NO$_x$ reduction in the exhaust of mobile heavy-duty diesel engines by urea-SCR

M. Koebel[a], M. Elsener[a], O. Kröcher[a,*], Ch. Schär[b], R. Röthlisberger[c], F. Jaussi[c], and M. Mangold[d]

[a] *Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
[b] *Measurement and Control Laboratory, Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland*
[c] *Liebherr Machines Bulle SA, CH-1630 Bulle, Switzerland*
[d] *Oberland Mangold GmbH, D-82467 Garmisch-Partenkirchen, Germany*

A DeNO$_x$ demonstration system for a diesel engine used in construction machineries and mobile cranes was setup. In preliminary experiments various extruded and coated SCR catalysts were evaluated with and without oxidizing pre-catalyst. The data from stationary tests with two selected catalysts were used to establish various model-based control algorithms for the optimum dosage of urea in the ESC and ETC. A NO$_x$ conversion of > 93% at < 10 ppm average ammonia slip could be achieved at a converter-to-swept volume ratio of < 2.0.

KEY WORDS: selective catalytic reduction; SCR; urea; diesel; exhaust; vanadia; catalyst.

1. Introduction

Over the last years, great efforts have been made in order to reduce NO$_x$ emissions from lean exhaust gases. The most important techniques are HC-SCR [1], the selective catalytic reduction (SCR) with N-containing reducing agents [2,3] and the NO$_x$ storage and reduction catalyst (NSR) [4]. Urea-SCR is considered to be most promising for heavy-duty diesel engines and has intensively been investigated especially by the German truck industry [5,6]. Urea is a solid and safe storage compound for ammonia, which is the actual reactant in the SCR reaction:

$$H_2N\text{–}C(O)\text{–}NH_2 + H_2O \rightarrow 2\,NH_3 + CO_2$$

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$
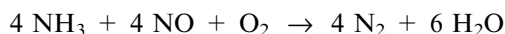
Urea-SCR has been approved in the last decade for the NO$_x$ removal from stationary diesel engine exhausts. One of the major demands for the application of this process to mobile engines is the reduction of the catalyst volume. This is made even more difficult by the varying loads and speeds in vehicles, resulting in changing volume flows, exhaust gas temperatures and NO$_x$ concentrations. Furthermore, the low deep temperature activity of SCR catalysts has to be enhanced.

In this project, a DeNO$_x$ demonstration system for a diesel engine used in mobile cranes has been setup and investigated. This development work was supplemented by laboratory studies on the improvement of the SCR catalyst activity.

*To whom correspondence should be addressed.

2. Experimental

2.1. PSI test bed "HARDI"

Preliminary tests were performed on the test bed "HARDI" at the Paul Scherrer Institute (PSI), whose setup is described in [3]. The experiments were carried out on a 6.64 L four-cylinder turbocharged diesel engine with intercooler (Liebherr D924 TI-E A2). The engine rated power output is 160 kW at 1900 rpm. Since the asynchronous generator was running at a fixed speed of 1500 rpm, the electric power was limited to 116 kW$_{el}$. The power range from 10 to 110 kW$_{el}$ was used on "HARDI". Since an asynchronous generator was used as a brake the engine is running at a fixed speed of 1500 rpm. NO and NO$_x$ concentrations were measured by a Tecan CLD 502, the urea consumption was determined gravimetrically and the ammonia concentration was measured by a wet chemical analyzer developed at PSI.

2.2. Liebherr Dynamometer

European steady state cycle (ESC) and European transient cycle (ETC) tests have been performed on a 9.96 L A4 six-cylinder turbocharged diesel engine with intercooler (Liebherr D926 TI-E). The rated power output is 270 kW at 2100 rpm. Fitted with its original electronic control unit, the engine achieves 5.8 and 0.08 g/kW h NO$_x$ and particles, respectively, on the ESC-13-modes test cycle. The main components of the SCR system were the dosing unit for urea solution (32.5%) and the SCR catalyst. The dosing unit was a modified prototype from Bosch. The test rig was controlled by a real time computer system from dSPACE. NO and NO$_x$ concentrations were measured by a Tecan CLD 502 and a Cambustion fNO400, equipped with a NCC400. Behind catalyst an additional

NO$_x$ sensor from NGK-Siemens was used. Urea consumption and ammonia concentration were determined as stated above.

2.3. Catalysts

A summary of the tested catalysts is given in table 1. E$_s$ and E$_l$ are commercial extruded SCR catalysts from Frauenthal, Austria. The catalysts C$_s$, M$_s$, and M$_l$ are coated ceramic and metallic honeycombs, respectively. They were prepared by a further developed method based on the equilibrium adsorption of polyvanadates on titania/tungstia from an acidic solution [7]. The pre-oxidation catalyst O$_s$ with platinum as the active component was delivered by OMG, Germany. Indices s and l designate the small and large version, respectively, depending on the installation of the catalyst in the small stationary or the larger dynamic test bed.

3. Results and discussion

3.1. Catalysts

The preparation procedure for SCR catalysts of Kleemann [7] could successfully be further developed for the coating of both cordierite and metal substrates. The preparation method was simplified and made more reproducible. The overall performance of these coated catalysts was better than that of most commercial types with an excellent temperature resistance up to 600 °C.

3.2. PSI Test Bed "HARDI"

Three different SCR catalysts were tested at the PSI test bed, each with and without precatalyst. Figure 1 shows the test results for seven loads/exhaust gas temperatures, respectively. Among the tested SCR catalysts without pre-catalyst the extruded type E$_s$ exhibited the highest DeNO$_x$ at low temperatures. Contrary, at the highest temperatures ($T = 465$ °C) the coated type M$_s$ showed the best result. The better performance of the extruded catalyst at low temperatures can be attributed to the fourfold amount of active mass, which is the rate limiting factor in this temperature regime. However, at high temperatures the SCR reaction is so much faster, that diffusion becomes rate limiting and only the outer catalyst layer participates in the reaction [8]. The higher DeNO$_x$ of M$_s$ compared to C$_s$ at high temperatures can be explained by the higher cell density of M$_s$ (400 cpsi).

The activity of the SCR catalysts is enhanced by introducing the pre-catalyst O$_s$. The effect is most pronounced at low and high temperatures, where the

Table 1
Specifications of tested catalysts

| Catalyst	Composition	Type	Substrate	Producer	Cell density (cpsi)	Volume (L)	Active mass (g)
E$_s$	~3%V$_2$O$_5$/WO$_3$/TiO$_2$	Extruded	–	Frauenthal	300	9.6	7000
E$_l$	~3%V$_2$O$_5$/WO$_3$/TiO$_2$	Extruded	–	Frauenthal	300	19.6	14,000
C$_s$	~2.5%V$_2$O$_5$/WO$_3$/TiO$_2$	Coated	Cordierite	PSI	300	9.85	1400
M$_s$	~2.5%V$_2$O$_5$/WO$_3$/TiO$_2$	Coated	Metal	PSI	400	10.0	2200
M$_l$	~2.5%V$_2$O$_5$/WO$_3$/TiO$_2$	Coated	Metal	PSI	400	19.9	2800
O$_s$	Pt	Coated	Metal	OMG	400	1.9	6.03
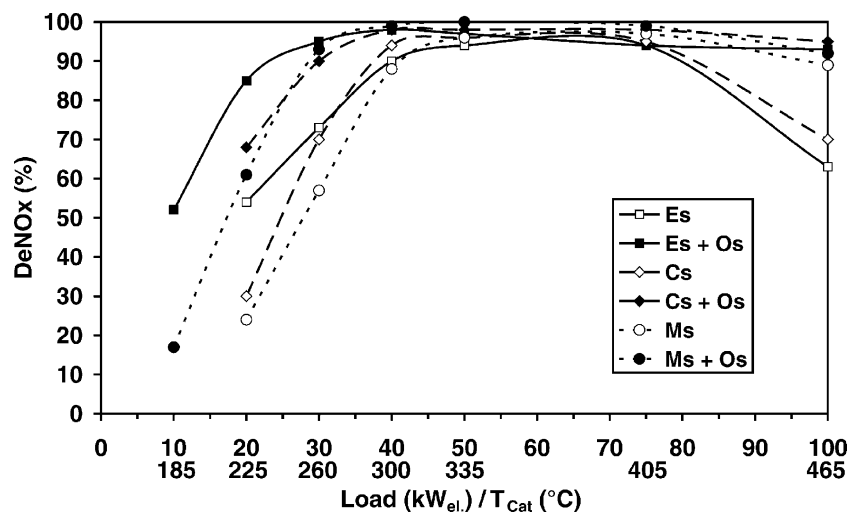
Figure 1. DeNO$_x$ (%) at 10 ppm ammonia slip for different types of SCR catalysts with and without pre-catalyst on the PSI test bed "HARDI".

SCR catalysts alone exhibited only low DeNO$_x$. For instance, at 20 kW/225 °C the activity of all catalysts could be increased by 30–40%, whereas the improvement was only a few percent in the optimum temperature range of 335–405 °C. It was proved in supplementing investigations, that this behaviour could be attributed to the increased NO$_2$ content after the pre-catalyst, which favours an additional reaction pathway, the so-called "fast SCR" reaction [9].

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

$$4\,NH_3 + 2\,NO + 2\,NO_2 \rightarrow 4\,N_2 + 6\,H_2O$$
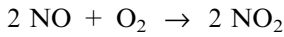
Surprisingly, at very low temperatures ($T < 200$ °C) the fraction of NO$_2$ was reduced over the pre-catalyst (figure 2). This effect was not observed in model gas experiments and can be explained by the oxidation of hydrocarbons and CO, present in the real exhaust gas, by NO$_2$.

$$HC/CO + NO_2 \rightarrow CO_2 + NO$$
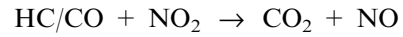
This reaction with HC and CO also took place over the SCR catalyst, accompanied by a further reduction of NO$_2$. Despite of this shift from NO$_2$ to NO over the pre-catalyst at very low temperatures, DeNO$_x$ of the SCR catalyst was improved due to the absence of deactivating hydrocarbons.

Experiments were performed with changing engine loads. The minimum injection temperature for the urea solution was set at 200 °C. This temperature was reached even faster after a cold start than after a warm start of the engine, since the efficiency of the cold engine was lower resulting in higher exhaust gas temperatures. Another reason for the faster temperature rise was the release of heat when water and hydrocarbons adsorbed on the catalyst and when the hydrocarbons started to oxidize (figure 3).
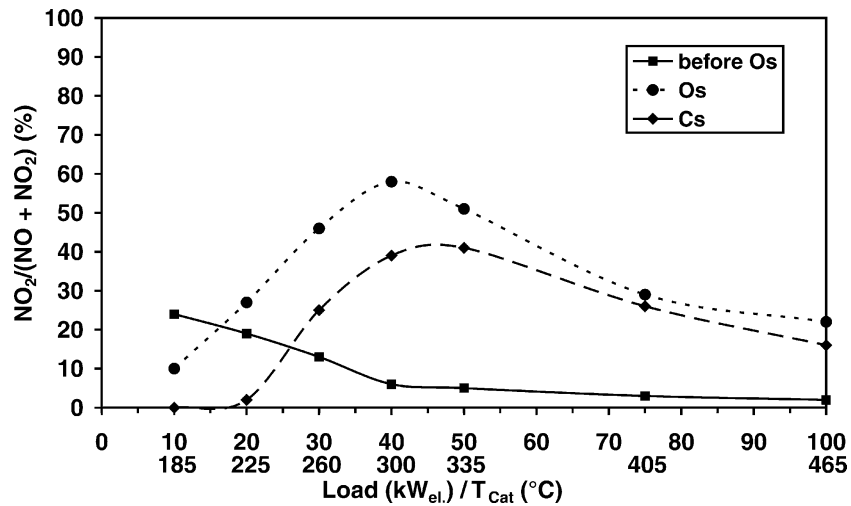

Figure 2. Fraction of NO$_2$ behind pre-catalyst O$_s$ and behind SCR catalyst C$_s$ on the PSI test bed "HARDI".
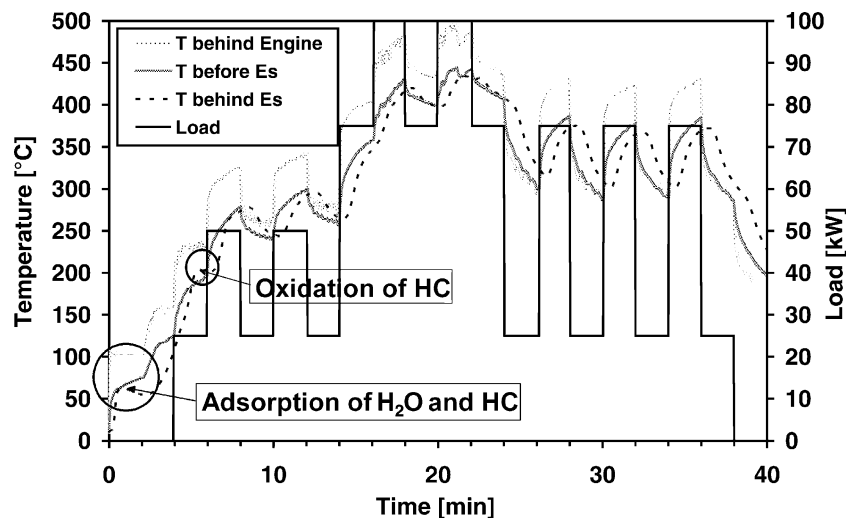

Figure 3. Temperatures before and after E$_s$ in a cold start test with changing loads on the PSI test bed "HARDI".

The average $DeNO_x$ in the stationary tests was calculated from the integrated NO_x concentrations before and behind catalyst for all three SCR catalysts and varied between 80 and 88%. The promoting effect of the pre-catalyst was smaller than expected and only significant for the coated catalyst C_s and M_s with much less active mass compared to the extruded E_s.

The main result of the tests at the PSI test bed "HARDI" was the mathematical model of the exhaust gas after treatment system, which could successfully be parameterised. For a detailed description refer to Lit. [10,11].

3.3. Liebherr dynamometer

For two SCR catalysts M_l and E_l dynamic control strategies were designed for the injection of urea solution. Figure 4 depicts the characteristic maps displaying the activity of the catalysts as a function of catalyst temperature and the gas hourly space velocity

(GHSV). Comparing these plots reveals that the coated catalyst M_l exhibits a stronger decline in activity than the extruded catalyst E_l at $T < 300$ °C. However, at low temperatures the extruded catalyst E_l needs more than 30 min for reaching equilibrium conditions, which prevents attaining maximum $DeNO_x$ under transient conditions. Consequently, in practice both catalysts showed a comparable performance in the ESC and ETC. Also, similar N_2O concentrations were found behind both catalyst types. At temperatures below 500 °C, 3–22 ppm N_2O was detected, rising to 140–200 ppm at the highest catalyst temperature of 560 °C.

Based on these activity maps a mathematical model and subsequently different dynamic, model-based feed-forward control strategies could be developed for catalyst M_l.

In an SCR system several sources of error can occur. The most severe are a wrong estimation of the NO_x concentration in the raw exhaust gas and a deviation in the urea dosage. In order to prevent the implications of
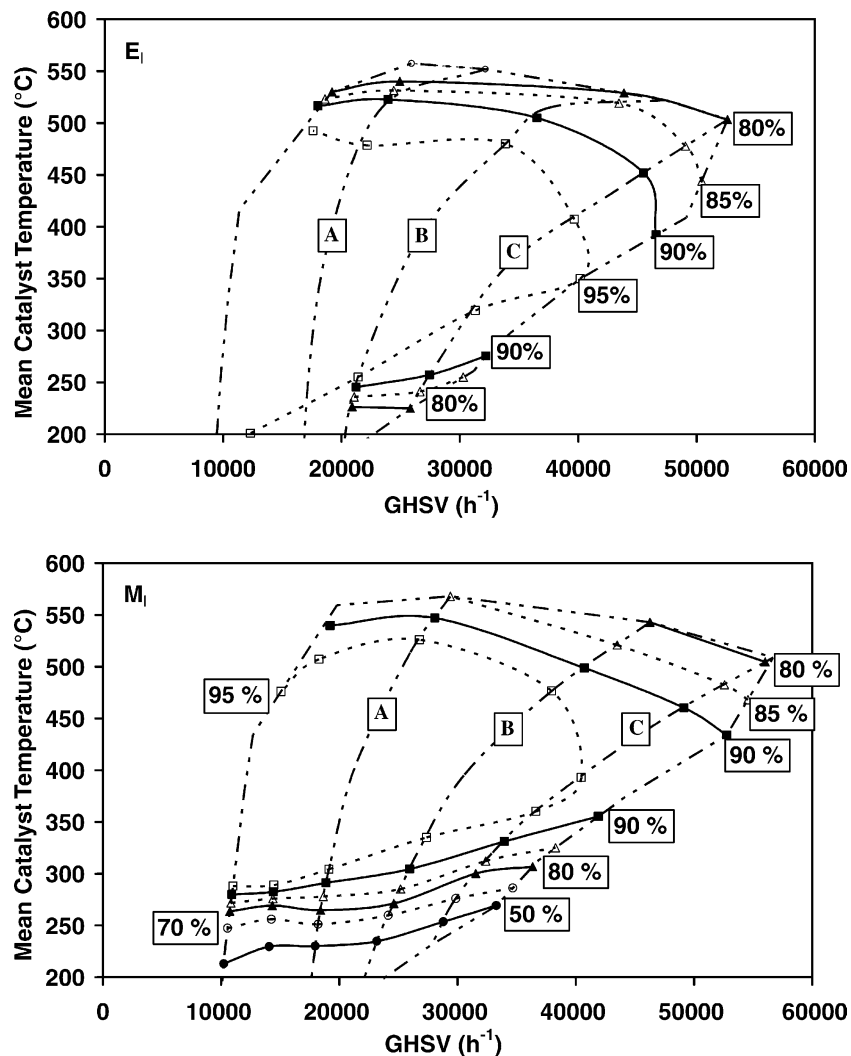

Figure 4. $DeNO_x$ (%) at 10 ppm ammonia slip as a function of catalyst temperature and GHSV for the extruded (E_l) and the coated catalyst (M_l). A, B, and C mark the three characteristic ESC speeds.
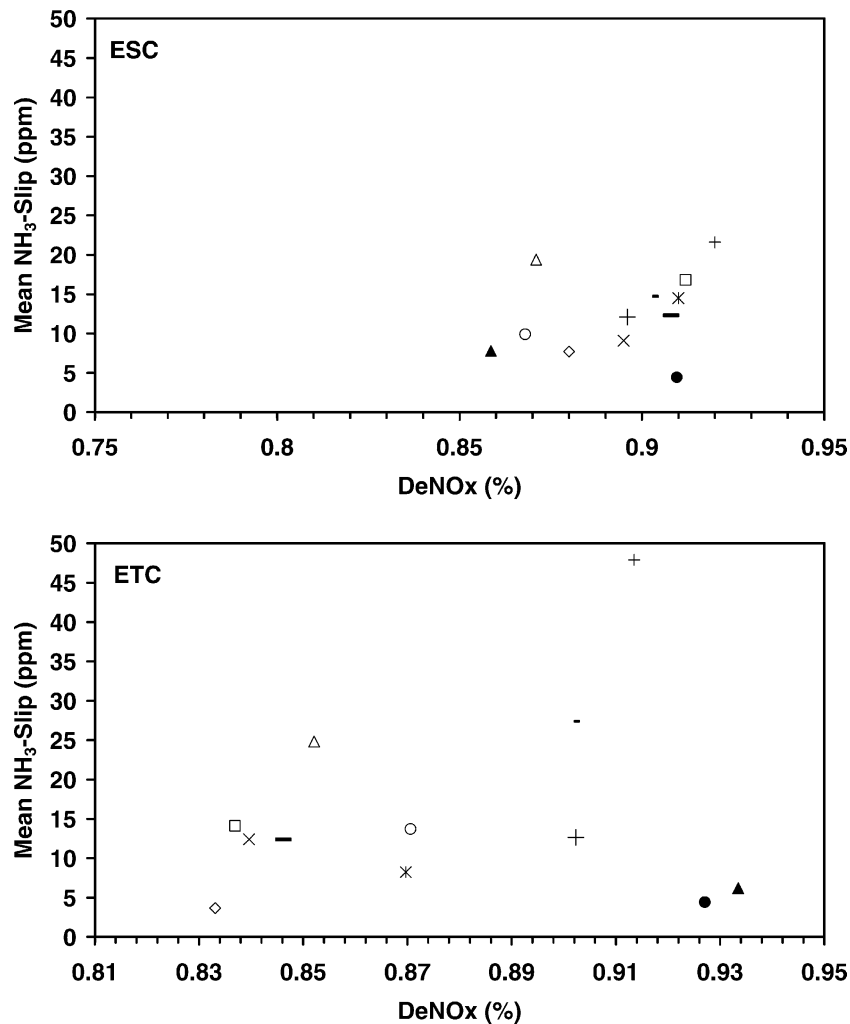
Figure 5. Specific emissions in the ESC and ETC for coated catalyst M$_l$ (open symbols) and extruded catalyst E$_l$ (filled symbols). The form of the symbols represents different control strategies: (+) static feedforward control, (−) feedforward control with ammonia storage estimator, (△,▲) static feedforward control and feedback control with a static prefilter, (○,●) feedforward control with ammonia storage estimator and feedback control with a static prefilter, (–) feedforward control with constant ammonia slip, (□) feedforward control with constant ammonia slip and feedback control with a static prefilter, (×) feedforward control with constant ammonia slip and feedback control with a model-based prefilter, (+) feedforward control with constant NO$_x$/NH$_3$ emissions, (*) feedforward control with constant NO$_x$/NH$_3$ emissions and feedback control with a static prefilter, (◊) feedforward control with constant NO$_x$/NH$_3$ emissions and feedback control with a modelbased prefilter.

these errors a feedback control is necessary, which could be realized by the utilization of a Siemens-NGK Smart NO$_x$ sensor. This sensor developed for the detection of NO$_x$ is cross-sensitive to ammonia, thus enabling the measurement of both components by applying an electronic filter to the primary signal. Originally, this control strategy was designed for the coated catalyst M$_l$, but it could easily be adapted to the extruded catalyst E$_l$.

Figure 5 depicts the mean ammonia emission as a function of mean DeNO$_x$ in the ESC and ETC for M$_l$ (open symbols) and E$_l$ (filled symbols) for different control strategies. The results of the ESC and ETC are comparable. However, the overall performance of the system strongly depends on the design and the tuning of the control strategy, e.g. the use of an advanced feedforward controller results in less mean ammonia slip than the use of the static feedforward controller. It

can clearly be seen that the extruded catalyst E$_l$ performed a little better than the coated catalyst M$_l$.

A detailed description of the experimental results on the Liebherr dynamometer and the development of the different control strategies can be found in [12–14].

4. Conclusions

The effectiveness of an SCR-system for the application in a mobile crane could successfully be demonstrated. With a robust single-type SCR catalyst of the size of a typical silencer a NO$_x$ conversion of > 93% at < 10 ppm ammonia slip could be reached. In order to guarantee a good DeNO$_x$ performance advanced control strategies containing a model-based feedforward as well as a feedback control are required.

Acknowledgment

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