

NO_x Reduction with the Combinations on LNT and SCR in Diesel Applications

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ABSTRACT

Stricter emission limitations for NO_x and particulates in mobile diesel applications will require the combinations of active aftertreatment methods like Diesel Particulate Filters (DPF), Selective Catalytic Reduction (SCR) with urea and Lean NO_x Trap (LNT) in the 2010's. A new concept is the combination of LNT+SCR, which enables on-board synthesis of ammonia (LNT), which is then removed on the SCR catalyst. The main application for this kind system will be light-duty vehicles, where LNTs are already used and the low temperature deNO_x is a main target. That combinatory system was investigated by developing and selecting PtRh/LNT and SCR catalysts for that particulate application, where the maximum temperature may reach 800°C and SCR should proceed without NO₂ assistance. Pt-rich, PtRh/LNT with reasonable high loadings above 80g/cft resulted in a high NO_x efficiency in the experimental laboratory conditions which created also on LNTs a higher NH₃ concentration for the SCR unit. The SCR catalyst with copper as an active metal (Cu- SCR) showed the good durability up to 800°C and a wide operation window without the NO₂ assistance. Fe-SCR and VSCR catalysts were more dependent on NO₂, which is not present after LNT and DPF. An optimized concept had an air injection after LNT to keep SCR condition always lean side, where the SCR reaction was promoted by oxygen with a high selectivity without NH₃ emissions. The simulations in reaction conditions and system design resulted in the proposals for the optimal design and main reaction mechanism.

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INTRODUCTION

The good fuel economy of diesel engines has resulted in their wide use in addition to heavy-duty also in light-duty applications. Efficient and economic NO_x and PM (particulate matter) removal methods are the main challenges of future aftertreatment systems for diesel engines. The demand for the simultaneous fuel consumption (CO₂) and emission decrease limits the possibilities to apply many of introduced methods.

The selective catalytic reduction of NO_x by urea (urea-SCR) on chemically stable V-SCR or thermally stable zeolite-SCR catalysts is world-widely in commercial use. Urea acts as a source for the actual reductant, ammonia (NH₃), which selectively reacts with NO instead of oxygen in lean exhaust gases. The SCR operation is enhanced particularly at low temperatures with the assistance of NO₂, which is formed on DOC. In heavy-duty applications, the

SCR efficiency has been usually above 85 - 90%, which has enabled a fuel-efficient engine calibration. The exhaust gas recirculation (EGR) matches better to smaller diesel engines to decrease NO_x emissions with the costs of higher fuel consumption and PM emissions. Urea-SCR for light-duty vehicles has limitations due to urban driving conditions, where the low-CO₂ engines have exhaust gas temperatures below 200°C (1). An external heating of the SCR system is a method to keep conditions in SCR window (>200°C) in urban driving phases (2). Urea/NH₃-SCR is thus a very selective and efficient method but it will also require additional urea distribution, on-board storage and injection systems, which may be difficult to build with light-duty applications. Urea hydrolysis to ammonia has also limitations (evaporation, thermolysis, hydrolysis and deposits) at lower temperatures.

Lean NO_x traps (LNT) have been also applied for NO_x removal, particularly for passenger cars, where the fuel economy is not that critical than with heavier trucks. LNTs

operate in the heterogeneous lean-rich conditions. However, the fuel acts as a reductant 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 (2 - 5 s). A high precious group metal (PGM, usually platinum and rhodium) loading is necessary to form efficiently NO_2 in lean and to operate in NO reduction during rich peaks. The NO_x adsorption sites adsorb efficiently also almost all SO_x in exhaust gas, which results in the sulfation of LNT. Desulfation in rich conditions above 600°C is a method to regenerate LNT again for active state. The periodical rich peaks for denitration and desulfation increase the fuel consumption up to 10% compared to completely lean combustion. The high selectivity for wanted nitrogen is more difficult to control than in the case of NH_3 -SCR. The reduction in rich peaks may result in NH_3 formation and NO reduction on Pt catalysts causes a potential for N_2O formation particularly at lower temperatures ($<300^\circ\text{C}$). Control strategies for reduction have been tailored to avoid these side products but usually that limits also the maximum available NO_x reduction.

Recently, the combination of LNT and SCR catalyst has been introduced as a method to utilize in situ formed NH_3 for NH_3 -SCR (3, 4, 5). NH_3 formed in rich peaks are stored on the SCR catalyst where it subsequently reacts with NO_x that breaks through LNT (6). Copper (Cu) and iron (Fe) zeolites have been mainly used as SCR catalysts due to the high temperature conditions ($>600^\circ\text{C}$ in regenerations) after LNT and DPF. The high ammonia adsorption capacity and strength are important for the SCR catalyst to maximize the NH_3 shift to lean NH_3 -SCR. The use of reformer unit and by-pass for LNT are the ways to enhance the LNT regeneration, even if NO_x in by-pass during regeneration may slightly decrease the total NO_x efficiency (7). The reformer modifies also the fuel to CO and hydrogen which are more efficient, final reductants for NO_x compared to HCs. The direct injection of fuel into exhaust may cause a HC inhibition on LNT at low temperatures. Enrichments with LNT and by-pass makes possible to have engine independent LNT regeneration (no need for engine throttling to reach λ values below 1 in LNT). In the same presentation it was also introduced the first commercial light-duty DOC+LNT+DPF+SCR concepts for US markets. In the commercial systems, a key question is also the order of LNT and DPF. The regeneration and thermal management of the upstream unit is much easier than the downstream unit. Both DPF and LNT are quite massive compared to the engine size, which makes difficult to heat up the downstream unit in light-duty applications and driving cycles. Secondary air injection between LNT and DOC or catalyzed DPF has been used as a way to oxidize HC (CO) slip.

The LNT based systems are summarized by the functional units and LNT regeneration types in Figure 1. Every system

may be also in the order, where LNT is in close-coupled position located before DPF, which improves the low temperature NO_x efficiency of LNT but makes DPF regeneration more demanding. For the simplicity, the reversed order was shown in that figure only for the last LNT+SCR systems. The LNT regeneration is based on engine enrichment and throttling in system A, C and D, on throttling and reformer gas in system B and on reformer gas in system E and F. However, DPF regeneration is usually made every 500 - 1000 km but LNT regeneration in every 1 - 2 minutes, which gives more possibilities for DPF regeneration strategies. Active DPF regeneration requires conditions to oxidize soot above 600°C . This is usually conducted by enrichment by engine or fuel injection in exhaust gas and throttling similar to LNT regeneration but in lean side. It is possible to integrate partly DPF, nitrate and sulfate regenerations (8). The DPF regeneration (max. $700 - 800^\circ\text{C}$) is the main reason for the thermal ageing of LNT and SCR, which needs to be considered in system design too.

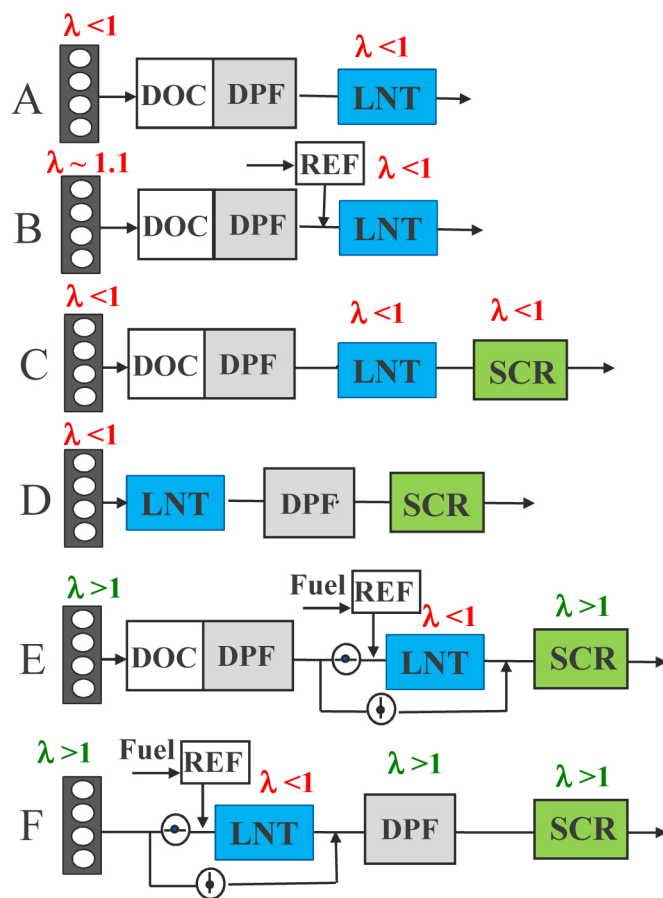


Figure 1. Possible LNT and LNT+SCR configurations for diesel applications (7). The shown λ values are related to the LNT regeneration period.

In this study, the LNT and SCR catalyst formulations were screened to find the optimal compositions and combinatory activity for LNT+SCR. The reaction studies were carried out to interpret the limiting factors, design and

key reaction paths of the method. The role of λ value for the LNT and SCR operations was also simulated with LNT+SCR systems in laboratory reactors.

EXPERIMENTAL AND METHODS

Catalysts

The LNTs in the experiments consisted of metal foils (500 cpsi, 50 μm), where a porous washcoat (about 40-50 g/m^2), active metal and NO_x trap compounds were added. Commercial stable alumina was the main compound in the washcoat. 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 added by chemisorption methods resulting in an even dispersion on washcoat (9). Finally, the samples were dried and calcinated at 550°C in air. The surface area (BET) of LNT coating was between about 130-140 m^2/g .

SCR catalysts were also based on metallic substrates (600 cpsi, 50 μm), where Cu, Fe and V catalysts were coated with binders. The coating amount was about 40 g/m^2 . The surface area (BET) of Cu and Fe catalysts was about 400-500 m^2/g and the BET area of TiO_2 based V-SCR catalyst was about 100 m^2/g . The type of support (Beta, ZSM-5, $\text{TiO}_2\text{-WO}_3$, other oxides) was also a variable in the experiments.

Laboratory Experiments

Laboratory simulations were conducted in the mixtures, which were created by mass flow meters controlled with data acquisition program as a function of time with a frequency of about one second. 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 , CO_2), chemiluminescence (NO_x , NO , NO_2) and FTIR (e.g. NH_3 , N_2O , individual HCs, with quartz reactor).

The activity of samples were evaluated in laboratory experiments, where a cycle includes longer lean and short rich periods simulating LNT and LNT+SCR system conditions. The lean-rich cycles were repeated for five times with the mixtures presented in table 1. The feed gas mixtures simulated typical lean exhaust gas compositions like analyzed with diesel engines. The absence of NO_2 simulated the D or F systems (no DOC+DPF before LNT). Light hydrocarbon, propene was solely used as a HC in the feed gas to be able to vary fast the inlet composition in transient condition. The total flow rate was 5.3 L/min.

Table 1. Experimental conditions in laboratory simulations.

Mixture	Lean	RichA	RichB	RichA+air
NO_x , ppm	500	1500	500	1065
C_3H_6 , %	0.1	0.1	3.75	0.07
CO_2 , %	0.25	5.73	5.73	4.07
H_2 , %	0.08	2.0	2.0	1.42
CO_2 , %	10	10	10	7.1
H_2O , %	10	10	10	7.1
N_2	bal.	bal.	bal.	bal.
λ	1.41	0.81	0.47	1.20
Period, s	30-120	5-15	5-10	5

NO was replaced with NO_2 in few experiments simulating the effects of DOC located before LNT.

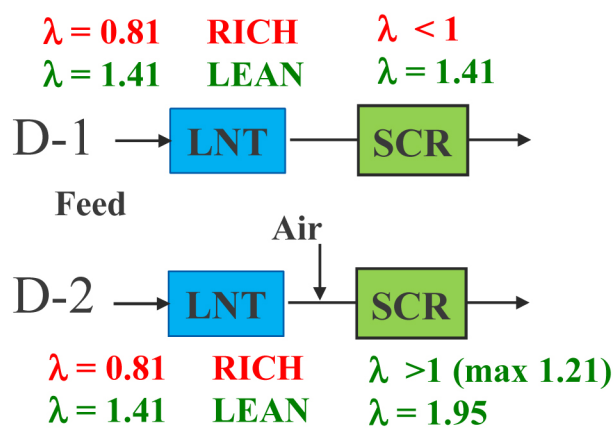


Figure 2. Laboratory simulations of LNT+SCR systems with LEAN-RICH-A and LEAN-RICH-A+air based on system D in Figure 1.

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 NH_3 adsorption-desorption was detected by the activity testing reactor by adsorbing NH_3 at 200°C by a step exchange experiment ($0 \rightarrow 500$ ppm NH_3 in nitrogen, 42,000 h^{-1}) and then the desorption of NH_3 was detected in the presence of oxygen by a ramp up to 600°C (10).

RESULTS AND DISCUSSIONS

The Effect of LNT Properties on NO_x Efficiency

The basic compositions of LNTs have been earlier developed for lean gasoline and diesel applications and NO_x adsorbent containing LNTs have been used also commercially e.g. by Toyota and VW (9). Platinum and rhodium are the most active metals in varying lean-rich conditions to have in lean high NO_2 formation, efficient HC/CO oxidation and in rich three-way catalyst properties.

Palladium has a limited activity for NO_2 formation and other reactions in diesel conditions at low temperatures. Therefore, the focus in the experiments was on PtRh catalysts with higher loadings like above 80 g/cft. Ceria based oxygen storage compounds (OSC) promote the LNT performance. OSCs are partly reduced in rich periods and oxidized again in lean periods, which property may have an effect on the NH_3 formation on LNT.

In diesel applications, the rich periods are decreasing fuel economy and their duration should be minimized to reach the target NO_x conversions. The rich periods may also cause high CO, HC, PM and ammonia peak concentrations which are usually controlled by adjusting the lean-rich timings. Therefore, nitrates in LNT are not usually totally reduced to avoid the flow-through of reductants and NO reduction to ammonia but some nitrates may stay on the surface after enrichments.

The screening of LNTs was based on fixed lean-rich conditions (L60s/RA5s, L = Lean, RA = Rich A) with hydrothermally aged (700°C/20h) samples. The basic study about the role of LNT composition (Alumina with Ba and rare earth elements), Pt and Rh was studied by varying the catalyst composition (Fig. 3). Pt and Rh were needed to activate the reactions in LNT. NO_x traps elements were not active alone (PGM-free LNT). Rh-only LNT with a higher loading (42 g/cft) had a limited activity too. Oppositely, the Pt-only LNT showed very high NO_x efficiency, being the most active at high temperatures. The variation of Pt:Rh ratio and the increase of the total loading from 85 up to 130 g/cft had minor effects. The results with the Pt+Rh loadings of 80+5 (16:1), 70+15 (4.7:1), 60+25 (2.4:1) and 125+5 (25:1) g/cft were almost identical with minor differences. The variation of enrichment and ageing conditions might reveal more about the optimum. A high Pt loading resulted in a slight improvement in light-off region below 200°C, which is important for light-duty driving conditions.

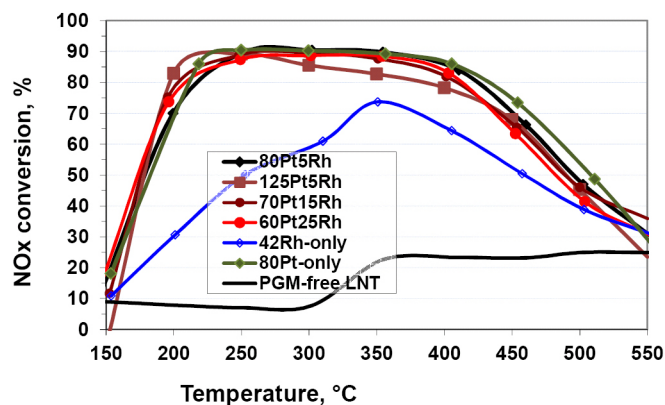


Figure 3. NO_x efficiency by Pt and Rh loadings (g/cft) on Ba and rare earth containing LNT (hydrothermally aged at 700°C/20h, 30.000 h⁻¹, L60s/RA5s, reactor 2).

The effect of oxygen storage compounds (Ceria) was also investigated and it was found that ceria in fact promoted NH_3 formation even if the oxygen storage capacity (OSC) might also have a buffering effect. Due to our very rich peak conditions, OSC was evidently consumed fast and NH_3 or reduced N compounds were stored on LNT at the end. The same promotion with ceria was proposed also with Pt catalysts with the property of on-board NH_3 synthesis by Breen et al. 2002 (11).

Potential SCR Catalysts for LNT+SCR Concept

NO_x efficiency in LNT+SCR

The effect of the SCR catalyst types was screened to select the right combination for further studies. A comparison was based on the same total catalyst volume (30.000 h⁻¹ with LNT only and 60.000+60.000 h⁻¹ for LNT+SCR). When the total volume is the same, it is possible to analyze which is the best way to divide the total volume, which requires space and causes costs and pressure drop. At low temperatures, the combinatory NO_x efficiency with the assistance of SCR was higher than with LNT only (Fig. 4). In addition, the fraction of wanted N_2 as a reaction product was higher than with LNT only (higher NH_3 and N_2O). At high temperatures, LNT only with a double LNT volume was better than the combinations. The best combinatory high temperature promotion was observed with Fe-ZSM-5 catalyst. In these screening studies, FTIR was not connected and thus NH_3 and N_2O emissions were not available.

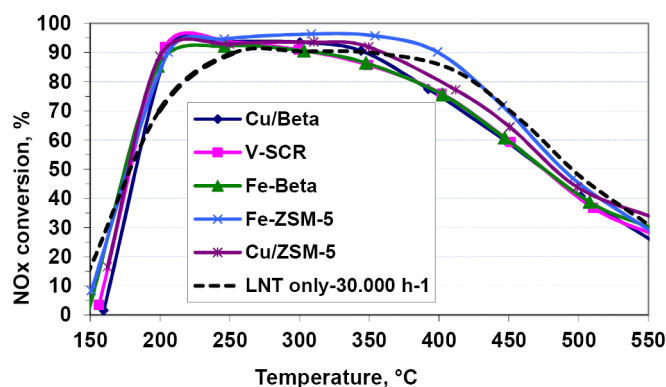


Figure 4. The combinatory effect of the same 80Pt5Rh/LNT and varying SCR catalysts in lean-rich (L60-RA5) laboratory simulation (LNT HT700 aged/20h-SCR catalysts fresh, SV 60.000+60.000 h⁻¹).

NH_3 adsorption capacity

The NH_3 adsorption capacity was measured at 200°C with a step exchange method. Even if many SCR catalysts were active as fresh, they may lose the activity and NH_3 adsorption capacity in ageing, which is evident after LNT and DPF in