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Comparison of Vehicle Aged SCR Catalyst on a Particulate Filter (SCRf) with Oven Aged Equivalent

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ABSTRACT

To meet forthcoming Euro 6 Diesel engines NO_x emissions legislation; highly efficient after-treatment systems are required. The use of urea or ammonia SCR is a well-established solution for high NO_x abatement for diesel engines. The combination of a Cu-Zeolite SCR catalyst and a diesel particulate filter has been widely investigated in recent years to respond to the European NO_x emissions regulations especially for those on light-duty vehicles. The after-treatment systems are preferred to be durable during the entirety of vehicle use. Indeed, the SCRf system must withstand the temperature resulting from the active regeneration of the particulate filter continuously. A 160,000 km vehicle aged SCRf catalyst which has endured more than 91 hours at temperatures superior to 600°C during the regeneration of the particulate filter was compared to an SCRf catalyst aged in the laboratory oven for 16 hours at 800°C with 10% H₂O. The vehicle aged SCR has not only been exposed to the hydrothermal ageing generated by the diesel particulate regeneration but also has seen chemical elements from urea decomposition, soot accumulation, engine oil and fuel residues. In this paper, deeper comprehension of the behaviour the SCRf catalyst during vehicle ageing was exposed. It is evident that the loss of NO_x activity is not only due to the regeneration of the particulate filter but also to the possible contamination from the urea injection and the elements present in the diesel fuel and engine oil. XRF results demonstrate that the concentrations of poisoning elements coming from the engine oil or fuel are concentrated mainly at the outlet of vehicle aged SCRf catalyst. Also, results reveal that the poisoning elements have affected the SCR activity of the vehicle aged SCRf catalyst. Finally, it was possible to establish a correlation between a 160,000 km vehicle aged SCRf catalyst and an equivalent SCRf aged for 16 hours at 800°C.

Keywords: SCR; exhaust after-treatment; DPF regeneration; chemical poisoning; NO_x reduction; NH₃ storage capacity.

NOMENCLATURE

CUC	clean up catalyst
DeNO _x	technologies to nox abatement
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
N ₂ O	nitrous oxide
NH ₃ -SCR	ammonia – selective catalytic reduction
NO _x	nitrogen oxides
OEM	original equipment manufacturer

SCR	selective catalytic reduction
SGB	synthetic gas bench
TPD	temperature programmed desorption
PM	particulate matter
XRF	x-ray fluorescence

INTRODUCTION

The removal of NO_x and particulate matter (PM) from the exhaust gas is an important concern for diesel car manufacturers due to the tightening constraints of emission regulations. It can be achieved by combining urea-SCR (selective catalytic reduction) and DPF (diesel particulate filter) in order to reduce the volume of the exhaust line and to be closer to the engine. Among the NH₃ SCR catalysts, Cu-Zeolite systems are considered to be the best option to reduce NO_x emissions at low temperature [1]. Moreover, the OEM (original equipment manufacturer) must ensure the durability of their after-treatment technologies up to at least 160,000 km and 700,000 km for light and heavy-duty vehicles, respectively. In the exhaust line, the SCR catalyst go through numerous constraints such as variable temperature which can be high at times in the case of the SCRf [2-5], water in the feed stream and poisonous compounds [6-8] that lead to alteration of its micro-structure and catalytic performance. The exposure of the zeolite catalyst to high temperatures can deactivate the catalyst by destroying the active sites, by sintering the metal ions and, finally by destroying its structure [9-14]. Schmieg et al. [9] have found a possible correlation between a laboratory and a 135,000 miles vehicle aged SCR catalyst which was exposed to a temperature peak near 700°C for about 200 times during the particulate filter regeneration.

On the other hand, the possible contamination of the SCRf catalyst by the elements coming from the diesel fuel and the diesel engine oil could be relatively high. Recently, Shwan et al. [15] have studied the deactivation of the Fe-zeolite by phosphorous and potassium elements. They found that phosphorous atoms can replace or block the iron active sites present in the zeolite even at low grade (~50ppm). The decrease of SCR activity, mainly at low reaction temperatures, was attributed to an important decrease of the monomeric iron species. They proposed two explanations: (i) the deposition of the phosphates species blocking the porosity and thus rendering the active iron sites inaccessible or (ii) the phosphates species replacing the hydroxyl groups leads to sintering of the iron species. They also observed an increase in the ammonia storage capacity after phosphorous exposure. As far as the durability and the stability of Cu-exchanged zeolite catalyst is concerned, a deep understanding of the effect of the hydrothermal ageing on the SCRf catalyst could help to develop a stable material. Small-pore zeolite-based catalysts such as Cu-SSZ13 are known to exhibit very high NO_x conversion and high hydrothermal stability at high temperature [16].

This work studied a commercial catalyst aged either on an engine bench with real driving conditions to an equivalence of 160,000 km, or in a laboratory oven with ageing of 16 hours at 800°C. The vehicle aged SCRf catalyst has seen numerous active regeneration and soot accumulation compared to an SCR catalyst. Thus, it is important to evaluate the hydrothermal ageing of an SCR catalyst combined with a diesel particulate filter. It is also important to check if the possible elements coming from the engine oil or the fuel can have an impact on the activity of the SCR catalyst. Indeed, XRF technique was employed to evaluate the type of poisoning elements and their concentrations all along the SCRf catalyst and NH₃-TPD technique was used to evaluate the impact of the poisoning on the ammonia

storage capacity of the Cu-zeolite catalyst. Finally, a correlation between the vehicle aged and the oven aged SCR/CUC catalysts is proposed.

EXPERIMENTAL TEST

Engine Bench Test

The diesel exhaust line includes a diesel oxidation catalyst (DOC) placed upstream the particulate filter coated with a selective catalytic reduction catalyst (SCR/CUC) and finally a clean-up catalyst (SCR/CUC) is placed downstream the SCR/CUC catalyst in order to prevent the ammonia slip (Figure 1). Gas composition was checked upstream and downstream of the different parts. Thermocouples were also specifically added to measure the temperature variation of the SCR/CUC catalyst during the engine bench endurance. The soot mass limit (SML) was controlled by the pressure sensors in order to launch the regeneration of the SCR/CUC catalyst. The regeneration of the SCR/CUC catalyst is carried out approximately every 600 km for 20 minutes at 650°C. Taking into account that the full exhaust diesel line was aged for about the equivalent of 160,000 km, the SCR/CUC catalyst was submitted to a temperature of approximately 650°C for over 91 hours due to the successive regenerations.

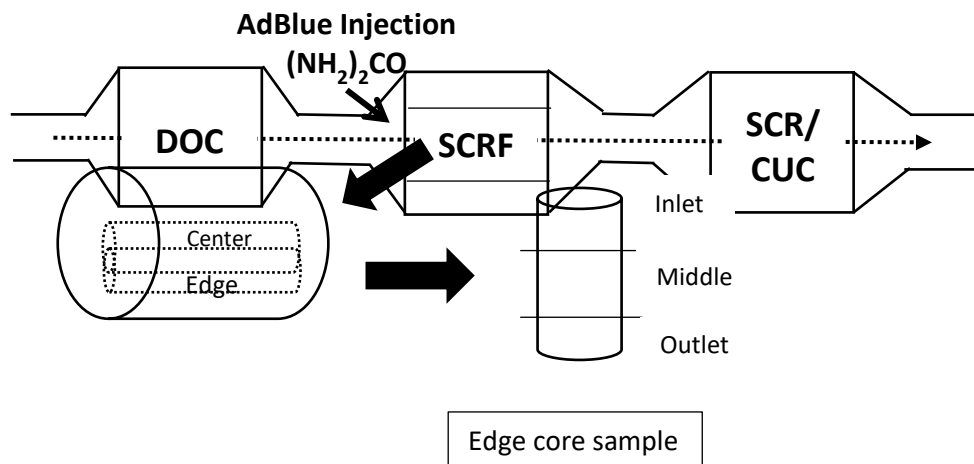


Figure 1. Diesel exhaust after treatment line.

Synthetic Gas Bench Test

To compare the vehicle aged SCR/CUC catalyst and the equivalent SCR/CUC aged in the oven, both catalysts were characterised on a synthetic gas bench. Two core samples of 0.4 L each, one from the centre and one from the edge of the part was cut from the engine size SCR/CUC. The gas concentrations were analysed by a fourier transform infrared spectrometer (multigas MKS 2000 FTIR). The activity of the core samples was investigated with an NH_3/NO_x ratio of 1.5, NO_2/NO_x ratio of 20% in presence of 10% O_2 , and 5% H_2O , balance with N_2 ; the space velocity being of $60,000\text{h}^{-1}$.

Laboratory Reactor Test

The soot is mainly accumulated at the end of the DPF catalyst and when the soot oxidation occurs, it is then the outlet of the part which displays the highest thermal gradient generated

by the soot combustion. Moreover, some chemical elements which can come from the diesel fuel or the diesel engine oil might poison the SCRF catalyst. In order to confirm these assessments, the different SCRF either aged on the vehicle or in the oven were divided into three different parts, inlet, middle and outlet. The full exhaust line, with individual parts aged in the oven, was also characterised for engine bench, with exposure to engine exhaust of a few hours. In order to study the NO_x conversion in a laboratory reactor, the catalytic tests were carried out using 80 mg of SCRF powder with the following gas composition: 1000 ppm of NO and also 1000 ppm of NH₃, 10% H₂O and a VVH of 60,000 h⁻¹. A mass spectrometer (Pfeiffer Vacuum OmniStar) was used to measure the gas concentrations as shown in Figure 2.

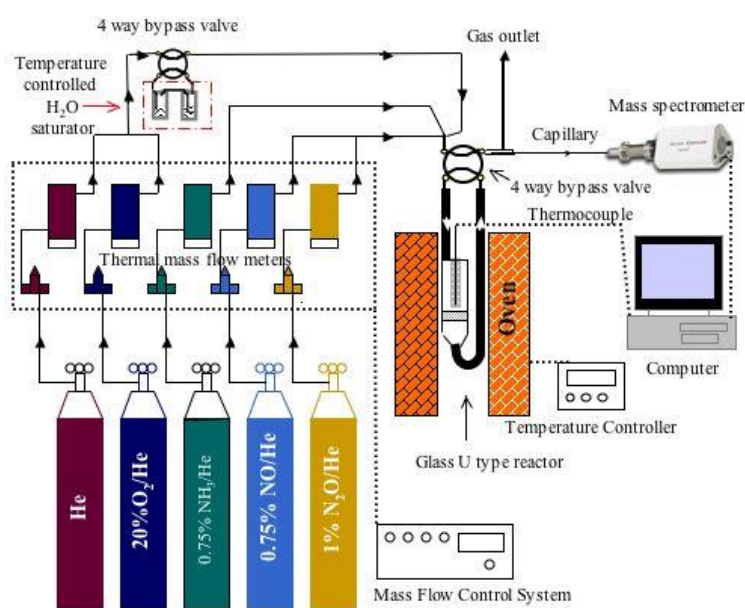


Figure 2. Laboratory reactor test.

Physico-Chemical Characterisations Techniques

The NH₃ storage was characterised by NH₃-TPD for: the SCRF catalyst aged on the vehicle which is an equivalent to 160,000 km (centre and edge of the part) and; oven aged SCRF. The different analyses were made with an Autochem 2910 micromeritics. Before the NH₃ adsorption, the samples were calcined for two hours at 550 °C (10 °C/min) under airflow at 30 cm³/min. The NH₃ adsorption was performed at 100°C for 45min with 5% vol NH₃ in helium with a flow rate of 30 cm³/min followed by two hours under a helium flow at 30 cm³/min to remove NH₃ that was not adsorbed by the catalyst. Finally, the ammonia desorption step occurs from 100 to 600°C using a heating rate of 10°C/min in a helium flow of 30 cm³/min. To determine the poisoning by the engine oil, the fuel or by the possible platinum released by the ageing of the diesel oxidation catalyst (DOC) [10-14, 17-18], different SCRF catalysts were analysed by x-ray fluorescence. The samples were done on pellet which is a mixture of SCRF samples and lithium borate and were analysed by Panalytical Axios advanced apparatus.

RESULTS AND DISCUSSION

DeNO_x performances of SCR catalysts

Synthetic gas bench results

To compare the SCR aged on vehicle and in the oven, both catalysts were characterised on a synthetic gas bench. Two core samples of 0.4 L each, one from the centre and one from the edge of the part were cut from the engine size SCR. It is important to understand the ageing along with SCR catalyst in real-driving ageing conditions.

The activity of the different core samples was evaluated in the gas composition of the NO₂/NO_x ratio of 20% to approach the real conditions supposed to be generated by the diesel oxidation catalyst upstream in the exhaust line. The NO_x efficiency of different SCR core samples is represented in Figure 3. It is clear that there is a difference in the activity between the edge and the centre part of the vehicle aged SCR, especially for the NH₃ storage capacity profile. This observation confirms that under realistic conditions, the effect of the hydrothermal ageing is not the same for all SCR catalyst, contrary to what was observed for laboratory oven aged where the hydrothermal ageing is uniform for all catalyst. Figure 3 also shows that the NO_x efficiencies are very close for all catalysts at different reaction temperatures up to 450°C, where the NH₃ oxidation is much higher for the core taken from the centre of the vehicle aged SCR and the oven aged SCR.

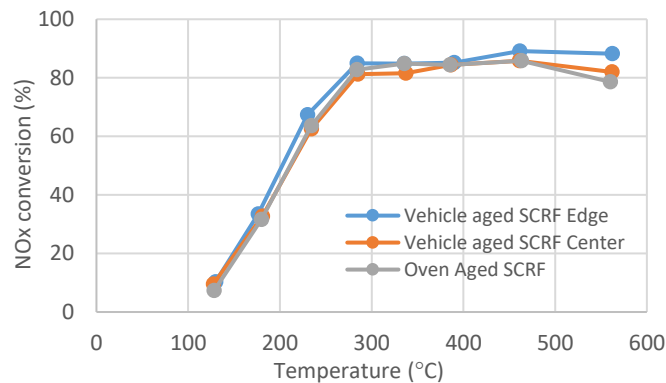


Figure 3. NO_x efficiency with an NH₃/NO_x ratio of 1.5 and NO₂/NO_x of 20% evaluated on the edge and centre cores from the vehicle aged SCR and the oven aged SCR.

Laboratory Reactor Results

In order to investigate the effect of the regeneration and the possibility of poisoning, catalysts were divided into three different parts: inlet, middle and outlet. The performances of the inlet of different SCR catalysts were plotted versus temperature as shown in Figure 4(a). All different SCR catalysts exhibit nearly the same NO_x conversion profiles. The vehicle aged (edge and centre) SCR catalysts have approximately the same NO_x conversion than the oven aged SCR. However, the ammonia oxidation is more elevated for the cores taken from the edge rather than those taken from the centre of the vehicle aged SCR catalyst. The ammonia oxidation impacts strongly on the NO_x conversion at the higher reaction temperatures. The inlet of the edge part of the vehicle aged SCR has probably been impacted by the urea injection. Indeed, as the reducing agent is a urea solution, it is possible

that the products coming from its decomposition or the deposition of urea crystals elements might be responsible for the poisoning of the edge of the part.

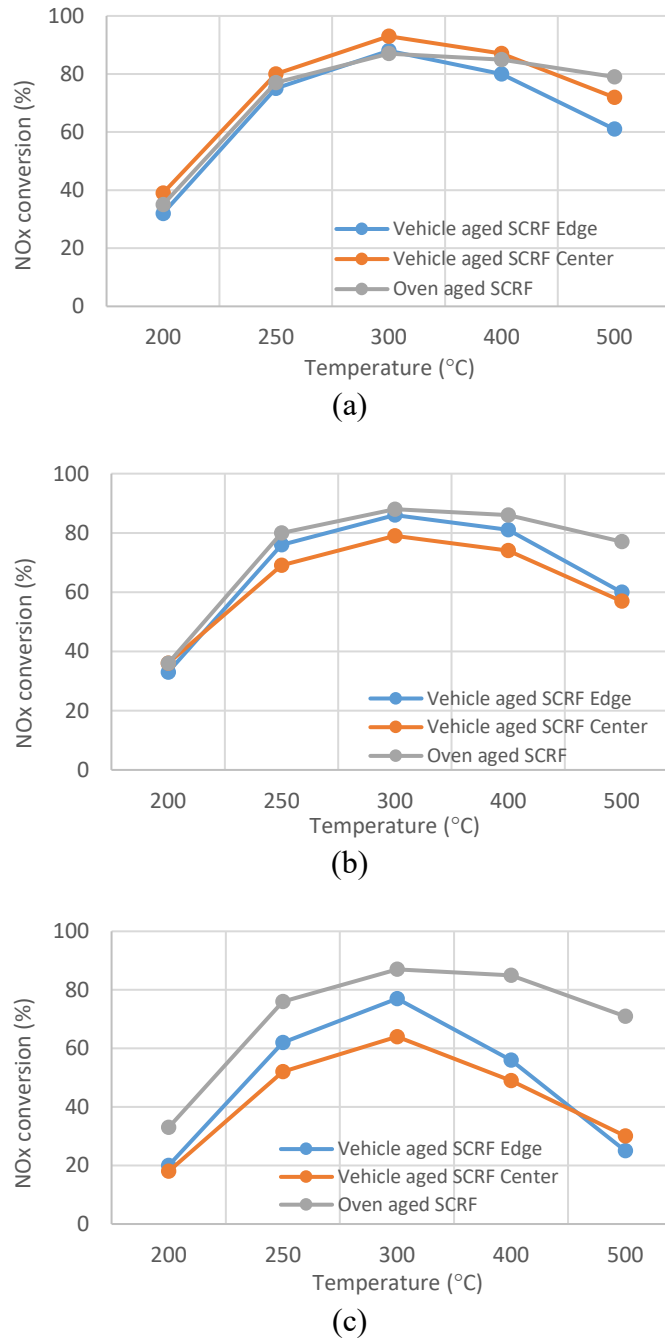


Figure 4. NO_x conversion over the inlet (a), middle (b) and outlet (c) part of different SCR catalysts in the standard NH₃-SCR reaction.

The standard NH₃-SCR activities of the centre part of different SCR catalysts are reported in Figure 4(b). The centre of the part of the vehicle aged SCR catalyst has the lowest NO_x conversion among all. This difference might come from the thermal gradient, the centre of the part being more exposed to elevated temperatures than the edge of the part. In addition, at a high temperature of >400°C, the NH₃ oxidation has a greater impact on NO_x conversion mainly for the SCR catalysts that have seen the engine test bench.

The NO_x conversions of the outlet part of the different aged SCRf catalysts are reported in Figure 4(c). The vehicle aged centre part has also the lowest NO_x conversion. The regeneration (soot oxidation) of the vehicle aged SCRf has had a greater effect on the centre than on its edge. Surprisingly, the different outlet parts, that have seen the engine bench, exhibit a volcano-type curve, typical of a NO_x reduction profile obtained over a catalyst containing copper oxide aggregates. On the other hand, the equivalence oven aged SCRf catalyst has a usual activity profile but with greater ammonia oxidation activity. These observations show that the different SCRf catalysts tested on the engine bench have been poisoned by chemical elements from the diesel engine oil or/and by the diesel fuel. This effect was particularly prominent for the outlet of the SCRf. The hydrothermal sequences, due to the regenerations, are not solely responsible for the ageing of the catalyst in real driving conditions since some chemical poisons (present in both the engine oil and the fuel) agglomerated to the particulate matter (PM) can also impact the performance of SCRf catalyst, especially at the outlet part of SCRf catalyst where the PM loading is the most elevated. Xie et al. [19] found in recent work that phosphorous poisoning is more severe on ammonia and NO oxidation. And also, they have shown that phosphorous poisoning lowers the hydrothermal stability of Cu-Zeolite SCR catalyst.

Physico-chemical Analysis Results

Ammonia-Temperature Programmed Desorption (NH₃-TPD)

The NH₃-TPD was used to evaluate the impact of the hydrothermal ageing on SCRf catalyst. The NH₃-TPD profiles of the inlets as presented in Figure 5 have a similar shape. Nevertheless, the inlet of the edge part of the vehicle aged has the lowest NH₃ desorption among all, whereas the inlet of the centre part, has the highest. This result confirms also that the ageing of an SCRf catalyst in a real driving condition is not homogeneous and the urea injection could have an impact on the inlet of the edge part of SCRf catalyst. On the other hand, the inlet of centre part is not that much affected by the hydrothermal ageing compared to the inlet of the oven aged SCRf catalyst.

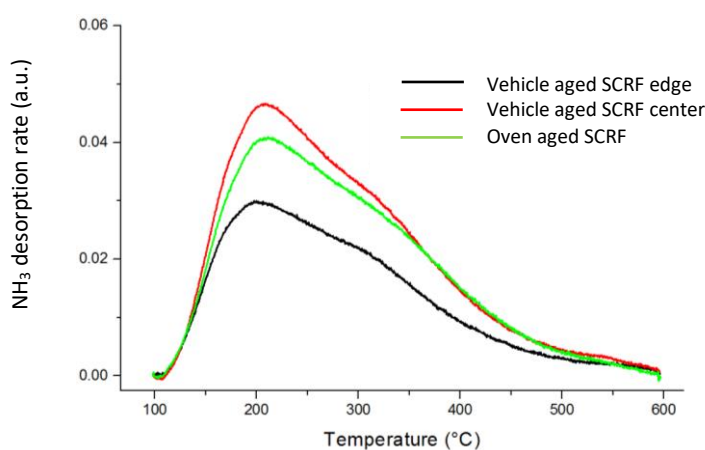


Figure 5. NH₃-TPD curves of the inlet part for different SCRf catalysts.

Nevertheless, the different middle NH₃-TPD curves have the same profile and the total NH₃ desorbed values are very similar (Figure 6). The Middle parts of the SCRf

catalysts whether aged in the oven or aged in real driving condition are only altered by the thermal ageing.

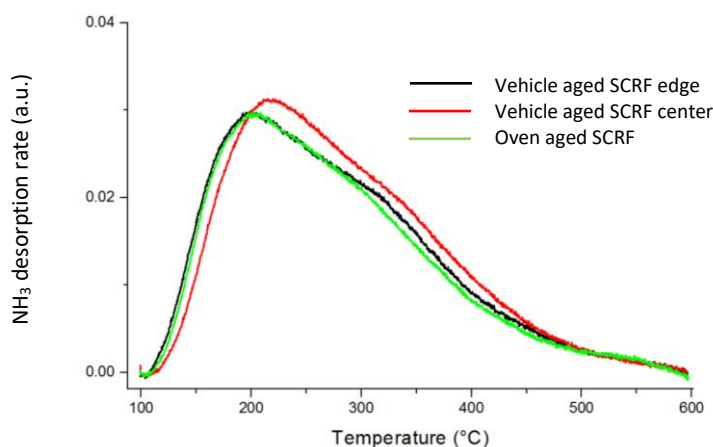


Figure 6. NH₃-TPD curves of the middle part for different SCRf catalysts.

The outlet NH₃-TPD curve profiles of both edge and centre parts of the vehicle aged are different from those of the oven aged SCRf catalyst (Figure 7). From the elemental analysis results, it is seen that the outlet of the different parts of the vehicle aged catalysts (Edge & Centre) are more poisoned than the oven aged catalyst. It could be possible that these chemical poisons could retain ammonia and consequently would increase the quantity of desorbed ammonia in the temperature range of 300 to 400°C, mainly the centre part of the vehicle aged SCRf catalyst. In this case, the value of NH₃ desorption does not fully represent the value of the copper zeolite catalyst. In conclusion, the outlet part of a vehicle aged SCRf catalyst can be poisoned by the elements from the engine oil and/or the fuel. These elements are also responsible of the ageing of the Outlet of SCRf catalyst aged in real driving conditions.

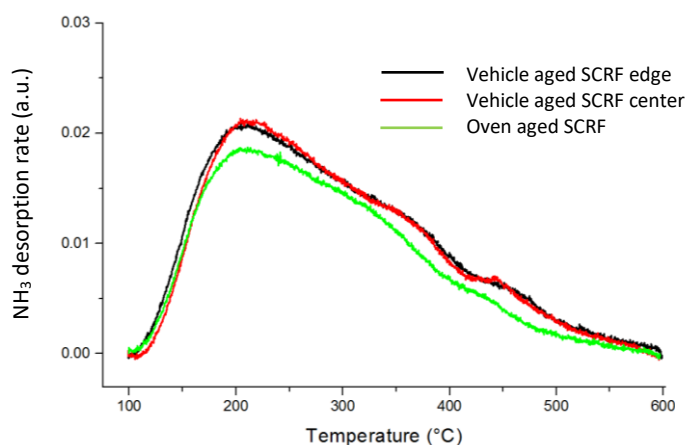
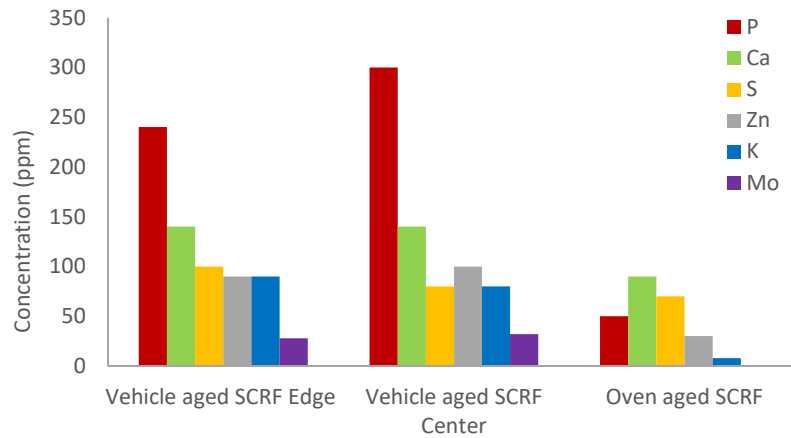


Figure 7. NH₃-TPD curves of the outlet part for different SCRf catalysts.

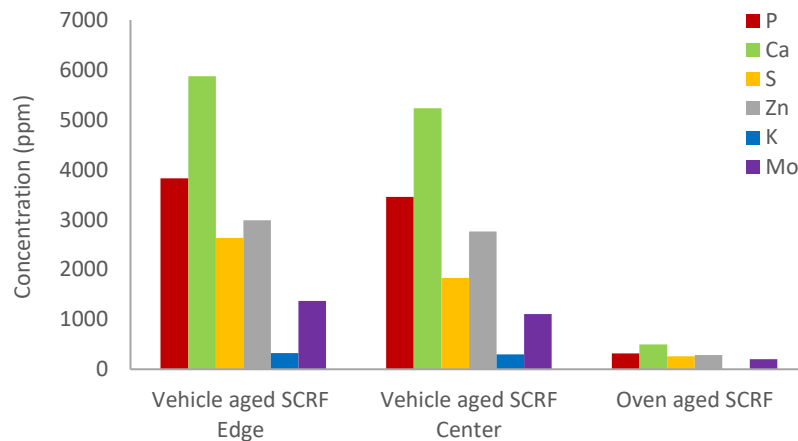
X-ray fluorescence (XRF)

To confirm the contamination of SCRf catalysts, the poison concentrations were analysed, by XRF. The concentration of elements present in the SCRf catalysts after the engine bench

test increases from the inlet to the outlet part as shown in Figure 8(a) and Figure 8(b). The elements which were retained significantly are phosphorus (P), calcium (Ca), sulfur (S), zinc (Zn), potassium (K) and molybdenum (Mo).



(a)



(b)

Figure 8. The concentration of the elements presents in the (a) inlet and; (b) outlet of different SCRf catalysts.

Their concentrations at the inlet of the edge and centre part of vehicle aged SCRf catalyst and the oven aged SCRf catalysts are shown in Figure 8(a). The maximum concentration is about 300 ppm. The phosphorous has the greatest concentration, especially for both parts of the SCRf catalyst aged at real driving conditions, followed by calcium. Both parts have accumulated more chemical elements than the equivalent oven aged SCRf catalyst (less than 100 ppm). The concentrations measured for the equivalence oven aged SCRf correspond to the value limits detected by the apparatus.

The concentrations at the outlet of the different SCRf catalysts are reported in Figure 8(b). The concentration values at the outlet have increased about 8 times more than at the inlet. At the outlet part, the calcium concentration is the highest followed by phosphorous. Other contaminants were also present in high concentrations at the outlet part. The maximum concentrations, for the edge part of the vehicle aged SCRf catalyst, are of about 5900 ppm and 3800 ppm for Ca and P respectively whereas, for the centre part, 5240 ppm of Ca and 3460 ppm of P. However, at the outlet of the equivalent oven aged SCRf, the chemical

poisoning concentrations have also increased to 500 ppm of Ca and 320 ppm of P. Finally, the percentage of chemical poisons is elevated at the outlet part showing that under real driving conditions, they accumulated more elements coming from diesel engine oil or diesel fuel.

In the literature, the contamination by platinum (Pt) at very low concentration (<10ppm) was observed mainly at the inlet part of the SCR catalyst due to the ageing of diesel particulate filter (DPF) or from the ageing of diesel oxidation catalyst (DOC) [9]. But, in our case, only a Pt contamination from the ageing of the DOC can occur. XRF results have shown that there is no contamination by platinum in the different SCRf catalysts. When the vehicle aged SCRf catalyst is divided into different parts, the NO_x conversion profiles do not have the same shape. The ammonia oxidation starts relatively earlier and it is more significant at the outlet where the poisoning of the SCRf catalyst was relatively high. To conclude, the comparison of the NH₃-SCR activity of the different aged catalysts and the XRF results imply that both chemical poisoning and the regeneration of the DPF catalyst play a role in the deactivation of the SCRf catalyst. The volcano type curve of a catalyst containing copper oxide aggregates suggests that phosphorous or calcium elements have changed the nature of copper species. Hans et al [20-21] have observed that after a hydrothermal ageing treatment on Cu-SSZ13 SCR catalyst, especially with a high Si/Al ratio, part of isolated Cu²⁺ ions were transformed to agglomerated Cu_xO and finally, these species might destroy the catalyst structure leading to its complete deactivation. Dahlin et al. [22] have shown that Cu-SSZ13 SCR catalysts are more sensitive to deactivation by sulfur and the SO₂ exposure temperature of 220°C have an important impact on the deactivation of the SCR catalyst. Also, Chen et al [23], have demonstrated that phosphorus accelerates the deactivation of Cu-SSZ13 in the presence of SO₂ at low temperature. They have observed that the deactivation was due to a severe decrease of the Cu²⁺ ions and by a partial coverage of the active sites by phosphate and sulfate species.

Effect of the chemical poisoning

In order to check if some regeneration of the catalyst is achievable, the outlet of the vehicle aged SCRf edge and centre parts were calcined at 750°C for 5 hours. On these solids, the NO_x conversions were measured with a laboratory reactor device. The NO_x conversions before and after calcination are represented in Figure 9. Before calcination, NO_x conversion decreases rapidly for both SCRf parts after 300°C. After the calcination, the SCRf parts have partially recovered their activities. The NO_x conversions start at higher above 250°C and reach a maximum at 400°C. Above this latter temperature, the ammonia oxidation still remains relatively high. According to Shwan et al. [15], the metaphosphates can block or replace the active sites. Also, Xie et al. [18] found that phosphorous tends to interact with Cu sites but also could partially form AlPO₄ phase when inserts into the zeolite framework. They demonstrate also that metaphosphates is the main compounds formed at the surface of phosphorous poisoned catalysts. After calcination at 750°C, the observed improvement in NO_x conversion may suggest that copper species have partially returned to their exchanged position (exchange between P and Cu). To conclude, the calcination step at 750°C can help to recover some NO_x conversion for the SCRf contaminated by engine oil or fuel elements.

In order to verify that the poisoning elements are really at the origin of the increase of the value of the NH₃ desorbed from the outlet of the vehicle aged SCRf centre part, calcination at 750°C for 5 hours was made. The total NH₃ desorption value of this sample was diminished by about 11.2% and the NH₃-TPD profile obtained in Figure 10 is close to the profile of the oven aged SCRf catalyst. However, the calcined catalyst at 750°C was

slightly damaging since the NH_3 desorption from strong acid sites (see Figure 10 at high temperature) had significantly decreased. Finally, the ammonia storage of the vehicle aged centre part may have increased with the effect of phosphorous exposure.

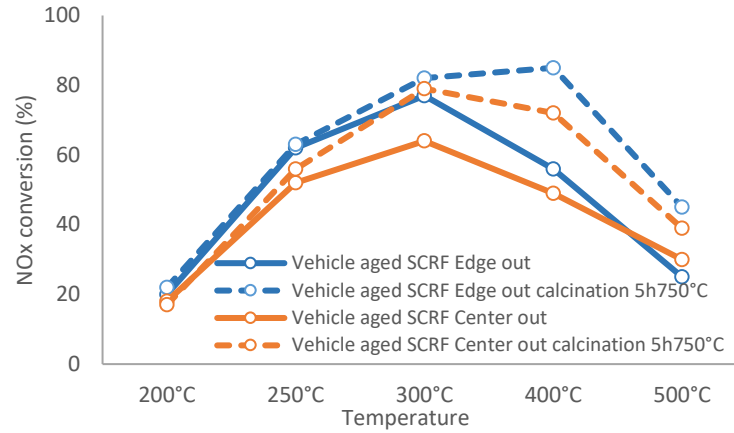


Figure 9. NOx conversion at the standard SCR reaction of 160,000 km vehicle aged SCR for edge and centre parts before and after calcination at 750°C for 5 hours.

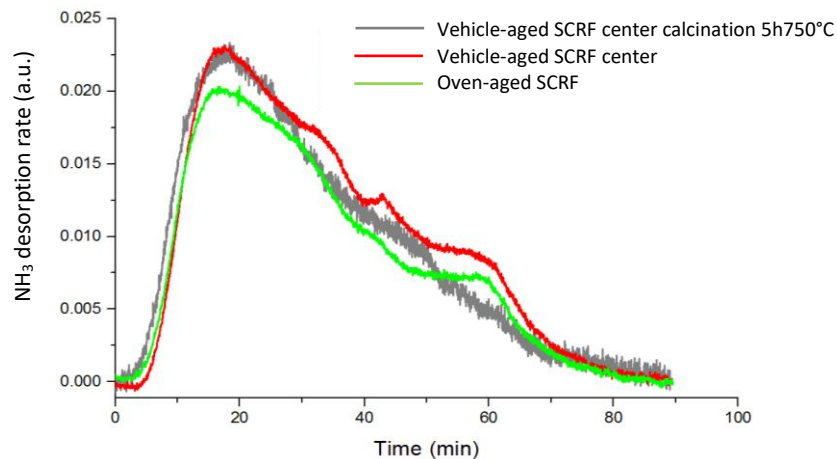


Figure 10. NH_3 -TPD curves of the outlet of vehicle aged centre part before and after calcination.

CONCLUSION

The different results of this work provide a good explanation for the ageing of an SCR catalyst that had accumulated about an equivalent of 160,000 km and was exposed for about 160 times to temperature peaks near 650-700°C for about 20 minutes each during the active regeneration of the particulate filter. It is quite clear that this ageing of the SCR catalyst is not homogeneous along with the catalyst whereas, in a controlled atmosphere oven, the hydrothermal ageing is homogeneous for all SCR catalyst. The vehicle aged SCR catalyst suffered from the impact of the flow distribution of the urea injection at the edge of the part. Furthermore, at the outlet part, damage was observed by the chemical poisoning from both diesel engine oil and diesel fuel by elements including calcium, phosphorous and sulfur. The NOx conversion profiles of the different outlet parts that have been tested in the bench engine

exhibit a volcano-type curve, typical of the NO_x reduction profile obtained over a catalyst containing copper oxide aggregates, with ammonia oxidation very significant at high temperature. After calcination at 750°C for 5 hours, the NO_x conversion of the outlet part of the vehicle aged catalyst was enhanced at 250-400°C temperature range. However, the ammonia oxidation is still significant at above 400°C.

These results might show that the poisoning elements, mainly phosphorous, have replaced or blocked the copper active sites in the structure of the zeolite. After calcination at 750°C, the NH₃ desorption from NH₃-TPD result has decreased by about 11.2%. According to the literature, if the Cu-Zeolite catalyst is poisoned by phosphorous elements, the ammonia storage capacity could increase since the phosphorous species could exchange with the Brønsted acid sites [4]. The NH₃-TPD analyses enable us to confirm that the thermal distribution is not homogeneous for all SCRF catalyst aged in real driving conditions. The active regeneration of the particulate filter is not exclusively responsible for the ageing of the SCRF catalyst. However, both urea injection and chemical deactivation have an impact on the durability of the SCRF catalyst. An equivalent 16 hours at 800°C oven aged SCRF catalyst was also compared with the vehicle aged SCRF catalyst. The NH₃-TPD characterisation and the DeNO_x performance results indicate a good correlation between the oven aged and the vehicle aged SCRF catalyst.

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