ppm NO + 15% O_2 + N_2 balance).

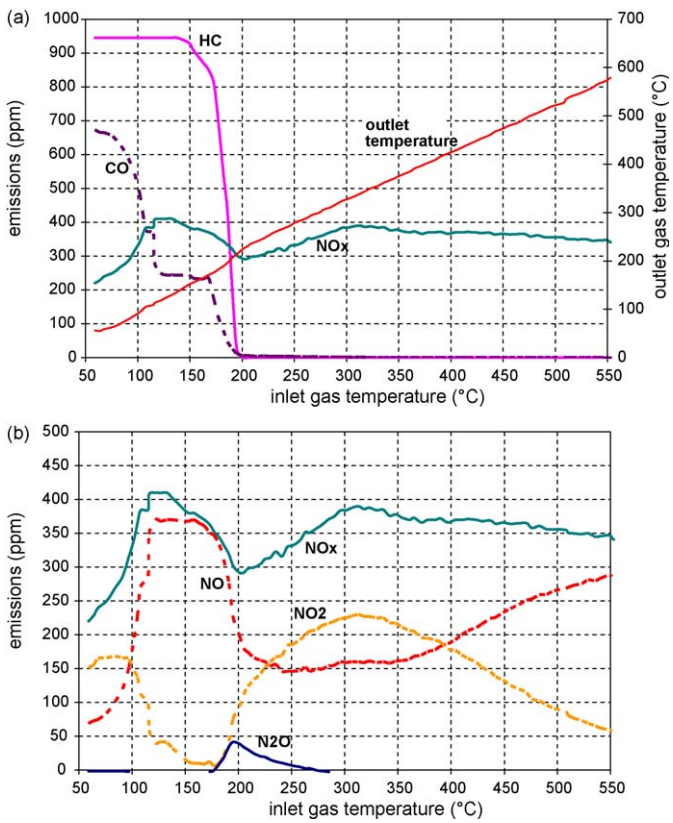

Fig. 4. Pollutant emissions measured downstream from the 4WCC during a light-off test with NO_2 replacing NO in the feed – ER = 0.3.

This mechanism was established to explain NOx storage on sorption sites where there was no dissociated O_2 available due to equivalence ratio away or full Pt sites. In our case it is not a matter of distant Pt sites since no NO formation was observed in a light-off test conducted with only NO_2 and O_2 in the feed (results not displayed). At these low temperatures CO more likely scavenged Pt sites preventing them from dissociating O_2. For that same reason the "nitrite" route mentioned earlier in this paper and involving both NO_2 and dissociated O_2 found itself limited at low temperature:

$$BaO + 2NO_2 + 1/2O_2 = Ba(NO_3)_2 \quad (2)$$

In Eqs. (1) and (2) BaO is shown as an oxide but is more likely under the form of a Ba carbonate or hydroxide.

3.2.2. Isothermal NOx storage

An example of isothermal NOx storage test at 360 °C is given in Fig. 5. The NOx trap saturated after around 150 s when the total amount of inlet NOx slipped through the catalyst. This period is quite low compared to some other commercial lean NOx traps which do not filter particulate matter and typically saturate after about 500–600 s in such conditions [13]. The outlet temperature increase was due to CO and HC oxidation. NO_2/NOx rates downstream from the engine and NOx storage capacities were determined from these tests at various temperatures, and gas compositions.

3.2.2.1. Impact of NOx. The NOx storage capacity is displayed on Fig. 6 for two different amounts of NO in the feed and three storage times: 60 s, 170 s and until NOx trap saturation. The NOx storage capacity evolves together with the ability of NO to oxidize (Fig. 2) in agreement with the general consensus that NO_2 is the main

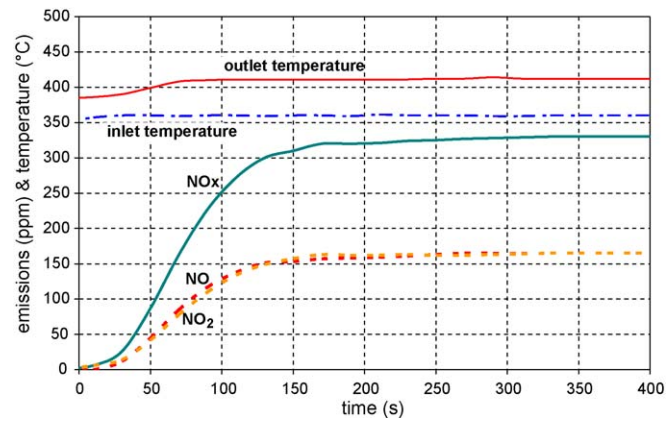

Fig. 5. NOx and temperature vs. time during an isothermal NOx storage run at 360 °C. ER = 0.3 with 340 ppm NO.

intermediate in the Ba trapping process [2]. The catalyst is still able to trap some NO at low temperature: at 170 °C the NSC is 4 mol m^{-3} of monolith while no NO_2 is produced. This adsorption probably occurred on alumina. A recent study by Lindholm et al. [14] pointed out the dominant trapping ability of the alumina support compared to barium sites at temperatures below 200 °C. Lindholm did not distinguish NO from NO_2. However, a former Fourier-Transform study by Westerberg and Fridell [15] demonstrated that NO adsorbed on Pt/Al_2O_3 samples at low temperatures (150 °C) and low coverage of nitrates.

The comparison of the plots in Fig. 6 indicates that the first 60 s of NOx storage were limited by a low NO amount present in the feed: the 350 ppm NSC reached a plateau above 200 °C unlike the 750 ppm NSC. NO oxidation was also a limiting stage before thermodynamic equilibrium was reached. A marked increase of the NSC with the amount of NO in the feed was observed: +30% after a storage time of 170 s and still +15% after saturation.

3.2.2.2. Impact of CO_2 and reducing agents. CO_2 amount was changed to 0% and 8% in the ER = 0.3 reference lean feed and NOx storage isothermal tests were run at 250 and 360 °C. The NOx storage capacity remained unchanged at both temperatures (not displayed). This is quite surprising since it is commonly demonstrated in the literature that CO_2 in the feed gas inhibits NOx adsorption because of a competition between the formation of barium carbonate and nitrate [16].

No effect of CO was observed either on NOx storage at constant temperature. On the other hand HC appeared to have a significant impact on the NSC as shown on Fig. 7. The largest effect is found at an inlet gas temperature at 200 °C where the final NSC is multiplied

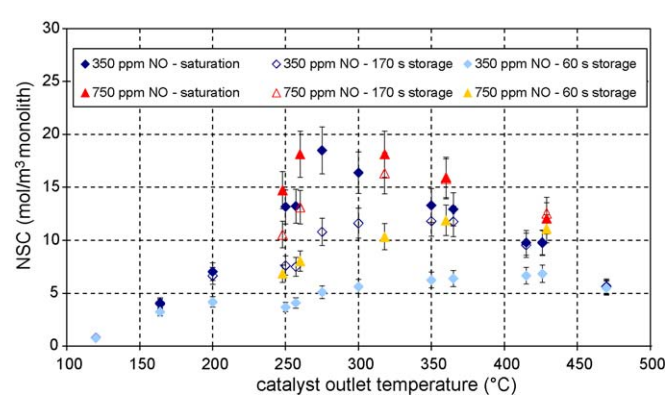

Fig. 6. NSC vs. catalyst outlet temperature for two lean feeds: ER = 0.3 with 350 and 750 ppm NO and three storage times: 60 s, 170 s and until NOx trap saturation.

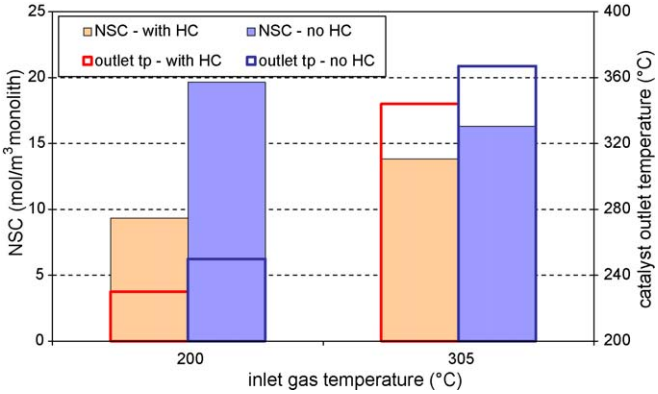

Fig. 7. HC impact on saturated NSC at two inlet gas temperatures with corresponding catalyst outlet temperatures – ER = 0.3.

by 2.1 when HC are suppressed from the feed. Several reasons may explain this difference:

(i) Non-selective partial reduction of 23% NOx into N_2O occurs at this temperature when HC are present but completely stops when HC are suppressed. This deNOx lowers the amount of NOx available for storage and hence the NSC as was demonstrated in Fig. 6, but not enough to explain such a large difference. DeNOx also disappears for an inlet gas temperature at 300 °C at which an NSC difference is still observed.

(ii) The catalyst temperature increase due to catalytic oxidation is lower when HC are suppressed: 230 instead of 250 °C for a 200 °C inlet gas temperature, leading to a 40% decrease of the NO_2/NOx ratio. Again, this decrease may be partly responsible for the NSC drop but not completely since it is not observed for a 300 °C inlet gas temperature. The catalyst temperature varies between 345 and 365 °C in this case where the NO_2/NOx ratio looks relatively stable.

(iii) Last but not least, CO_2 emissions were monitored during the N_2-TPD following the isothermal NOx storage test and a CO_2 peak was observed around 340 °C behind the 200 °C inlet gas temperature with HC only. This peak diminished behind the 300 °C test but was still visible. No CO_2 desorption was detected when HC were suppressed. These observations are quite interesting as they highlight a competition for sorption sites via HC oxidation to CO_2 with subsequent barium carbonate formation. As mentioned earlier in this section, such a competition had not been observed with CO_2 present in the gas phase unlike what is commonly described in the literature [16].

3.3. Rich operating conditions without soot: catalyst light-off during temperature ramp

An illustration of light-off test results is given in Fig. 8. Pollutant, H_2 and O_2 emissions measured downstream from the catalyst are given as a function of the inlet gas temperature for an equivalence ratio ER = 1.1. H_2 emissions were monitored in rich operating conditions. In this example NO and O_2 were used to oxidize all H_2 and a part of CO at 190 °C. As the temperature kept increasing, HC oxidation began to compete with H_2 and CO oxidation. A variation in the slope of HC and H_2 emissions around 500 °C indicates the action of water via C_3H_6 steam reforming:

$$C_3H_6 + 3H_2O = 3CO_2 + 6H_2. \quad (3)$$

No evidence of the water gas shift reaction activation could be found, if any. Further tests should be conducted with simpler feeds to demonstrate whether this reaction takes place or not.

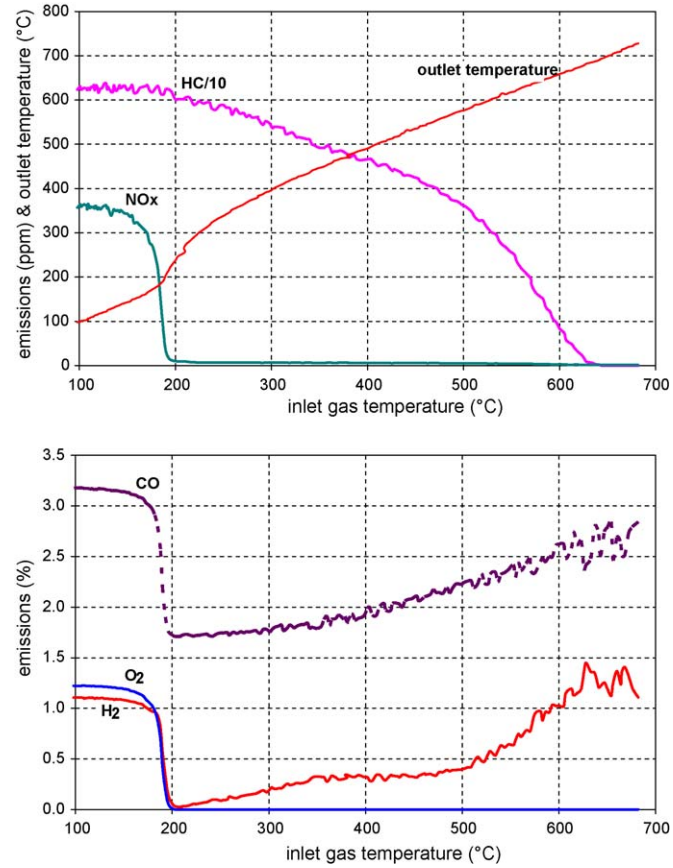

Fig. 8. Gaseous emissions measured downstream from the 4WCC during a light-off test – ER = 1.1.

A light-off test was done with a simplified gas composition (no oxygen, no CO_2, no water) to better distinguish the various reactions involving pollutants. Results are displayed in Fig. 9. An oxygen mass balance between reactants and products allowed us to estimate H_2O emissions. An ammonia analyzer was used for this test. NH_3 emissions were detected and correlated perfectly with the NH_3 determined from a hydrogen mass balance. NH_3 formation was due to reaction between H_2 and NO:

$$2NO + 5H_2 = 2NH_3 + 2H_2O \quad (4)$$

Such results facilitate the understanding of the reaction mechanism involved in rich feed conditions. Here is a suggestion to explain reductant conversion above 300 °C (catalyst outlet temperature) once all available NO is reduced:

(i) C_3H_6 starts to compete with other reducing agents to reduce NO inducing a CO and H_2 increase. C_3H_6 oxidation is partial because of the lack of oxygen and yields CO instead of CO_2, and H_2O.

(ii) Above 500 °C the slowly decreasing H_2O matching with increasing NH_3 formation points out a diminishing selectivity towards N_2. Thus Eq. (4) replaces:

$$2NO + 2H_2 = N_2 + 2H_2O \quad (5)$$

(iii) The sharper decrease of H_2O production around 550 °C may indicate the starting of steam reforming yielding CO and H_2 again and finishing HC conversion. Steam reforming had been detected at this same catalyst outlet temperature in the test conducted with a complete lean feed (Fig. 8).

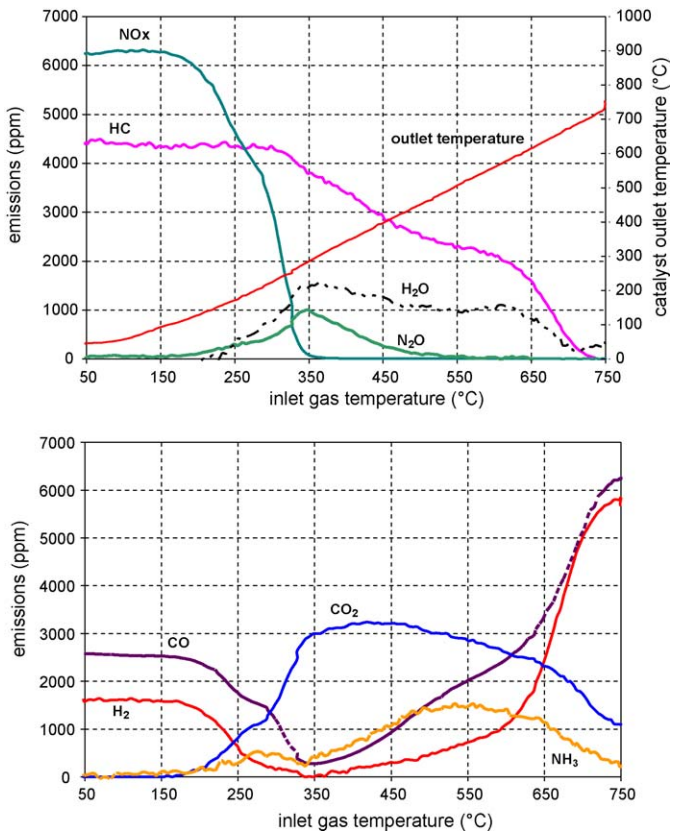

Fig. 9. Gaseous emissions measured downstream from the 4WCC during a light-off test – H_2O is evaluated – simple rich feed is 4400 ppmC C_3H_6, 2600 ppm CO, 1600 ppm H_2, 6300 ppm NO, balance N_2.

A complete mass balance allowed us to determine the temperature ranges and relative importance of all reactions involving NO in these specific conditions. Results are presented in Fig. 10. It is important to keep in mind that this NO reduction mechanism was established in a steady state and might change during transition conditions like during a short rich pulse to reduce the stored NOx. Such a different behavior was observed by Tonkyn et al. [17] (and also Scholtz et al. [18]) who used H_2 as a unique reductant. They detected NH_3 only in steady state and in cycles with 8 s or longer rich periods. They concluded that the appearance of ammonia was an indication that nitrogen production from stored NOx was complete, and that the optimal rich period had been reached or exceeded. Cumaranatunge et al. [19] gained

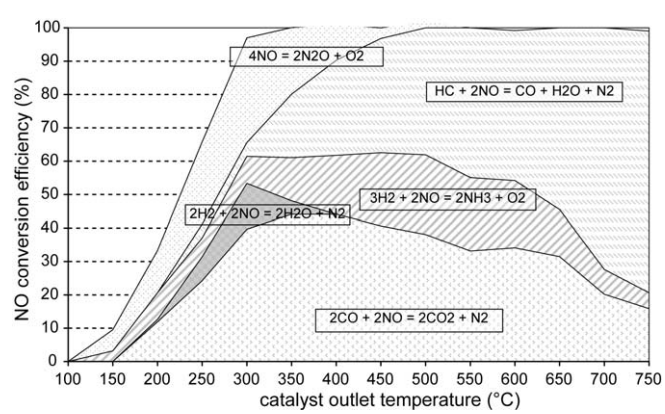

Fig. 10. Distribution of reactions involved in NO reduction in a rich feed vs. catalyst outlet temperature.

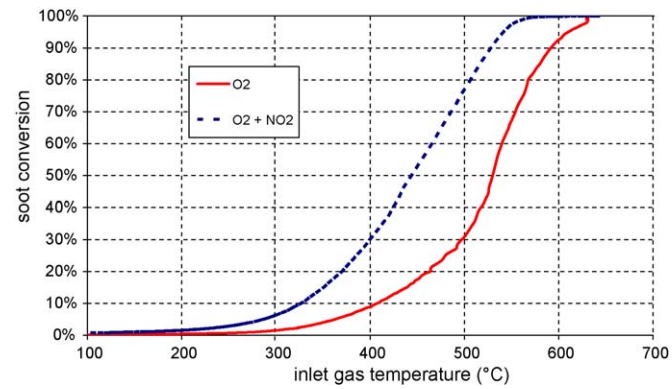

Fig. 11. Soot oxidation during a light-off test on a soot loaded sample with 15% O_2 in N_2 ("O_2") and 15% O_2 + 4% H_2O + 300 ppm NO_2 in N_2 ("O_2 + NO_2").

further insight into the actual mechanism when they demonstrated that the regeneration of a $Pt/BaO/Al_2O_3$ NOx trap in H_2 occurs through the formation of NH_3 as an intermediate and that an oxygen source on the catalyst support, usually the stored NOx, is necessary for the oxidation of NH_3 to N_2.

3.4. Impact of soot

3.4.1. Soot oxidation

Specific tests with simple gas feeds were conducted to emphasize O_2 and NO_2 ability to oxidize soot. The soot conversion ratio vs. temperature is displayed in Fig. 11 with different oxidizing feeds: O_2 alone and $O_2 + NO_2$. The soot conversion ratio was deduced from CO_2 emission measurements. Light-off temperatures were respectively 530 and 445 °C: a significant decrease was obtained by only adding 300 ppm NO_2. NO_2 is well known to react with soot leading to CO_2 and NO formation [20,21]. In real exhaust gas conditions, where NO is dominant compared to NO_2, NO must be at first oxidized into NO_2 on Pt sites.

3.4.2. Catalyst light-off runs

The light-off of a 4WCC sample loaded with soot was further investigated in a lean feed (ER = 0.3). Results are displayed in Fig. 12. CO_2 emissions due to soot were evaluated by deducting CO_2 emissions (ppm) due to HC and CO oxidations and CO_2 in the inlet feed from the CO_2 measured downstream from the catalyst (signal given in %). This is the reason why the corresponding curve is so hectic and can only be used as qualitative information. Soot oxidation becomes significant at 300 °C, i.e., well after catalyst

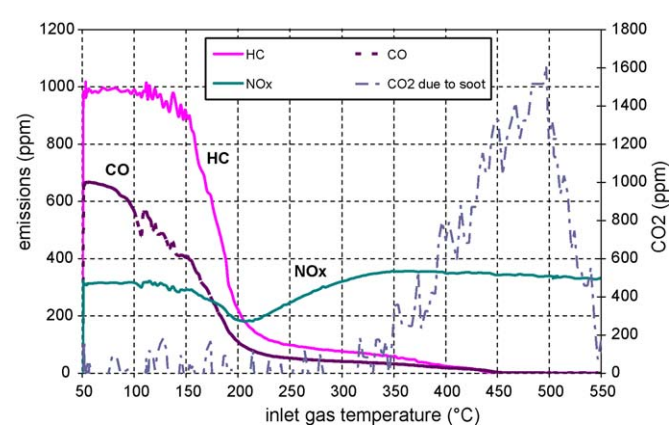

Fig. 12. Pollutant emissions measured downstream from the 4WCC during a light-off test on a soot loaded sample, including CO_2 due to soot oxidation – fuel–air equivalence ratio ER = 0.3.

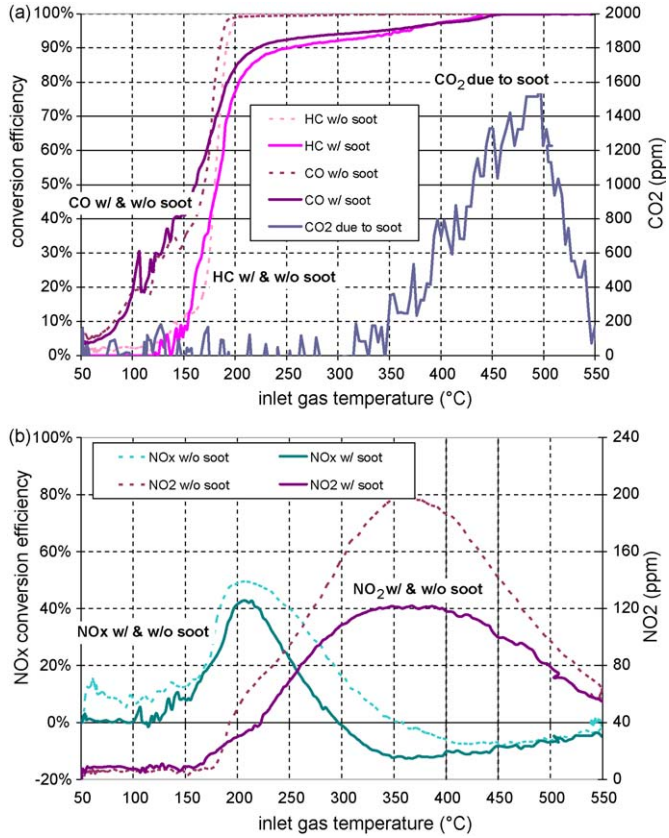

Fig. 13. Comparison of 4WCC conversion efficiency obtained during a light-off test on a soot loaded sample ("w/soot") and an unloaded sample ("w/o soot", derived from Fig. 2(a)) – fuel–air equivalence ratio = 0.3.

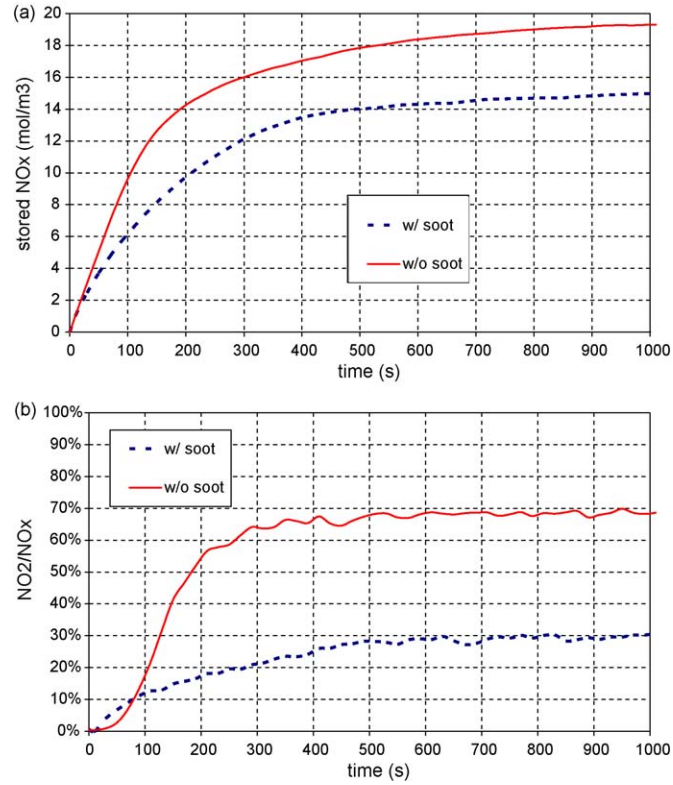

Fig. 14. Comparison of NOx storage quantities (a) and NO_2/NOx ratios (b) obtained during an isothermal NOx storage run on a soot loaded sample ("w/soot") and an unloaded sample ("w/o soot") – fuel–air equivalence ratio = 0.3 with 300 ppm NO, inlet gas temperature = 300 °C.

light-off which occurs around 180 °C. It still has an impact on the ends of CO and HC oxidations which are slowed down. This effect is more apparent in Fig. 13, where the 4WCC conversion efficiencies for all three pollutants with and without soot are compared. CO and HC light-off curves evolve the same way until the inlet temperature reaches 180 °C (Fig. 13(a)). NOx conversion is due to storage. Its diminution when soot is present is related to NO_2 emissions which are 40% lower (Fig. 13(b)) above 180 °C. Soot hence seems to have an inhibiting effect on both NOx storage and CO and HC oxidations as soon as it starts to oxidize, i.e., around 200 °C according to Fig. 11 and at even lower temperature according to Fig. 13. The soot impact on NOx storage was further investigated with isothermal NOx storage tests on soot loaded samples.

3.4.3. Isothermal NOx storage

As already observed in the previous section, soot oxidation and NOx storage compete for NO_2. The following graphs (Fig. 14) further illustrate this phenomenon. They display the time evolution of stored NOx and NO_2/NOx ratio during an isothermal NOx storage test at 300 °C with a 0.3 equivalence ratio. The presence of soot reduces the NOx storage rate and the NOx storage capacity at saturation (by 22% in this case). Sulfur emitted by the engine during sample soot loading was not held responsible for this NOx storage decrease because the engine loading phase only lasted about 45 min with a low sulfur fuel. The competition for NO_2 is obvious in Fig. 14(b) where the NO_2/NOx ratio measured downstream from the 4WCC is divided by 2.3. Part of the NOx storage capacity decrease may be due to the adsorption over Ba sites of the CO_2 produced by soot oxidation with formation of $BaCO_3$ as suggested by Castoldi et al. [20]. Further tests with simpler feeds would be necessary to verify whether this competition takes place in our case or not. It is also significant to observe such a large impact on NO oxidation and subsequent storage even though soot only deposit on inlet channels: all channels are actually wash-coated with active and storage sites and are hence able to treat NOx. However, outlet channels are not able to compensate the NOx storage loss due to the soot deposit in inlet channels, maybe because of a too short residence time.

3.4.4. Rich pulses

The impact of soot was also investigated in conditions close to real use, i.e., by periodically switching between 40 s lean feed periods and 2 s rich pulses to regenerate the NOx trap. Pollutant emissions are displayed in Fig. 15. Tests began with no NOx stored. Results confirmed those obtained in steady state conditions. At the beginning the sample without soot was a better NOx trap than the one with soot (not displayed) as expected from our previous results. After a few cycles the results stabilized. NOx storage appeared to be about the same for both samples despite the large increase of NO (Fig. 15(a)) meaning a much lower amount of NO_2 available in the presence of soot. During rich pulses a NOx slip was observed only when no soot was there: NOx were better reduced in the soot loaded sample and the storage capacity better regenerated. This observation correlates with lesser HC and CO oxidations which are hindered by soot oxidation at this temperature (Fig. 12) in both lean and rich feeds. This additional HC and CO available may take part in the better reduction of NOx and thus compensate the effect of soot. H_2 emissions could not be monitored because the analyzer response time was not fast enough.

Two second rich pulses appeared too short to efficiently regenerate the NOx trap. Other results obtained without soot showed that 8–10 s rich pulses were more effective.

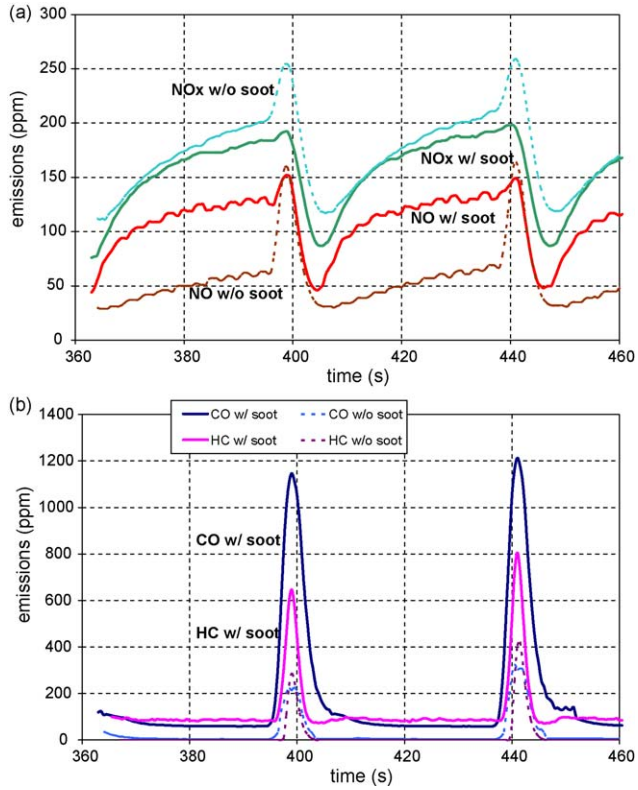

Fig. 15. Comparison of NOx (a) and HC and CO emissions (b) measured during NOx storage stages and rich pulses on a soot loaded sample ("w/soot") and an unloaded sample ("w/o soot") – inlet gas temperature = 260 °C and outlet gas temperature = 315 °C.

4. Conclusions

The behavior of a commercial 4-way catalytic converter was investigated in terms of reaction mechanisms involving all reactants present in vehicle exhaust gases: CO, HC, NOx, O_2, soot, etc. Reaction interactions and competitions were emphasized depending on gas composition and temperature. Besides the oxidation reactions which are classically dominant in a lean feed, the dependency of NOx storage on NO_2 production and its inhibition due to CO oxidation by NO_2 at low temperature was highlighted. CO_2 produced during HC oxidation appeared to compete with NOx for sorption on barium sites. In a rich feed several reactions took place to convert pollutants: NOx reduction by H_2 and CO, the possible formation of NH_3, steam reforming of unburned hydrocarbons.

The few tests conducted on soot loaded samples so far gave quite interesting results about the significant interaction between soot oxidation and catalytic reactions, such as soot oxidation by NO_2 inducing a slower NOx storage rate. Further results are needed to complete our global understanding of the 4WCC behavior for a better soot and NOx control on diesel engines. To perform this next study, the experimental set-up will be enhanced by inserting additional thermocouples in the monolith sample so as to get more precise reaction light-off temperatures and improve the interpretation of the interrelationship between the different simultaneously occurring reaction and storage steps, such as: does the CO_2 released during soot oxidation compete with NOx storage? Does the released NO_2 oxidize soot during rich pulses? In which conditions is there continuous soot oxidation? An engine test bench study is necessary to study the 4WCC behavior while it is loading and find in which conditions the particulate filter is continuously regenerating. Furthermore, a thorough analysis of soot would allow us to correlate their structure and composition to their kinetic reactivity (Huguet et al. [22]).

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