

Combination of LNT and SCR for NO_x reduction in passenger car applications

The removal of NO_x and particulate emissions in light-duty diesel vehicles will require the use of aftertreatment methods like Diesel Particulate Filters (DPF) and Selective Catalytic Reduction (SCR) with urea and Lean NO_x Trap (LNT) (Euro 6 and beyond). A new concept is the combination of LNT + SCR, which enables on-board synthesis of ammonia (NH₃), which reacts with NO_x on the SCR catalyst. The main application for this kind system will be lighter passenger cars, where LNTs may be used instead of full urea-SCR system. That particular combinatory system was investigated by developing platinum (Pt) and rhodium (Rh) containing LNTs and SCR catalysts in this study. In the use conditions, the maximum temperature may reach temperatures up to 800 °C and NO_x reduction reactions should proceed without NO₂ assistance in the SCR position after LNT and DPF. PtRh/LNT with the total loadings of 85 g/cft (2.8 g/L) and higher resulted in a high NO_x efficiency above 80–90% with a broad operation window in the laboratory simulations. In the experimental conditions, a higher NH₃ concentration after LNT was essential to simulate well the operation of SCR catalysts. The developed Cu-SCR catalyst showed a high hydrothermal durability up to the ageing temperature of 800 °C and a wide operation window without the NO₂ assistance (NO only in feed). Fe-SCR and V-SCR catalysts were more dependent on NO₂. A studied concept had an air injection after LNT to keep SCR condition always in lean side, where the SCR reaction was promoted by oxygen resulting in high reduction selectivity to nitrogen (N₂) without NH₃ emissions. The simulations in reaction conditions and system design resulted in the proposals for the optimal design and main reaction mechanism in DOC + DPF + LNT + SCR systems.

Key words: NO_x, SCR, LNT, catalysts, diesel

1. Introduction

Fuel consumption (CO₂, price) has become a driving force in engine and vehicle development. A low fuel consumption of diesel engines has resulted in their wide use also in light-duty applications, even if the fuel economy savings are increasing as a function of the weight of vehicle [1]. Efficient and economic NO_x and PM (particulate matter) removal methods are the main challenges of future aftertreatment systems (ATS) for diesel engines. The demand for the simultaneous fuel consumption (CO₂) and emission decrease limits the possibilities to apply many of developed ATSs.

The selective catalytic reduction (SCR) of NO_x by urea on sulfur-tolerant vanadium-SCR or thermally stable zeolite-SCR catalysts has been applied commercially world-widely. Urea is the source for ammonia, which selectively reacts with NO forming nitrogen (N₂) in lean exhaust gases. The SCR reactions are promoted at low temperatures by NO₂ formed on diesel oxidation catalysts (DOC). The exhaust gas recirculation (EGR) in diesel engines decreases NO_x emissions by decreasing combustion temperatures with the costs higher PM emissions. Urea-SCR for light-duty vehicles has limitations in urban driving conditions, where exhaust gas temperatures are below 200 °C [2]. An external heating of the SCR system is a method to maintain conditions in SCR window (> 200 °C) in urban driving or light-off region [3]. Urea/NH₃-SCR is thus a very selective and efficient method but it requires urea solution stored in the vehicle and injection systems. Ammonia formation by urea hydrolysis has also limited rate (evaporation, thermolysis, hydrolysis and deposits) at low temperatures.

Lean NO_x traps (LNT) have been also applied for NO_x removal particularly in light-duty applications, where the required periodic enrichments ($\lambda < 1$) are not able to harm the fuel economy with the same magnitude like in heavy-duty applications. However, the injected fuel forms reductants for

NO_x and no additional reductant tanks are needed. NO_x is first adsorbed in lean on alkali or earth alkaline metals (like barium) as nitrates, which are then reduced to nitrogen during short rich peaks (for 2–5 s at 1–3 min intervals). Precious group metals (PGM, like platinum and rhodium) as active metals are necessary to form efficiently NO₂ in lean and to catalyze NO reduction during rich periods. The NO_x adsorption sites adsorb efficiently also almost all SO_x in exhaust gas, which results in the known S-poisoning (sulfation) of LNT. Sulfur regeneration in longer rich periods above 600 °C regenerates LNT back to active state to adsorb again NO_x. The periodic rich peaks for nitrate and sulfate regeneration increase the fuel consumption up to 10% compared to fully lean diesel combustion. However, the longer rich peaks result in the risk of NH₃ emissions. Control strategies for LNT regeneration have been tailored to avoid these drawbacks but the prevention of harmful side product formation limits also the possible NO_x reduction capacity.

The combinatory properties have been applied in new systems utilizing ammonia, formed on LNT, downstream on SCR catalyst [4–6]. NH₃ formed during rich periods are stored on the SCR catalyst where it subsequently reacts with NO_x passing LNT [6]. Copper (Cu) and iron (Fe) zeolites have been mainly used as SCR catalysts due to high thermal durability requirements (> 700 °C). The high ammonia adsorption capacity is important for the SCR catalyst to maximize the NH₃ buffer for lean NH₃-SCR. The use of reformer unit and by-pass for LNT may enhance the LNT regeneration [7]. Fuel is converted in a reformer to CO and hydrogen which are more efficient, final reductants for NO_x. Periodic enrichments on LNT during the by-pass flow makes possible to have engine independent LNT regeneration (no need for engine throttling to reach λ values below 1 in LNT). A key question is also the order of LNT and DPF in final systems. The regeneration and thermal management

of the upstream unit is much easier than the downstream unit. Because both DPF and LNT units are large (> engine volume), it is difficult to heat up efficiently the either unit in the downstream position.

The LNT based systems are compared by the order of units and LNT regeneration strategies (Fig. 1). LNT may be also in close-coupled position before the diesel particulate filter (DPF) in systems A-C. That set-up improves the low temperature NO_x performance of LNT but limits DPF regeneration. LNT can be coated on DPF structure, which is also a commercial solution and integrates PM filtration and NO_x removal by LNT (8). The LNT regeneration varies and can be based on engine enrichment (fuel), throttling and/or introduced reformer gas.

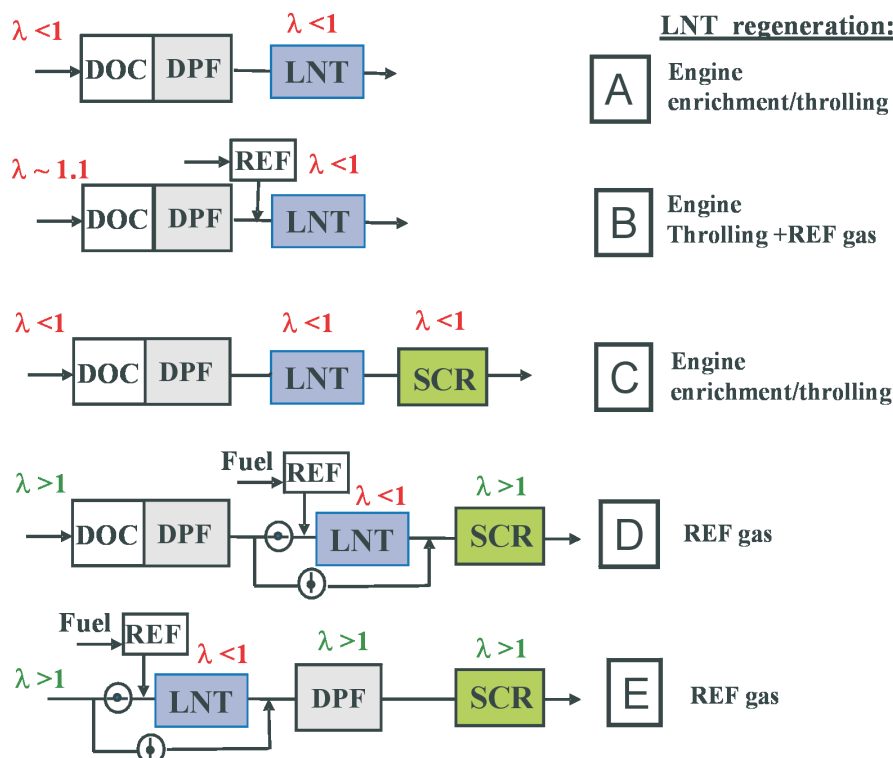


Fig. 1. LNT and LNT + SCR configurations together with DOC + DPF for diesel applications. The shown λ values are related to the LNT regeneration period [9]. REF = Reformer

Carbon (soot) accumulated in DPF is oxidized by short active regeneration periods (1–2 min by the interval of about few hundreds kilometers) at temperatures above 600 °C or passively by the NO₂ assistance in normal driving conditions when the exhaust temperature is above 250 °C. The DPF regeneration (max. 700–800 °C) causes the main thermal durability requirements for LNT and SCR catalysts in these kinds of systems.

In our studies, the development of LNT and SCR catalysts were summarized and optimized for the combinations of LNT and SCR. The reaction studies were a tool to interpret key reaction paths in this combinatory system. The laboratory simulations were targeting to develop the full-scale catalysts to be applied in FEV, VKA and VW in the same work package in this EU funded Powerful project.

2. Experimental and methods

2.1. Catalysts

The LNTs in the experiments were based on metal substrates (500 cpsi, foil thickness 50 μ m), where an alumina based porous coating (about 150 g/L), active metal and NO_x trap compounds were added. Thermally stable rare earth element (REE, e.g. Ce) based oxygen storage and thermal stabilizer material were added as promoters for LNT. Platinum and rhodium were impregnated on catalysts resulting in an even noble metal dispersion on washcoat [10]. Finally, the samples were dried and calcinated at 550 °C in air. The surface area (BET) of LNT coating was between about 130–140 m²/g.

SCR catalysts were also based on metallic substrates (600/500 cpsi, 50 μ m), where SCR catalysts with V, Fe and Cu as active metals were coated (about 170 g/L). The surface area (BET) of Cu and Fe catalysts was about 400–500 m²/g and the BET area of TiO₂ based V-SCR catalyst was about 100 m²/g. The support for Cu and Fe was optimized in the development to reach the target properties (stability and promotion of Cu and Fe, operation window) for NO_x reduction.

The same optimized catalyst compositions were further coated on 500 cpsi metallic substrates and canned for a converter for full-scale engine experiments, where LNT was 1.4 L and SCR catalyst 1.9 L by the volume.

2.2. Laboratory experiments

Simulated gas mixtures were created from bottle gases by mass flow controllers. The catalyst samples were located in metallic or quartz reactors heated by conventional resistance or fast IR furnaces, where the diameter of samples was 14 mm. The compositions of exhaust gases were analyzed by FID (HC), IR (CO, CO₂), chemiluminescence (NO_x, NO, NO₂) and FTIR (e.g. NH₃, N₂O, individual HCs).

The activity of samples were measured in laboratory experiments, where a cycle includes longer lean and short rich periods simulating conditions in LNT and LNT + SCR systems. The lean-rich cycles were repeated for five times with these mixtures (Table 1). The feed gas composition simulated common lean exhaust gas analyzed with diesel engines. The absence of NO₂ simulated the D or F systems (no DOC + DPF before LNT). A light hydrocarbon, propene was the only HC in the feed gas to make the fast variation

of the inlet composition possible in transient condition. The total flow rate was 5.3 L/min.

Table 1. Experimental conditions in laboratory simulations

Mixture	Lean	Rich	Rich + air
NO _x , ppm	500	1500	1065
C ₃ H ₆ , %	0.1	0.1	0.07
CO, %	0.25	5.73	4.07
H ₂ , %	0.08	2.0	1.42
CO ₂ , %	10	10	7.1
H ₂ O, %	10	10	7.1
N ₂	bal.	bal.	bal.
λ	1.41	0.81	1.20
Duration, s	30–120	5–15	5

Hydrothermal ageing was performed parallel for 12 samples using 10% water in air at 700–800 °C for 20 h

The surface area and pore size distribution were detected by the standard BET (Brunauer-Emmet-Teller) method with nitrogen adsorption-desorption isotherms (Sorptomatic 1990). The NH₃ adsorption-desorption was detected by the activity test reactor by adsorbing NH₃ at 200 °C by a step exchange experiment (0 → 500 ppm NH₃ in nitrogen, 42.000 h⁻¹) and then the desorption of NH₃ was detected in the presence of 10% oxygen in nitrogen (Temperature programmed Oxidation (TPO) experiment) by a ramp of 20 °C/min up to 600 °C [11].

2.3. Engine-bench experiments for catalyst development

The engine experiments were conducted with a 1.2L turbocharged diesel engine equipped with DOC+DPF system before LNT+SCR [12]. The experimental conditions were simplified for catalyst development purposes and these experiments were done using all-in-line system together with the assistance of engine management system to make periodic enrichments to purge LNT. After system development, the lean period was 150 s and rich period 15 s with λ of 0.95 in the selected conditions. The emissions after engine, DOC+DPF, LNT and SCR were measured by the sample gas collected to the FTIR analyzer (Gasmet) calibrated for exhaust gas components. λ values and temperatures were detected also in these positions.

3. Results and discussions

3.1. Development of Lean NO_x Traps

NO_x adsorbent containing LNTs have been used also commercially since 1990's, first for lean gasoline and later for diesel passenger car applications. Platinum and rhodium are the most active platinum group metals (PGMs) to form NO₂ in lean phases and reduce NO_x in rich periods. The development was thus focused on PtRh catalyst compositions with higher loadings like above 80 g/cft. Ceria containing oxygen storage compounds (OSC) were used as promoters in the coating to enhance LNT performance.

The rich periods are decreasing fuel economy and their duration should be minimized together with the target NO_x

conversion. The rich periods cause higher CO, HC, PM and ammonia peak concentrations which magnitude can be controlled by adjusting the lean-rich timings. Usually nitrates in LNT are not completely reduced during rich peaks to avoid the flow-through of reductants (CO/HC) and NH₃ emissions but a part of nitrates remains on the catalyst surface. The presence of a SCR catalyst after LNT enables to utilize more complete reduction steps because ammonia will be cut down by SCR.

The development of LNTs was based on periodic lean-rich excursions (L60s/R5s, L = Lean, R = Rich) with hydrothermally aged (700 °C/20 h) samples. Pt as a main catalytic metal together with Rh was needed as well as NO_x adsorbents, oxygen storage compounds to have an active LNT (Fig. 2). The co-operation of Pt, Rh, OSC and NO_x adsorbent were optimized tailoring the relative concentrations, raw materials and preparation methods. The Pt-only LNT showed also quite high NO_x efficiency, being the most active at high temperatures. Even if Rh had minor effect in these laboratory simulations, it has a role in transient enrichment peaks to maintain a high efficiency with a low amount of unwanted side products. It was seen that a high Pt loading resulted in a slight improvement in light-off region below 200 °C, which is important for light-duty driving conditions (9). In addition, the Pt reserve has also a role to improve the durability of LNT in long-term use.

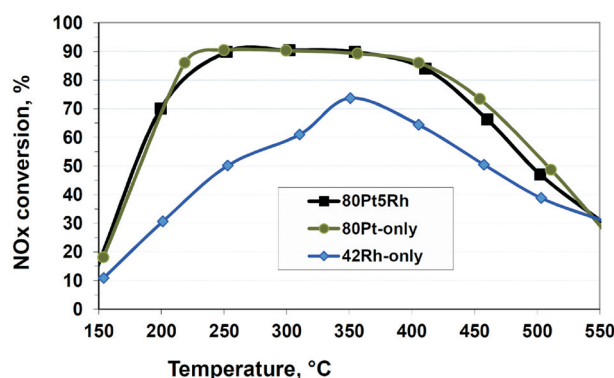


Fig. 2. NO_x efficiency by Pt and Rh loadings (g/cft in the legend) on Ba and rare earth containing LNT by a laboratory simulations (samples hydrothermally aged at 700 °C/20 h, SV 30.000 h⁻¹, timing L60s/R5s)

In our simulations, the oxygen storage compounds (Ceria) were found to promote the total NO_x conversion to nitrogen and NH₃. Therefore, the oxygen storage capacity (OSC) has not a buffering effect like detected in a passive TWC + SCR system in near to stoichiometric mean conditions with lean gasoline application [13]. It is important to use thermally stable, sulfur-resistance oxygen storage compounds in LNTs. The ceria promotion for LNT reactions has been also proposed for Pt catalysts earlier [14].

3.2. Development of SCR catalysts for LNT + SCR concept

Various copper, iron and vanadium based SCR catalysts were screened by NH₃-SCR, LNT + SCR and durability stud-

ies (surface area, ammonia adsorption capacity and activity with NO and NO + NO₂) in the preliminary studies [9]. Because LNT + SCR systems are mainly applied for light-duty applications which test and driving conditions are focused on low temperatures (100–250 °C), the catalyst evaluations were also zoomed in that region. In DOC + DPF + LNT systems, the peak temperatures are above 700 °C on DPF and LNT. The SCR catalyst located after LNT should be active in NO only SCR reactions (standard SCR), because NO₂ formed on DOC or catalyzed DPF have been consumed in LNT. Copper based SCR catalyst showed a wide operation window without NO₂ and also a good low temperature functionality (Fig. 3). The Fe-SCR catalyst was more dependent on the promotion of NO₂ at low temperatures. Therefore, the iron catalyst had a limited low temperature SCR activity in the absence of NO₂. However, NO₂ promotion was clear both on Cu and Fe SCR catalysts aged at 800 °C. It can be assumed that NO₂ promotion has a higher effect on aged than on fresh catalyst, which has more active catalyst surface available. Cu and Fe catalyst showed stable SCR activity up to ageing temperatures of 800 °C. V-SCR had a limited durability and it was similar to Fe-SCR catalysts also highly dependent on NO₂ promotion at low temperatures [9]. As a summary, copper and iron based SCR catalysts were thus most durable for the target application. Therefore, the Cu-SCR1 catalyst was applied for full-scale LNT + SCR studies with diesel engine due to the observed properties at low temperatures and for SCR after LNT.

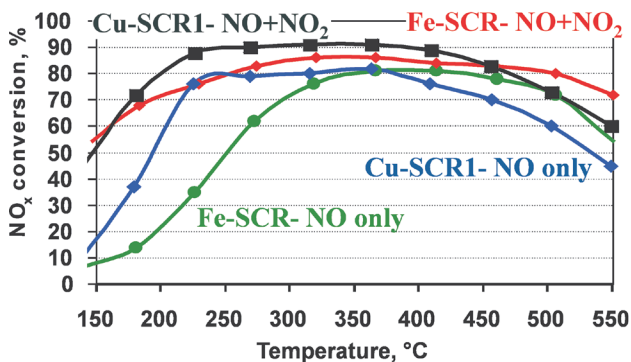


Fig. 3. NO_x efficiency on hydrothermal aged (800 °C for 20 h) copper and iron SCR catalysts in standard SCR reaction (no NO₂, SV 50.000 h⁻¹, NH₃/NO = 1)

Many SCR catalysts may lose NH₃ adsorption capacity in the ageing conditions in the SCR position after LNT and DPF. The Cu-SCR catalysts showed a stable NH₃ adsorption capacity at 200 °C up to the ageing temperatures at 800 °C (Fig. 4). A V-SCR catalyst had lower adsorption ability at 200 °C and it still lost the adsorption capacity after ageing at 700 and 800 °C. PtRh/LNT had also a low ability for ammonia adsorption but that was only 5% of that of Cu-SCR1 as fresh.

After adsorption steps, SCR catalysts were treated in temperature programmed oxidation (TPO) in lean gas mixture (Fig. 5). The ammonia desorption as a function of temperature at 200–600 °C is a fingerprint about the ammonia

adsorption strength on catalyst surface. A part of ammonia was oxidized to NO and N₂O (not shown here), which relative amounts varied by the catalyst type and ageing state. The Cu-SCR catalysts with a high adsorption capacity and strength after ageing at 700–800 °C were thus the most potential for LNT + SCR applications, where NH₃ formed in rich periods will be adsorbed downstream on the SCR unit and further utilized in SCR reactions in lean periods.

Relative NH₃ adsorption capacity

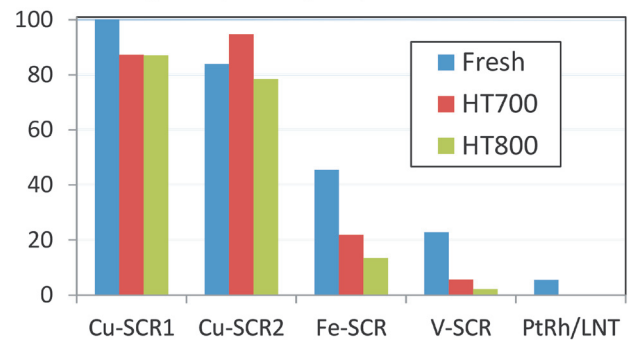


Fig. 4. Relative, coating weight based NH₃ adsorption capacity of studied SCR catalysts and PtRh/LNT at 200 °C as fresh and hydrothermally aged

Ammonia desorption

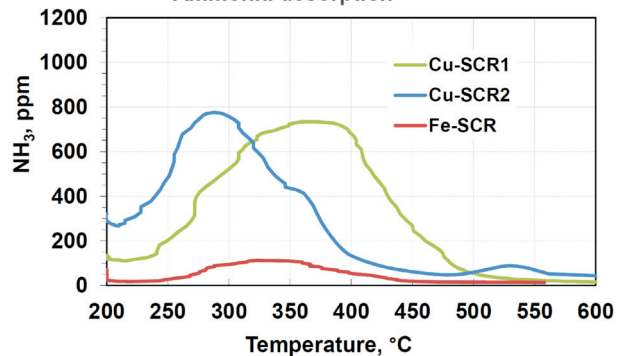


Fig. 5. Ammonia desorption from HT800 aged SCR catalysts in TPO experiments between 200–600 °C (10% oxygen in nitrogen). Adsorption capacity totally filled by NH₃ at 200 °C before that TPO

3.3. Effect of reaction conditions on LNT+SCR performance

Duration of lean phase

After optimizing the PtRh/LNT and SCR catalyst composition [9, 12], the selected, most active catalysts were applied for LNT + SCR simulation with synthetic feed gases. The lean-rich timing has the direct effect on the NO_x storage and reduction abilities. In real-life, the lean-rich timing correlates directly to fuel economy: the shorter is the rich period and the longer is the lean period, the better is the fuel economy. Enrichments increase always the fuel consumption with diesel engines optimized to economic lean combustion. Both the duration and frequency of rich periods are meaningful. NO_x adsorption capacity depends on the duration of lean period, if the surface is mainly emptied of adsorbed NO_x by the efficient reduction. The long, two minutes lean period resulted in lower NO_x activity in the laboratory simulations particularly at high temperatures, where the NO_x storage

capacity became limiting and the real residence time is shorter due to the temperature effect (Fig. 6). The relative NH₃ formation was lower with 120 s lean experiments. Too short 30 s lean period did not anymore improve the mean NO_x conversion compared to the standard 60 s lean one but that short lean period between efficient enrichments (5 s with $\lambda = 0.86$) had a slight negative effect.

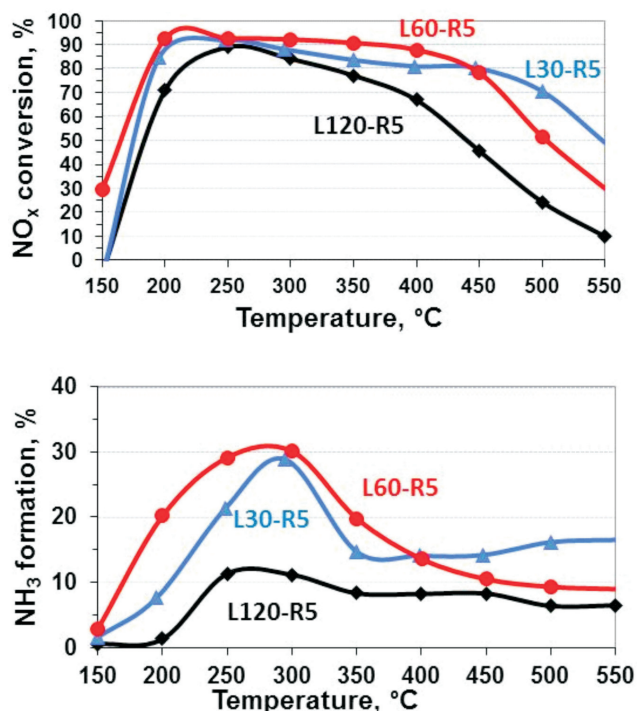


Fig. 6. The effect of the lean phase duration (30–120 s, rich 5 s) on NO_x efficiency and NH₃ formation with 80Pt5Rh/LNT1 + Cu-SCR1 (30.000 + 60.000 h⁻¹)

LNT+SCR simulations

The NO_x efficiency was higher with the assistance of SCR than with LNT only with the same total space velocity at low temperatures. At high temperatures, LNT only were detected to reach higher NO_x efficiency with the same total catalyst volume but the presence of SCR unit prevents the ammonia emissions. The NO_x adsorption (storage) capacity per coating amount (grams) on NO_x adsorbents decreases a function of temperature, which limits the high temperature NO_x conversion. This is also a reason together with the fuel economy, why LNTs are not that competitive with urea-SCR catalysts in heavy-duty applications (highway trucks) which have exhaust gas temperatures of about 300–550 °C in the driving conditions and test cycles.

NO_x conversion and the emissions of NH₃ and N₂O were detected in the comparison between LNT only and the LNT with a varying SCR unit (Fig. 7) LNT only resulted in high mean NH₃ formation due to very rich peaks ($\lambda = 0.82$ for 5 s) in simulation. In these conditions, it was possible to utilize SCR functionality in reaction studies downstream LNT. Both copper and iron based SCR catalysts were able to cut ammonia down and increased particularly the low temperature activity, which is important for passenger car

applications. The LNT volume was the same in every experiment (30.000 h⁻¹) and SCR was an additional volume after that fixed LNT. When that SCR unit was added after the LNT only, the NO_x conversion was higher and NH₃ slip still lower but that design meant 50% larger total volume. In this simulation, N₂O formation was related solely to HC-SCR (propene as HC) at low temperatures in lean side, almost no side reaction to N₂O was detected during enrichment peaks and the type of SCR catalyst had negligible effect on N₂O formation. However, in real exhaust gas HCs are less active for HC-SCR than one of most reactive HC, propene used in this simulation. Relative HC-SCR effect on N₂O formation may be about 10–30% (the fraction of HC-SCR reactive HCs in diesel exhaust) of these observed formation rates in real diesel exhaust gases. The same HC-SCR reaction will happen in the real system first on Pt-based DOC, located before LNT. Therefore, the presence of LNT in diesel system does not increase the potential for N₂O formation.

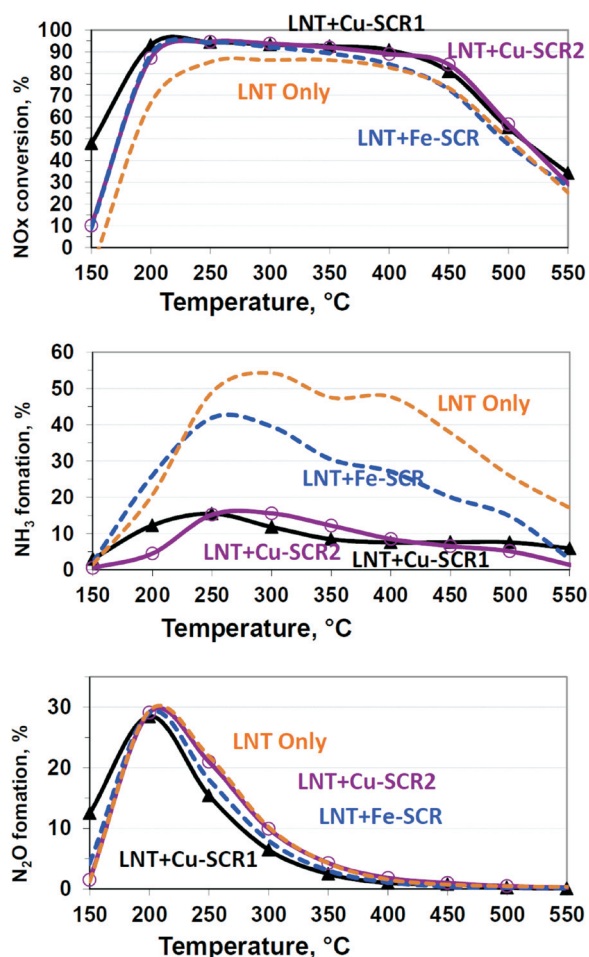


Fig. 7. The effect of SCR catalyst type on the NO_x efficiency together with NH₃ and N₂O formation in L60-R5 laboratory simulation (LNT + SCR = 75 + 75 mm = 30.000 + 30.000 h⁻¹, 80 g/cft Pt and 5 g/cft Rh on LNT, LNT only = 75 mm = 30.000 h⁻¹)

The Cu-SCR catalysts were able to promote the LNT performance with suppressed NH₃ formation particularly at low temperatures. In this lean-rich condition, the presence

of the SCR unit resulted in lower NH₃ formation compared to large LNT only. Cu-SCR catalysts are able to promote LNT also with a smaller volume (60.000 h⁻¹), opposite to Fe-SCR catalyst [9]. The NH₃ emissions were quite high (max. 40–50%) with LNT only, which experimental conditions made the effect of SCR quite dominating. NH₃ formation-% and N₂O formation-% were calculated by the inlet NO_x concentration. All detected N-O and N-H compounds originated from feed NO_x.

The promotion of Fe-SCR catalyst on NO_x conversion was similar like with Cu-SCR catalyst. The total NO_x efficiency was slightly lower than with the Cu catalyst at high temperatures. That large Fe-SCR unit (30.000 h⁻¹) was able to promote also low temperature SCR but our other studies showed that SCR below 300 °C was more limited with Fe-SCR than with Cu-SCR when SV was 60.000 h⁻¹ over SCR unit [9]. The use of Fe-SCR resulted in higher NH₃ emissions (max. 42%) than the use of Cu-SCR (max. 14%). This difference is a key property to use Cu-SCR in the further full-scale studies.

The LNT + SCR design was optimized in many other experiments by varying the volume of catalyst units and lean-rich timings. The optimal design was targeting the maximal NO_x efficiency and minimal NH₃ slip after the complete system. Any additional volume of units should be avoided to keep pressure drop and costs of the units low.

3.4. Shifting SCR unit to lean during the LNT regeneration-air addition

In LNT + SCR system the ammonia concentration can be adjusted to a higher level after LNT than in LNT-only systems, because formed ammonia will react on the SCR unit. This combination results in a higher total NO_x efficiency but traces of NH₃ may be left even after the SCR unit, because the conventional SCR catalysts are not good in long rich or stoichiometric periods. It is difficult to store all formed NH₃ on the SCR unit in rich and to have then the reaction with stored NH₃ and feed NO in lean. After the change from rich to lean the NH₃/NO_x (gaseous+adsorbed) ratio is very high, which results in NH₃ slip. In conventional NH₃-SCR systems, the NH₃/NO_x ratio is fixed near to the value of 1 with the known (model-based) NH₃ storage on the SCR catalyst surface. In LNT + SCR system, that NH₃/NO_x ratio varies in the wide range. The continuous lean SCR condition promoted SCR and thus total NO_x efficiency to N₂ with lower NH₃ emissions. Oxygen and NO₂ promote the SCR reactions on conventional SCR catalysts, which promotion is missing in rich.

Therefore, an approach is to keep the SCR unit continuously in lean side, also during LNT regenerations. In by-pass LNT + SCR systems [12] the SCR unit will be also always in lean side, which functionality we also simulated in this experimental procedure. In our laboratory simulations, λ was 1.2 on the SCR unit by the assistance of an additional

air injection for the SCR unit, when λ was at the same time 0.81 on LNT during regeneration periods (Fig. 8).

The lean condition had a minor effect on detected NO_x conversion, but the selectivity to desired N₂ instead of ammonia was higher with this air assistance. The use of air addition made the volume of the SCR unit more critical, opposite to the results without air addition. The increase of SCR catalyst volume (111.000 → 30.000 h⁻¹) dropped NH₃ formation degree from 30 to 5% in L60-R5 conditions [9].

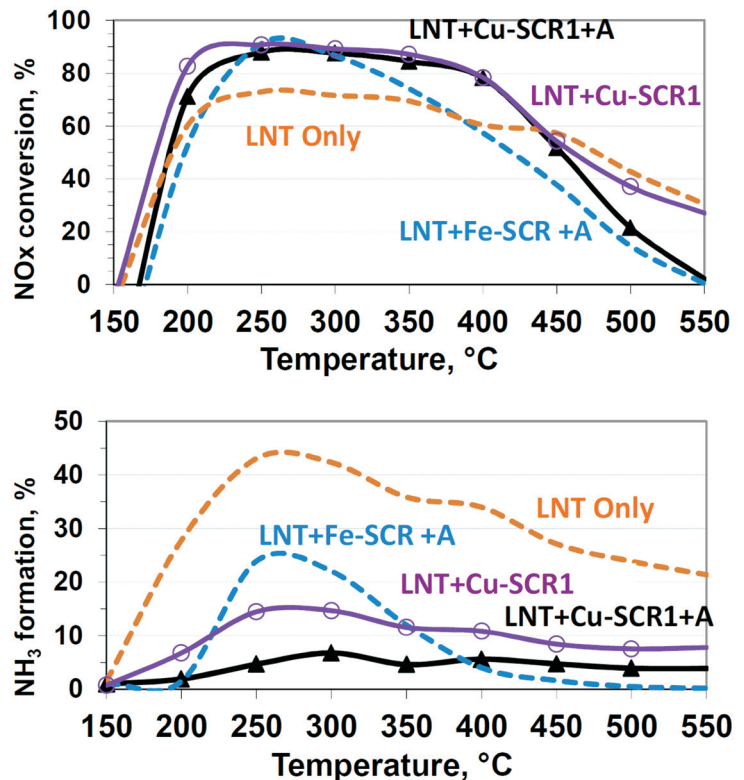


Fig. 8. The effect of air addition before the SCR unit on NO_x efficiency and NH₃ formation with fresh LNT and SCR catalyst combinations in L60-R5 conditions (37 mm + 75 mm = 60.000 h⁻¹ + 30.000 h⁻¹)

3.5. Engine experiments for catalyst development

LNT and SCR catalysts developed by the small-scale samples were further prepared as full-scale and examined as combinations with the 1.2 L engine in lean-rich operation. Higher NH₃ emissions were detected after LNT due to the long rich period (15 s), even if λ was not that low as in the rich mixture of laboratory experiments. The combination of LNT and SCR was installed in series by flow direction without any air addition, which was too complicated to add in this experimental set-up. However, ammonia adsorbed in rich period will react later in lean period also in this set-up.

The assistance of SCR unit for LNT performance was well seen in these experiments (Fig. 9). The Cu-SCR1 catalyst promoted NH₃-SCR reaction, which increased the total NO_x efficiency and removed NH₃, formed on LNT, out from exhaust outlet. In the selected two engine points the mean temperature was after SCR about 180 and 270 °C in that lean-rich operation. NO_x conversion increased from 43 to

95% in the point of 180 °C and from 80 to 96% in the point of 270 °C. In these experimental conditions, the SCR unit was necessary to reach the target NO_x conversion without ammonia emissions. These simulation results were used as a base for the LNT and SCR catalyst samples used in the partners' engine and vehicle studies in this joint Powerful EU program.

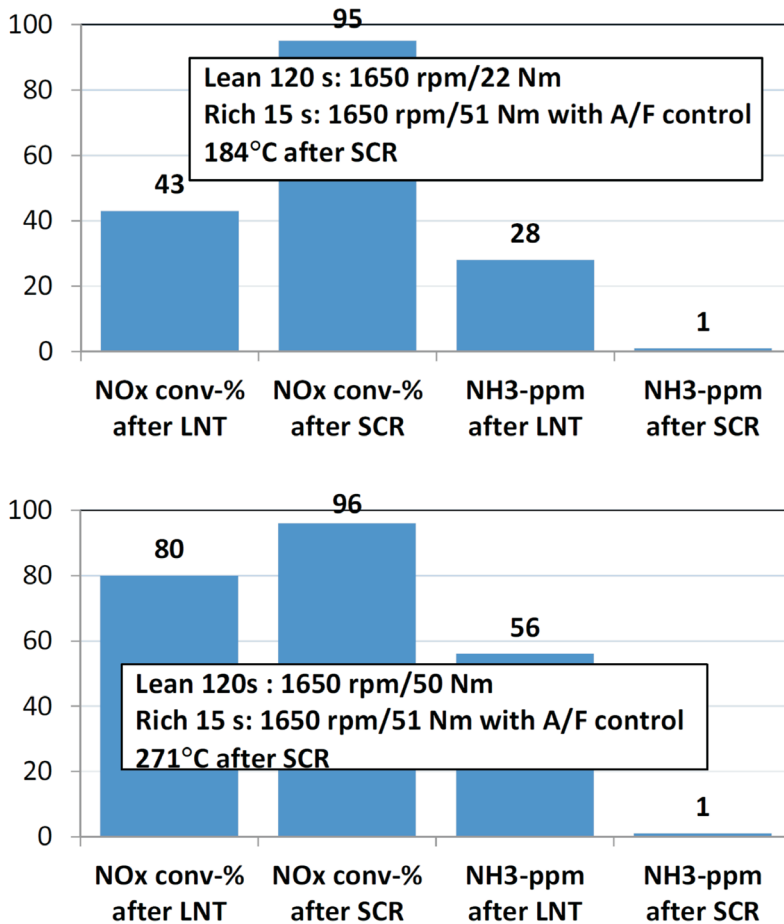
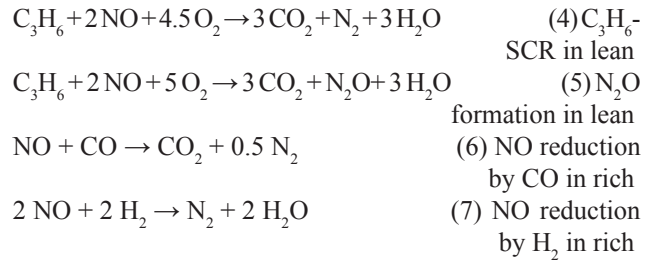
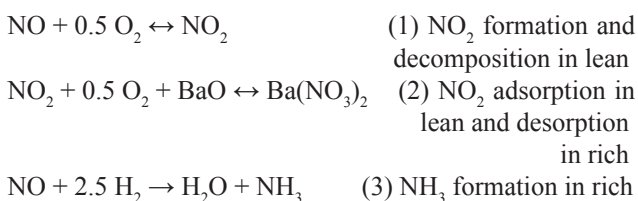


Fig. 9. The effect of Cu-SCR1 on the NO_x conversion and NH₃ formation with 80Pt5Rh/LNT in two engine points with a 1.2 L diesel engine (LNT 1.4 L, SCR 1.9L). The shown values are mean values by the last 5 cycles of 8 repeated cycles in L120-R15 cycling in both engine point

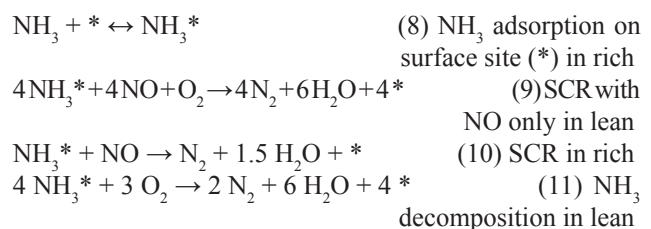
3.6. Reaction mechanism in LNT + SCR system

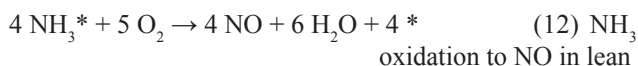
The reaction mechanism in this combinatory system can be described by the known LNT and SCR reaction paths. The LNT operation can be calibrated to form more ammonia than with known LNT only systems. The formed NH₃ will react on the SCR unit. NH₃ is formed with the λ values below 1 in known 3-way catalyst reactions. The main NO_x reactions on LNT can be presented as follows [9, 10, 15, 16]:



The adsorbed NO_x (nitrate, nitrite) on BaO will be desorbed and decomposed to NO in reducing conditions, which equilibrium is controlled by thermodynamics and kinetics. NO is reduced by CO or H₂ formed from partial HC oxidation, water gas shift and gas reforming reactions. The gaseous NO₂ concentrations in the LNT reactor outlet are very low in lean-rich conditions, due to adsorption (in lean) and reducing (in rich) conditions. Propene represents HCs in our experiments and those equations and it is also a source for the final reductants (H₂ and CO) of NO_x. C₃H₆-SCR on PtRh/LNT results also in a low NO_x conversion around at 200–300 °C (eq. 4). N₂O is a by-product in this reaction sequence (eq. 5). The oxygen storage capacity (OSC) has also a role in lean-rich excursions and 3-way catalyst performance but those reactions are not included in this general NO_x reaction path description. The detailed surface reaction mechanisms are much more complex [17] but the above reactions describe the main paths related to reaction rates of observed reactants and products in reactor inlet and outlet.

NH₃ formed in LNT will adsorb and react on SCR catalyst mainly in rich phase. Standard SCR is the main NO_x reduction path in that after LNT position. A part of NH₃ may be oxidized also back to NO, particularly at higher temperatures. NH₃ is presented below to react with gaseous NO as an adsorbed intermediate but it has been also presented mechanisms where both reactants are adsorbed or NH₃ is in gas phase. However, NH₃ adsorption step has a key role in this LNT + SCR system to move adsorbed NH₃ to be utilized in the following lean period. Therefore, ammonia adsorption was included in this simplified reaction set. The NO_x main reactions on SCR unit can be presented as follows:





In more detailed surface mechanism, many other surface intermediates and competing reaction paths exist. In fact, SCR reaction (on Cu) and NH₃ adsorption (on support) proceed on separate catalyst sites.

4. Summary

The LNT and SCR catalysts were developed and optimized for LNT + SCR applications. Pt-Rh catalysts with optimized support, PtRh loadings, NO_x adsorbents and oxygen storage compounds resulted in an efficient LNT composition. The Cu-SCR catalysts showed a good durability up to 800 °C and a wide operation window without NO₂ assistance. Fe-SCR and V-SCR catalysts had lower NH₃ adsorption capacity and they were dependent on NO₂, which promotion is not possible to apply in the SCR position after LNT and DPF. The SCR unit after LNT was able to increase total NO_x efficiency and remove NH₃ emissions during powerful enrichments.

The design of LNT + SCR was optimized for the developed concept by catalyst volumes (SV) and lean-rich timing. The concept variation for real diesel applications with DPF units was analyzed. The main application for this kind system

will be light-duty vehicles, where the use of LNTs is known and the low temperature NO_x removal is the main target. The use of a SCR unit after LNT enabled to reach higher NO_x efficiencies by the use of heavier enrichments without NH₃ emissions, because NH₃ is consumed in SCR. The detected N₂O formation in our simulations was mainly related to HC-SCR on PtRh/LNT in lean side because of the reactive propene, which was the only hydrocarbon in our feed gas. In real exhaust gas, the HC fraction active for HC-SCR is very low and N₂O will be much lower.

In a developed concept and simulation, air was injected between LNT and SCR to keep the SCR unit in lean side during LNT regeneration. As a consequence, SCR reactions were promoted by oxygen also during enrichments, when the main NH₃ formation occurs. The main benefit of the air addition was the improved NO_x reduction selectivity to N₂ with low NH₃ emissions in the final exhaust gas.

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