From the powder to the honeycomb. A comparative study of the NSRefficiency and selectivity over Pt–CeZr based active phase

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L. Masdrag[1], X. Courtois*[1], F. Can[1], B. Cartoixa[2], S. Raux[3], A. Frobert[3], D. Duprez[1]

1: Institut de Chimie des Milieux et des Matériaux de Poitiers (IC2MP), UMR 7285 CNRS-Université de Poitiers, Bât.B27, 4 rue Michel Brunet, TSA 51106, 86073 Poitiers Cedex 9
2: CTI, 382 avenue du Moulinas, La Resclause, 30340 Salindres
3: IFPEN, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize

(*) corresponding author: xavier.courtois@univ-poitiers.fr

Abstract

The efficiency and the selectivity of a model platinum based catalyst supported on a modified ceria-zirconia oxide was evaluated in the NOx storage-reduction (NSR) process at four catalytic scales: powder, (0.5”x1.5”) flow-through monolith (FTM) system, small size (1”x2”) and full size (5.66”x10”) catalysed Diesel Particulate Filter (DPF).

The washcoating of the active phase over FTM affects both the NOx storage properties and the NOx reduction step. The reduction step efficiency is especially decreased at low temperatures. It is associated with an incomplete regeneration of the storage sites and with a strong NOx desorption peak during the rich pulses of the NSR process for the FTM supported system. The NOx reduction selectivity is also strongly affected by the upscale, with an important N_2O selectivity detected over FTM. The recorded NOx profiles during NSR cycles indicate a probable diffusion limitation. However, same trends were observed for both powder and FTM systems concerning the effect of the reductant mixture, for both NSR efficiency and N-compounds selectivity.

After incorporation of the active phase in the porosity of the DPF, a sharp drop in NOx storage properties and subsequently in NSR efficiency are observed. Supplementary tests suggest that the diffusion from the platinum oxidizing sites to the storage sites is again very affected by the upscale. Finally, the engine bench tests confirm the low DeNOx activity of the DPF system.

Keywords: NSR; LNT; NOx, ceria-zironia; honeycomb; washcoat; DPF

1 Introduction

Regulations of passenger car pollutant emissions become stricter and stricter. Particularly, NOx emission from exhaust gas of Diesel and lean-burn engines is problematic and a specific catalytic process appears necessary to reach the new standards. One possible way to reduce NOx emissions in excess of oxygen is the use of a NOx storage reduction (NSR) catalyst [1]. It works mainly in lean condition. NOx are firstly oxidized on precious metals and then stored on basic compounds, mainly as nitrates. Periodically, the catalyst is submitted to rich conditions for few seconds so that the stored NOx are reduced into N_2 on the precious metals. Unfortunately, the process can be not fully selective into N_2. In fact, an incomplete reduction may be observed, leading to the formation of N_2O, a powerful greenhouse gas. In addition, an excessive reduction level can also be obtained, with emission of NH_3. Both N_2O and NH_3 emission during the NSR process must be obviously proscribed.

Depending on the reductant agent, its concentration and the duration of the rich excursion, both NH_3 and N_2O can be observed during the NOx reduction [2-7]. Ammonia formation is mainly favored when H_2 is used as reductant [8,9], whereas N_2O is rather obtained with CO as reductant [4,10]. In fact, on-board, the reductant is initially coming from the gasoline/Diesel fuel and the NSR catalyst is submitted to a mixture of hydrocarbons, CO and H_2 in various amounts. In previous studies [11,12], we have demonstrated that using complex rich and lean mixtures, the N_2O emission is mainly driven by H_2 at 200 °C, and by C_3H_6 at 300 °C. Unexpectedly, a large part of the N_2O emission at 300 °C was attributable to a NOx reduction occurring during the lean phases carried out with traces of reductant. Ammonia emission is related to the presence of residual hydrogen, whatever the introduced reductant. However, the ammonia selectivity is dramatically lowered since the catalyst exhibits high redox behavior brought by ceria based oxide for instance [13].

These previous studies were carried out using powders of platinum based catalysts. Nevertheless, the implementation of powdered catalysts in exhaust pipes requires the use of suitable support, such as honeycomb monoliths. It induces specific behaviors which are supposed to influence the catalytic activity, as mass transfers [14]. The objective of the current work is to study the influence of the catalyst shape on the NOx conversion and selectivity. With this aim, the same platinum (2.12 %) / ceria-zirconia based oxide catalyst was used as powder, or washcoated on a (0.5”x1.5”) flow-through ceramic monolith (FTM) system, with a special attention to the N_2O selectivity in regards on the nature of the reductant agents (C_3H_6, CO and H_2) composing the gas feed. The active phase was also introduced into the porosity of a Diesel Particulate Filter (DPF) substrate with the aim to have a DPF+DeNOx coupled system. Firstly, the catalyst was introduced in the porosity of a 1x2 inches silicon carbide (SiC) Diesel particulate filter (DPF) for NSR studies at a laboratory scale. Finally, the active phase was introduced in the porosity of a full size 5.66x10 inches DPF for tests with a four cylinder diesel engine.

2 Experimental

2.1 Catalyst formulation and characterization

The support used in this work is a ceria-zirconia based oxide provided by Solvay. It is denoted

CZ in this study. Platinum (2.12wt%) was impregnated at pH=10 using a $Pt(NH_3)_2(NO_2)_2$ aqueous solution. After drying, the catalyst was pre-treated at 500°C for 4h under synthetic air in order to stabilize Pt before the final hydrothermal treatment at 700°C for 25h (synthetic air and 10% H_2O).

Catalyst as powder was characterized by means of nitrogen adsorption-desorption isotherms, XRD, H_2 chemisorption, H_2-TPR and NOx storage capacity measurements as previously reported in [12]. The obtained catalyst is noted Pt/CZ and exhibits BET specific surface area of 82 $m^2.g^{-1}$ with a platinum dispersion of about 16%.

The upscale to a flow-through monolith (FTM) honeycomb and DPF cylindrical monolith was performed by the CTI Company. The catalyst was washcoated over a 0.5x1.5 inches cordierite honeycomb (400 cpsi) with a total loading of 150 g/L including 33% boehmite. It was also introduced into the porosity of a DPF (SiC, 300 cpsi, initial porosity and pore size of 45% and 15 µm, respectively). The obtained loading was 120 g/L, including 10% boehmite. The corresponding platinum loading is rather low compared with conventional NSR catalysts, at 60 g/ft^3. Two sizes were manufactured: a 1 x 2 inches DPF (denoted small size) for tests with a synthetic gas bench, and a 5.66x10 inches DPF (full size) for tests with an engine bench. The catalyzed DPF were stabilized at 700°C for 25h under 80% N_2 + 10% O_2 + 10% H_2O.

2.2 NOx storage capacity measurements

The NOx storage measurements were performed at 200, 300 and 400°C under 500ppm NO, 10% O_2, 10% H_2O, 10% CO_2 and N_2 after a pretreatment at the same temperatures under a rich mixture reported in Table 1. The gas analysis was performed by a Multigas MKS 2030 analyzer (FTIR). The NOx storage capacity (NSC) was then estimated by the integration of the recorded profile for the first 60 seconds, equal to the lean periods of the NSR test in cycling conditions (section 2.3). The NOx storage properties of the 1" x 2" DPF system were performed during laboratory tests using the lean mixture reported in Table 1, *i.e.* in presence of traces of reductants. The NSC is expressed either as the percentage of the stored NOx in 60s (for powder, taking into accounts that 99.2 µmol NOx per gram of catalyst were injected in 60 s) or in mg_{NOx}/L_{cata} (for monolith supported catalysts).

In addition, long time storages, which are not representative of the real-life NSR process, were also performed to access the oxidation activity estimated by the NO_2/NOx ratio (%) at saturation.

2.3 NOx storage reduction (NSR) experiments

The laboratory NSR tests were performed over powdered and FTM honeycomb samples, in cycling condition by alternatively switching between lean (60s) and rich (4s) conditions using electro-valves. The lean and rich gas compositions are described in Table 1. Most gases (NO, NO_2, N_2O, NH_3, CO, CO_2, C_3H_6 …) were analyzed using a Multigas FTIR detector (MKS 2030), except H_2 which was analyzed by mass spectrometry. NOx reduction into N_2 is calculated assuming no other N-compounds than NO, NO_2, N_2O and NH_3, neither HNCO which was never detected. For each tested temperature (200, 300 and 400°C), the activity of the catalyst was followed until stabilization and calculations were done taking into account ten cycles after stabilization. Supplementary tests were carried out with a simplified gas mixture, i.e. with only one reducing compound (C_3H_6 or CO or H_2), but keeping the same redox

equivalence ratio as used with the complete gas mixture (Table 1). The equivalence ratio is calculated using equation (1), and corresponds to 0.017 and 3.35 for the lean and the rich gas mixture, respectively.

$$\text{equivalence ratio} = (9*[C_3H_6]+[CO]+[H_2]) / ([NO]+2[O_2]) \quad (1)$$

Similar tests were also performed with the DPF system (1 x 2 inches). Note that due to the use of various catalytic apparatus for the different catalyst scales, tests were not performed exactly with the same (flow rate/active phase weight) ratio. The corresponding conditions are reported in Table 2. Very similar ratio was used for powder or DPF, whereas it is significantly lower with honeycomb. In addition, note that for powder and DPF, the gas flow passes through the catalyst, whereas the gas mixture licks the catalytic bed using the FTM honeycomb.

Finally, a full size DPF (5.66" x 10") was also coated in order to evaluate the catalyst behavior using an engine bench equipped with a Diesel common rail four cylinder 2.2 L engine (Euro 4 specification). Three consecutive cycles alternating rich and lean gas composition were imposed to assess the NOx storage capacity and the NOx reduction efficiency at 330 and 405°C. Details about the engine bench equipment and procedure are available in the Supplementary Material file.

Table 1: rich and lean gas compositions used for the NOx conversion test (60s lean/4s rich). The equivalence ratio is constant at 0.017 at 3.35 in lean and rich gas mixture, respectively.

Gas	C_3H_6	CO	H_2	NO	O_2	CO_2	H_2O	N_2
Lean mixture (60s)	300 ppm	500 ppm	167 ppm	500 ppm	10 %	10 %	10 %	balance
Rich mixture (4s)								
C_3H_6+CO+H_2, denoted as « full gas »	9000 ppm	4 %	1,33 %	100 ppm	2 %	10 %	10 %	balance
C_3H_6+H_2	9000 ppm		5,33 %	100 ppm	2 %	10 %	10 %	balance
CO+H_2		6 %	7,33 %	100 ppm	2 %	10 %	10 %	balance
H_2			13,4 %	100 ppm	2 %	10 %	10 %	balance

Table 2: laboratory catalytic tests: gas flow/catalyst weight conditions.

	Active phase (mg)	Total flow rate ($L.h^{-1}$)	Space velocity (h^{-1})	(Flow rate /active phase weight) ratio ($L.h^{-1}.g^{-1}$)
powder	70	20	200,000	285
FTM Honeycomb (0.5"x1.5")	480	84	17,500	170
DPF small size (1"x 2")	2,780	860	35,000	310

3 Results and discussion

3.1. Powder/ FTM honeycomb comparison

In a first part, the NOx storage and NOx conversion behaviors are presented and discussed. NSR tests were performed using the "full gas" rich mixture (Table 1). The selectivity of the NOx reduction is thereafter discussed in section 3.1.2. Various rich mixtures were then evaluated.

3.1.1. NOx storage and NOx conversion behaviors

The results obtained on powdered Pt/CZ are detailed in [12]. For further comparisons, the percentage of stored NOx in 60 s (duration of the lean period of the cycled NSR test) and NSR behaviors obtained with powder using the "full gas" rich mixture (Table 1) are summarized in Figure 1A. The NOx storage capacity is rather limited since less than half of the introduced NOx for the first 60s are trapped (41-48%). The maximum NOx storage rate is observed at 300°C (Figure 1A). Note that the NO oxidation rate, estimated by the NO_2/NOx ratio after saturation, also exhibits a maximum at 300°C, at 64%, and then decreases to 54% at 400°C due to the thermodynamic limitation of the NO + ½ O_2 = NO_2 reaction at this temperature. Long time storages indicate that the NOx storage at high temperature is rather limited by a lack of basic sites able to store NOx.

NOx conversion obtained in cycled NSR test also exhibits a maximum efficiency at 300°C, in accordance with the higher amount of stored NOx after 60s at this temperature. In fact, the observed NOx conversions are quite close to the percentages of stored NOx for the three studied temperatures. This indicates that the NOx storage step is the rate determining step, in opposition with previous results obtained with less complex mixtures [15]. At 300°C, the NOx conversion is slightly higher than the NOx storage rate. This observation can be attributed to a partial NOx reduction during the lean phases including traces of reductants, as previously demonstrated in [12].

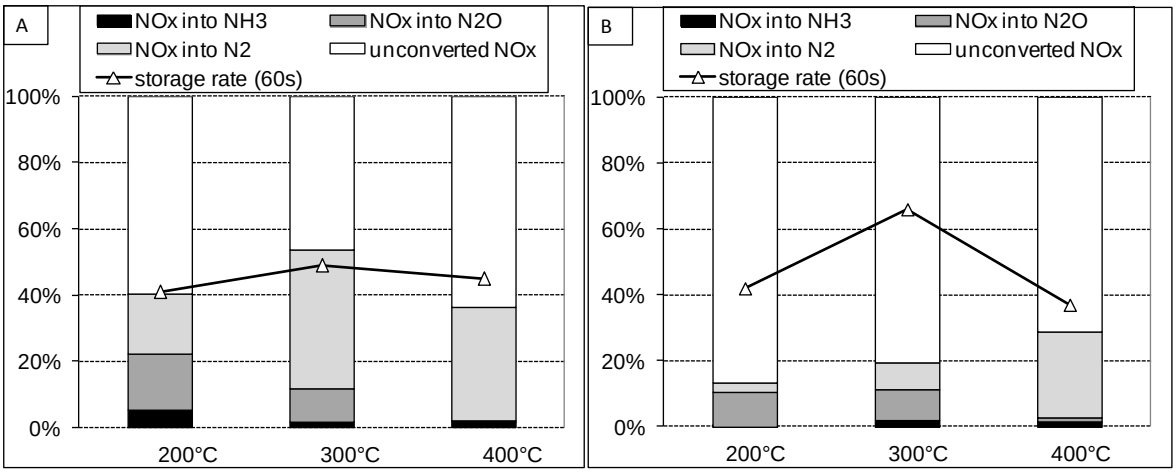

Figure 1: Percentage of stored NOx in 60s (△) and NOx storage/reduction efficiency in cycled condition at 200, 300 and 400°C with mixtures depicted in Table 1 (full gas) for Pt/CZ catalyst used as powder (A) and honeycomb (B).

Figure 1B reports the results obtained with the impregnated FTM honeycomb with the same gas mixtures, but with a lower "flow rate /active phase weight" ratio (Table 2). The percentages

of stored NOx for 60s still exhibits a maximum at 300°C, which is much more marked than with powder. Note that very similar storage rates are measured at 200 and 400°C for both systems (*i.e* powder and honeycomb) despite a lower "flow rate /active phase weight" ratio for the honeycomb sample. In fact, compared with the powder, a lower NO oxidation activity is observed over the honeycomb, especially for low temperatures. The outlet NO_2/NOx ratio measured at saturation is 46% and 28% lower over the honeycomb than with the powder at 200 and 300°C, respectively (corresponding to NO_2/NOx ratios of 22% and 46%, respectively). This ratio is similar for both catalysts at 400°C, close to the thermodynamic equilibrium at this temperature. This result seems to indicate that the apparent redox behavior of the catalyst is affected by the upscale from the powder to the honeycomb despite a lower "flow rate /active phase weight" ratio. However, two parameters may intervene to explain this activity loss: (i) the gas flow passes through the powder, whereas the gas mixture licks the catalytic bed using honeycomb, and (ii) a partial covering of the active phase is possible due to the use of boehmite as binder (33 wt% of the loading for the FTM honeycomb).
Figure 1 also shows that the NOx conversions obtained during the NSR test over the honeycomb supported catalyst are significantly lower compared with the storage efficiencies, especially at 200 and 300°C. Only half of the possibly stored NOx appears to be reduced in cycled condition for these temperatures. Then, in opposition with tests performed with powder, the reducing phase clearly appears to be the limiting step of the NSR process over the FTM honeycomb, in accordance with the increase of the NOx conversion with temperature, whereas a maximum is observed at 300°C using the powder.

In order to have a better understanding of the large differences observed on honeycomb between the storage and the reduction rates at low temperature (i.e. 200 and 300°C), information are obtained from the NOx profiles recorded during the NSR cycles. For instance, a comparison of the NOx profiles recorded at 300°C with the powdered and the honeycomb supported catalysts is depicted in Figure 2. Indeed, the NOx profiles corresponding to the lean periods exhibit higher concentrations on honeycomb compared with the powder, whereas the NOx storage tests at 300°C reveal higher NSC (in % of stored NOx for the first 60s) for the honeycomb (Figure 1). It indicates that, cycles after cycles, some storage sites are not regenerated during the rich periods and become unavailable for the subsequent lean storage phase. This observation indicates a probable diffusion limitation.

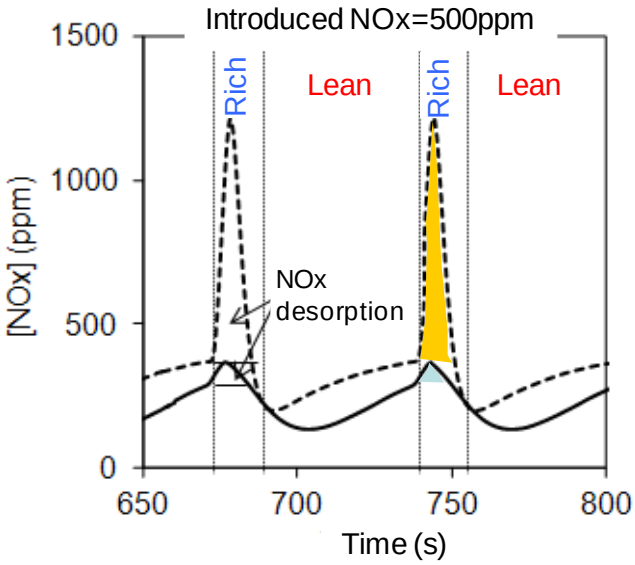

Figure 2: NOx concentration profiles recorded during the NSR tests at 300°C over Pt/CZ used as powder (—) or honeycomb (---).

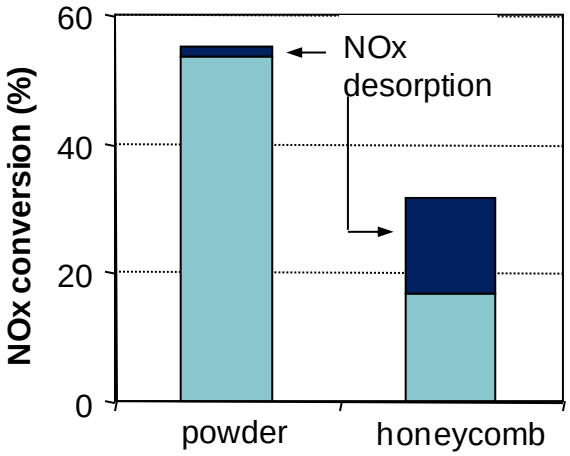

Figure 3: Comparison between NOx conversion and NOx desorption during the rich pulses at 300°C over powder or honeycomb.

In addition, Figure 2 also shows a strong NOx desorption peak during the rich pulses of the NSR test for the honeycomb system. Note that (i) rich pulses appear longer than 4s on Figure 2 due to the unavoidable mix between rich and lean gas mixtures, mainly due to the IR cell volume; (ii) flow rate /active phase weight ratio differs for the two samples. However, the integration of the desorption peaks indicates that, over honeycomb, there is as much converted NOx as desorbed (and unconverted) NOx over honeycomb (Figure 3). This NOx desorption is mainly related with a NO release. On the contrary, on powder, the amount of desorbed NOx corresponds to only 3% of the converted NOx, as illustrated in Figure 3. However, the sum of the NOx conversion and desorption is significantly lower over honeycomb compared with powder, in accordance with the fact that the percentage of NOx storage during the lean periods of the NSR cycles is in fact lower over the honeycomb than over the powdered catalyst.
Finally, the NOx conversions in NSR cycles are significantly lower at low temperature over

honeycomb than using the powder because the honeycomb supported catalyst exhibits both a lower effective NOx storage percentage and a higher NOx desorption without reduction during the rich pulses. Diffusion limitations are supposed to be the major cause of the deactivation.
At 400°C, over the honeycomb supported catalyst, the difference between the percentage of stored NOx and the percentage of reduced NOx is dramatically decreased. Both parameters tend to be similar. In addition, the catalytic behaviors obtained over powder and honeycomb are comparable at this temperature (Figure 1). This indicates that the diffusion phenomena are no more the limiting parameter at this temperature, and the NOx conversion limitation is then attributable to a lack of strong basic sites for both catalysts.

3.1.2. N-compounds selectivity

As previously mentioned, the powdered Pt/CZ catalyst behavior toward N_2O is fully detailed in previous works [11,12]. Figure 1 recalls that using complex mixtures as described in Table 1, the NOx reduction is not fully selective into nitrogen, especially at 200 and 300°C. Few amounts of ammonia are detected, and more problematic, the N_2O selectivity reaches high levels for low temperatures, at 45% at 200°C, and around 20% at 300°C.
Over the FTM honeycomb, in addition to the decrease of the NOx conversion previously discussed, some changes in the NOx reduction selectivity are also observed, especially for low temperatures. Indeed, the N_2O selectivity strongly increases, at 77% and 51 % at 200 and 300°C, respectively. In the same time, the ammonia selectivity decreases (nearly no ammonia is detected at 200°C). Then, the NOx reduction appears to be less deep over honeycomb than over powder. However, it was previously demonstrated that N_2O production is very sensitive to the reductant used [11,12]. In order to check the honeycomb behavior toward different rich mixture compositions, a comparative study was performed at 300°C using the different reduction mixtures detailed in Table 1. The obtained results are reported in Figure 4 and compared to the powdered catalyst behavior.

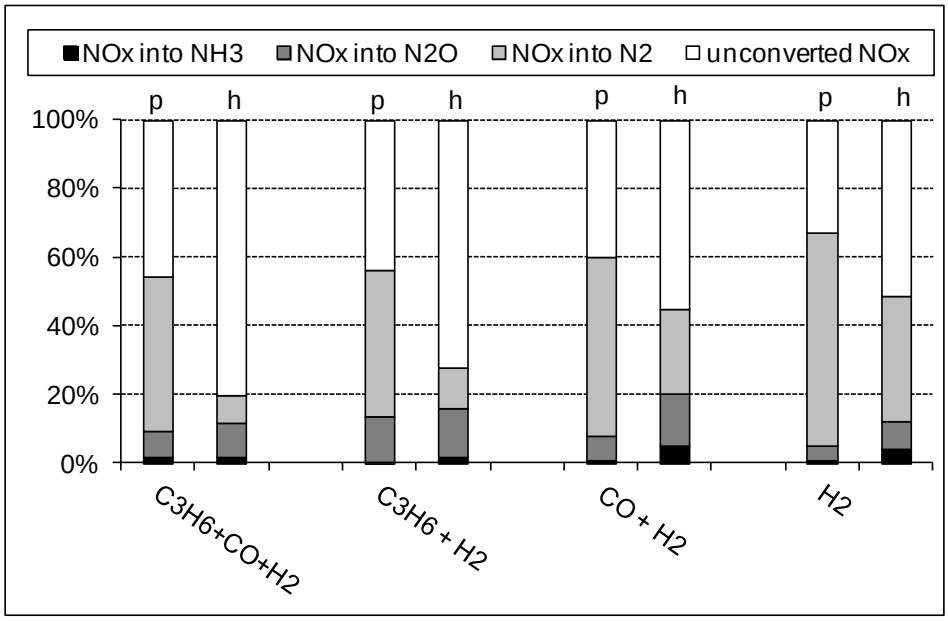

Figure 4: Comparative effect the reductant mixture in the rich pulses at 300°C over powder (p) or honeycomb (h). Detailed gas mixtures are reported in Table 1.

Whatever the reducing mixture used, Figure 4 shows that the NOx conversion is always significantly lower over the honeycomb supported catalyst than using powder, as previously reported in Figure 1. However, the gap between both catalysts is more marked when the rich mixture contains propylene rather than CO-H_2 or H_2 only as reductant.
Compared with the "full gas" mixture (C_3H_6+CO+H_2), the replacement of CO by the same amount of H_2 (C_3H_6+H_2 mixture) does not modify significantly the DeNOx behavior, especially toward the N_2O selectivity. Using powder, the N_2O selectivity reaches 22% and 19%, respectively, whereas over the honeycomb, it reaches 51 % and 50%, respectively. These values are dramatically higher than using only H_2 (3% N_2O selectivity over powder, 17% over honeycomb). Thus, CO is not really implicated into the N_2O selectivity at 300°C, whereas C_3H_6 appears to be the main contributor to the N_2O emission at this temperature, whatever the catalyst form (i.e. powder or honeycomb).
With powder as for honeycomb supported catalyst, an improvement of the NOx conversion is observed using reducing mixture containing CO-H_2 or H_2 only as reductant, with both a higher NOx conversion and a lower N_2O selectivity. The results obtained with these two mixtures are rather similar due to the water gas shift reaction which is favored on Pt/CZ [11], leading to a mix of CO and H_2 whatever the introduced reductant(s), CO-H_2 or H_2 only.
Results reported in Figure 4 are also in accordance with the assumption of a greater diffusion limitation over honeycomb since C_3H_6 appears to be largely responsible for both the activity loss and the increase in N_2O selectivity. Propylene is assumed to have a lower diffusion coefficient than CO or H_2 [16]. As a consequence, the availability of propylene at the active sites should be lower, leading to a limited regeneration of the storage sites, and then to less available storage sites for consecutive cycles. In addition, a lack of reductant at the active site level leads to an enhancement of the N_2O selectivity because of a lower reduction rate for the platinum particles. Indeed, according to Cumaranatunge *et al.*, N_2O is produced at the beginning of the rich periods [17], associated with the reduction of the precious metals.

Finally, similar tendencies are observed with both powder and honeycomb depending on the reducing mixture, with always a better DeNOx efficiency (conversion and selectivity) over powder than over honeycomb. C_3H_6 appears to be the major contributor to the N_2O emission in cycled condition. In order to confirm this observation, supplementary tests were performed with reducing mixtures containing C_3H_6 and H_2 with various concentrations, but always keeping the same equivalence ratio for all measurements: C_3H_6 was varied from 0 to 9000 ppm whereas in the same time, H_2 concentration was varied from 13.4 % to 5.33 %. NOx conversion and N_2O selectivity are reported in Figures 5A and 5B, respectively. When the propylene concentration is increased, both catalysts exhibit a decrease of the NOx conversion associated with an increase of the N_2O selectivity. As previously observed, the NOx conversion is lower using the honeycomb supported catalysts, and the N_2O selectivity is approximately twice compared with the powder (Figure 5B), confirming again that same trends are observed with both powder and honeycomb, C_3H_6 being the main contributor to the N_2O emission in cycled condition.

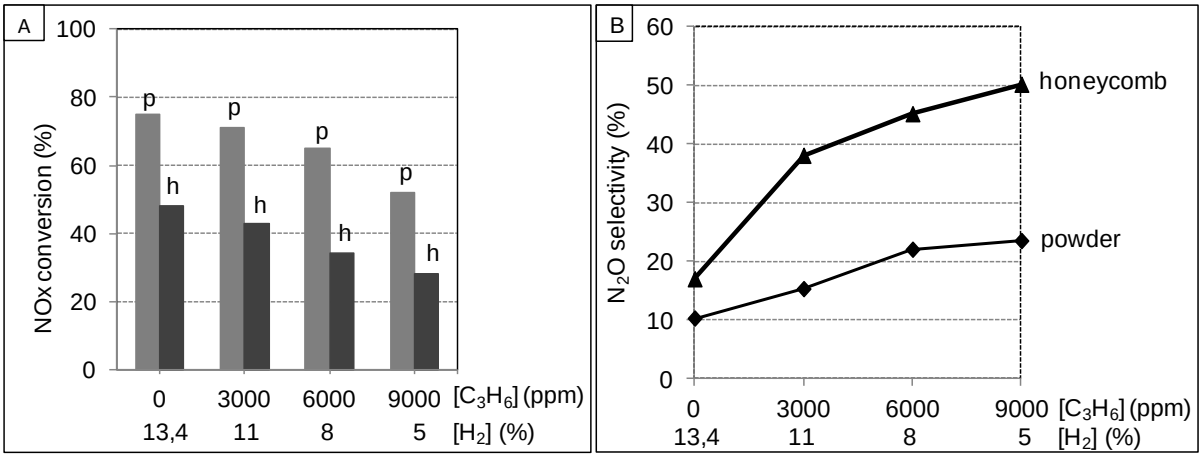

Figure 5: Comparative effect of propylene concentration in rich pulses over powder (p) or honeycomb (h). (A): NOx conversion; (B): N_2O selectivity. Test performed at 300°C with lean mixture depicted in table 1, and only C_3H_6-H_2 as reductant in the rich pulses, from 0 ppm C_3H_6-13.4 % H_2 to 9000 ppm C_3H_6-5.33 % H_2 (same reductant/oxidant equivalence ratio for all measurements).

However, as previously demonstrated [11,12], N_2O can be produced during the NOx storage phases in case of traces of reductants in the lean mixture. For instance, at 300°C, using powder Pt/CZ powder catalyst, it was observed that using lean and rich mixtures containing C_3H_6 (mixed with CO and H_2 or alone), 45% of the N_2O production takes place during the lean periods [11], mainly attributed to the NOx-C_3H_6 reactivity in excess of O_2. Same approach was applied to the honeycomb supported catalyst in order to check the possible N_2O emission during lean pulses. An illustration of the N_2O profiles during a NSR test using the "C_3H_6+H_2" rich mixture is depicted in Figure 6 for both the powdered and the honeycomb supported catalysts.

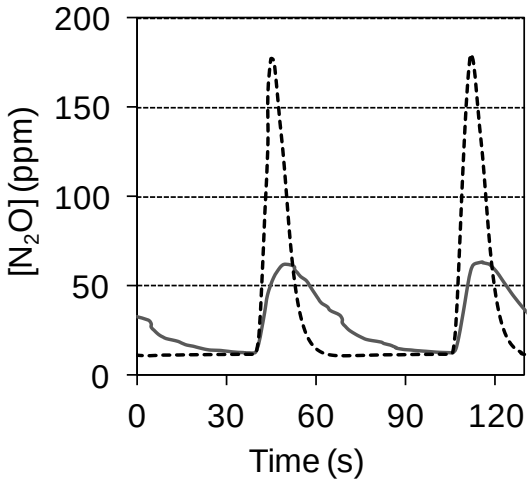

Figure 6: N_2O concentration profiles recorded during the NSR tests at 300°C over Pt/CZ used as powder (—) or honeycomb (---), rich mixture containing 9000 ppm C_3H_6-and 5% H_2.

It appears that the N_2O profiles recorded at 300°C exhibit the same N_2O concentrations at the end of the lean periods for both catalysts. The differences in the N_2O shapes are due to differences in the flow rate through the IR cell (Table 2). Integration of the N_2O profiles gives

similar values, indicating that the distribution of the N_2O emission between the lean and rich phases is not significantly changed by the catalysts shape (powder or honeycomb). In addition, it also indicates that the N_2O yields are in the same order of magnitude with both catalysts. For tests illustrated in Figure 3, the N_2O yield varies from 14% to 16% for the honeycomb supported catalyst, and from 11 to 14 % for the powder. Other illustrations of the N_2O yields are also available in Figures 1 and 4. However, the N_2O selectivity is significantly higher using the honeycomb supported catalyst (Figure 5B) because of lower NOx conversions.
Finally, similar NOx storage percentage were observed with both catalysts, but using a lower (flow rate/active phase weight) ratio for the FTM honeycomb catalyst. Taking into account this point, the lower NOx conversions obtained with the honeycomb is associated with a less deep reduction, with higher N_2O selectivities. However, similar trends are observed for both catalysts toward the rich mixture compositions and toward the participation of the lean periods on the global N_2O emission. A special focus on the reduction steps is detailed in the next section.

3.1.3 Focus on the reduction step

According to Epling *et al.* [18], four main parameters are involved during the rich periods: the nitrate decomposition, the NOx desorption, the NOx reduction and the reduction of the stored oxygen, especially in the case of materials with high oxygen storage capacity (OSC), which is the case of Pt/CZ catalyst. With the aim to obtain an optimal NOx conversion, a balance should be obtained between the decomposition and the reduction rates of the stored NOx species.
Over precious metal based catalysts (Pt and/or Rh supported over BaO/Al_2O_3), Fridell *et al.* [19] reported that the NOx desorption can be attributed to (i) a low reduction rate for the metallic sites compared with the decomposition rate of the stored nitrates; (ii) a NOx desorption from storage sites far from the metallic sites, *i.e.* to diffusion limitations. Finally, the assumptions from these two studies are strongly linked and correlated with our results comparing powdered and FTM honeycomb supported catalysts. Compared with the powdered Pt/CZ catalyst, the reduction rate appears to be significantly lower over the honeycomb due to a large NOx desorption without reduction, as also mentioned in other studies [20,21]. It is also reported that when the temperature is lowered, the rates of nitrate decomposition and subsequent NOx reduction are decreased, but nitrate decomposition is still occurring. On Pt/CZ, this lower NOx conversion over honeycomb is associated with a higher N_2O selectivity. As previously discussed, data recorded in this study are in accordance with a probable diffusion limitation over the honeycomb, in association with a decrease of the apparent redox activity. This should lead to a lower reduction rate for the platinum particles, which induces a limitation in the NOx dissociation. The probability of NO and N interacting is greater than N and N interacting, solely based on the concentrations of the two species on Pt and therefore N_2O can be formed.

Finally, the reduction step over the FTM honeycomb is characterized by a higher N_2O selectivity observed compared with the powder, and also by an important NOx desorption. In order to investigate a possible relationship between these two parameters, supplementary tests were performed with catalysts with various compositions: the metallic phase was varied considering bimetallic Pt-Pd formulations, and another support, based on modified alumina-ceria (AlXCe), was evaluated. On Figure 7 is plotted the N_2O yield depending on the amount of desorbed NOx during the rich pulses of the NSR test performed at 300°C with the “full gas”

mixture.

Figure 7 seems to indicate that the more the NOx desorb, the more N_2O yield is high. Note that this relation is not so evident comparing the catalysts tested as powder (results not shown). However, it also appears on Figure 7 that catalysts supported on the AlXCe support exhibit a lower NOx desorption compared with CZ supported samples. The ceria loading in CZ support is approximately three times higher than in AlXCe support and the oxygen storage capacities (OSC) is known to be improved when cerium is associated with zirconium. As a consequence, considering that the redox support should also be reduced during the rich pulses, oxygen from the support should delay the platinum surface reduction and a part of the introduced reductants are used for this reduction. Although the ceria reduction is an endothermic reaction [22], the oxidation of the introduced reductant is highly exothermic, leading to a globally exothermic process. Then, a high OSC should induce an increase of the temperature at the catalyst due to reaction between the reductant and the stored oxygen. It may increase the reaction rates but also favor the NOx desorption. Unfortunately, there was no possibility to record the temperature change of the catalyst with the apparatus used but it appears from Figure 7 that at 300°C, catalysts with high OSC rather favor the desorption than the reduction rate.

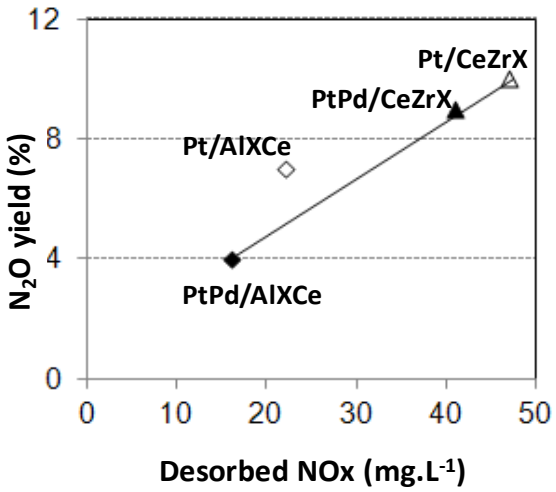

Figure 7: Relationship between, the N_2O yield and the NOx desorption recorded during the rich pulses. NSR tests performed over FTM honeycomb supported catalysts at 300°C using the "full gas" mixture.

3.2 Up-scale to DPF supported catalyst

The integration of the catalytic formulation into the porosity of a SiC DPF was performed by the CTI Company. Firstly, a small size DPF (1"x2") was prepared for test at the laboratory scale with a synthetic gas bench. A full size sample (5.66"x10") was also made for evaluation with an engine bench. Characterization of the DPF by SEM after the introduction of the catalyst shows a good distribution of active phase inside the SiC walls, with no accumulation at the surface of the channels (Figure 8).

3.2.1. (1"x2") DPF

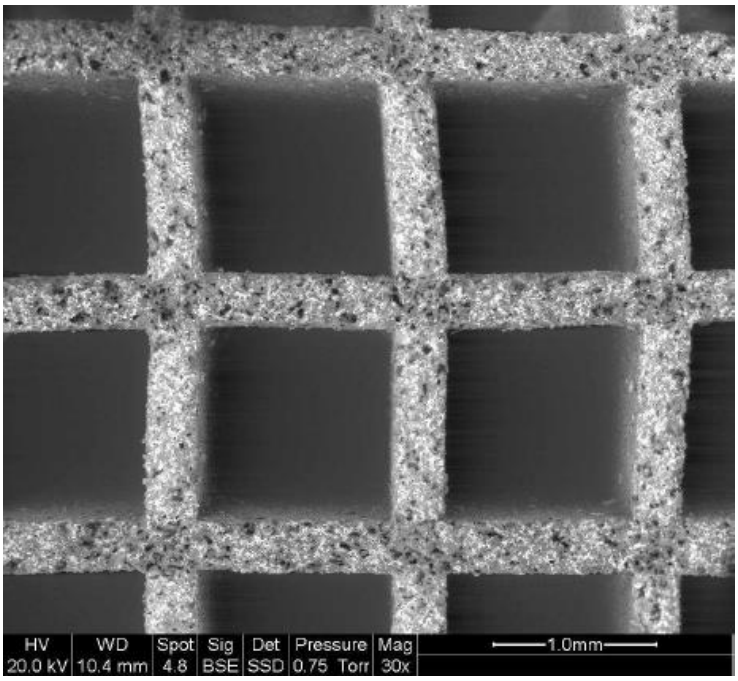

Figure 8: SEM image of a SiC DPF filter after introduction of the Pt/CZ catalyst in the wall porosity.

The small size DPF (1"x2") sample was evaluated in NOx storage capacity test and NSR experiments using a synthetic gas bench. Operating conditions are reported in Tables 1 and 2. Note that the space velocity was 35,000h^{-1} for the DPF sample, leading to a "flow rate /active phase weight" ratio close to that used with the powdered catalyst. Remind that the space velocity was lower for the honeycomb, at 17,500h^{-1}. NOx storage and NSR behaviors obtained between 200 and 400°C with the DPF are shortly compared with the honeycomb in Table 3.

Table 3: comparison of the NOx storage and NSR behaviors of (0.5"x1.5") FTM honeycomb and (1"x 2") DPF (small size) samples.

	FTM honeycomb (0.5"x1.5")			DPF (small size) (1"x 2")		
	200°C	300°C	400°C	200°C	300°C	400°C
NOx storage (mg_{NOx}/L_{cata}) for 60s	118	180	100	50	40	30
NOx conv. (%) in NSR cycles	13	19	28	15	13	5

The DPF sample clearly exhibits a supplementary deterioration of the DeNOx properties compared with the honeycomb supported catalyst, especially due to very low NOx storage capacities. In opposition with powdered and honeycomb supported catalysts, it appears that the NSC decreases with temperature, which could be interpreted as a decrease of the strong basic sites proportion or their accessibility. As a consequence, NOx conversions in cycled condition are limited at a low level (maximum NOx conversion: 15%) and also decrease with temperature.

Interestingly, the NO_2/NOx ratio measured at saturation of the NOx storage tests is not so affected with the up-scale. At 300°C, it reaches 64% using the powder, and 53% for the honeycomb supported catalyst and 48% using the DPF sample.
The N_2O selectivities measured with the small size DPF (1"x2") reach 67% at 200°C and 37% at 300°C. They appear lower than with the honeycomb. It corresponds to similar N_2O yields at 200°C, but the N_2O yield drops from 10% to 5% at 300°C with the scale-up.
In order to have a better understanding of the storage and/or reduction limitation over the DPF sample, additional NOx storage measurements were performed with various gas compositions (Table 4).

Table 4: NOx storage capacity (express as mg_{NO2}/L_{cata}) at 300°C measured over the (1"x 2") DPF (small size) sample depending on the reaction mixture.

Lean Mixture	mg $_{NO2}$ / L $_{cata.}$	NO_2/NOx at saturation
« full gas »	40	48 %
NO_2 (alone)	820	96 %
NO_2 (with reductants)	60	43 %
NO (without reductant)	100	44 %

It is worth noting that introducing only NO_2, the NOx storage capacity is very highly improved, by a factor 20, at 820 mg/L. Since the NO oxidation behavior is practically satisfactory, this result suggests that the diffusion from the oxidizing site, namely platinum particles, to the storage sites is very limited. However, another parameter is clearly identified: when NO_2 is associated with traces of reductants (C_3H_6+CO+H_2) as for the "full gas" mixture, the NSC drops to only 60 mg/L. In parallel, the NO_2/NOx ratio at saturation drops from 96% without any reductants to 43% when NO_2 is associated with reductants. Then, NO_2 is supposed to be partially reduced by traces of reductants, leading to a strong limitation of the NOx storage. When reductants are removed from the initial mixture, *i.e.* only NO and O_2 are introduced, the NSC is approximately doubled compared with the "full gas" mixture, but it remains low compared with measurements performed with only NO_2 (Table 4), confirming the limiting-step of the diffusion over NOx storage properties.

To conclude, the limited catalytic activity of the DPF sample is mainly attributed to very limited NOx storage capacities. Diffusion appears to be partially responsible of this limitation, in association with the presence of reductants which impacts the NO_2 stability at the catalyst level. Indeed, the NSC of this catalyst is very sensitive to the reaction mixture. It is strongly affected by the presence of traces of reductants, especially when NO_2 is used.

3.2.2. (5.66"x10") DPF

Finally, a full size impregnated DPF was tested using an engine bench equipped with a four cylinder Diesel engine (Euro 4 specification).
First, the filtration function of the DPF is not affected by the introduction of the catalyst in the

porosity. No smoke is measured at the DPF outlet. However, this impregnated DPF, based on a standard porosity filter (i.e. 45%), induces a higher back pressure than a standard bare DPF. As a consequence, the range of engine speed is limited. The DeNOx efficiency was measured using two engine conditions reported in section 2.3 and more detailed in the SI file. Three consecutive cycles alternating rich and lean gas composition were imposed to assess the NOx storage capacity and the NOx reduction efficiency. As expected, the NOx storage in real condition is very limited, leading to very low NOx conversions. Compared with a conventional NSR catalyst, the NOx storage capacity is around 8 times lower.

4 Conclusions

The behavior of a Pt-CeZr based catalyst was investigated at different scales in NOx storage reduction process, using suitable tests. From the powder to the (0.5 x 1.5 inches) FTM honeycomb system, the study evidenced a significant decreased of the DeNOx efficiency, associated with (i) a strong NOx desorption phenomenon due to the failover from lean to rich pulses and (ii) a higher N_2O selectivity compared with the powder system. These both behaviors seem to be correlated, and the more the NOx desorb, the more the N_2O yield is high. Diffusion limitations are assumed to be the main cause of the activity loss. However, both powder and honeycomb supported catalysts exhibit same behaviors toward the composition of the rich mixture.

The further upscale, with the integration of the active phase in the porosity of (1 x 2 inches) DPF, leads to a supplementary deactivation of the NSR efficiency, attributed to an important drop of the NOx storage capacity. Again, the results suggest that diffusion from the platinum particles to the storage sites is responsible of this limitation. Finally, engine bench tests confirm the low activity of a (5.66 x 10 inches) DPF system and the need of high porosity filter.

Acknowledgements

The Authors thank the French Ministry of Economy, Finance and Industry for its financial support (FUI contract n° 08 2 90 6669 NOSICA).

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Supplementary Material.

Engine bench equipment and procedure.

The activity of a coated full size DPF (5.66" x 10") was evaluated using an engine bench equipped with a Diesel common rail four cylinder 2.2 L engine (Euro 4 specification). Three consecutive cycles Alternating rich and lean gas composition were imposed to assess the NOx storage capacity and the NOx reduction efficiency. The reductants were introduced through an exhaust port injector located upstream of the turbine. The exhaust pipe was instrumented for temperature and pressure record. Gas analysis were performed using gas analyzers HORIBA MEXA 7100 DEGR (NO, NO_2, CO, CO_2, O_2, HC) and AVL SESAM (MKS FTIR detector), and smoke opacity was measured with an AVL 415S instrument.
Note that the equivalence ratio of the rich phases is somewhat difficult to assess due to injection of liquid HC for the rich pulses. The inlet measurements by lambda sensor and gaseous sampling do not allow a correct analysis, whereas, due to the mix of the rich and lean mixtures, the outlet analysis report equivalence ratios lower than 1.

Two representative conditions of the NEDC cycle were selected: 1500 rpm, 105 N.m (inlet catalyst temperature: 330°C; 160 ppm NOx; SV: 19,000h^{-1}) and 2250 rpm, 114 N.m (inlet catalyst temperature: 405°C; 225 ppm NOx; SV: 34,000h^{-1}).