RECENT IMPROVEMENTS OF THE LONG-TERM ROBUSTNESS OF NO_X STORAGE CATALYSTS SYSTEMS FOR DIESEL ENGINES

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ABSTRACT

The main focus of powertrain development is shifting gradually to the improvement of fuel economy and the reduction of CO_2 emissions. Lean burn combustion approaches such as the diesel engine or stratified spray-guided gasoline direct injection technology are an important element in achieving those goals due to the good fuel economy associated with these engine concepts.

A substantial success factor for both types of engines is the further improvement of innovative exhaust gas aftertreatment solutions able to convert nitrogen oxides, or NO_x under oxidizing conditions. The NO_x storage catalyst or lean NO_x trap (LNT) has become the most widely adopted choice for engines with gasoline direct injection systems and also for the current diesel Bluetec systems from DaimlerChrysler. In the heavy duty sector, as well as for the introduction of heavy passenger vehicles for the BIN5 legislation in the USA, urea-SCR technology is already in use in series production or is being developed for series production.

In this paper, requirements and trends for future NO_x aftertreatment technologies are being discussed. Ongoing development work focusing on improving the durability and sulfur resistance of LNT formulations will be presented and discussed in detail.

1. INTRODUCTION

The right plot in Figure 5 compares the conversion curves for different aging temperatures with the fresh catalyst. Except for one case, the catalysts were aged for 5 hours; only in the case of the 750°C aging the data for 10 hours aging were used since data for the 5h aging were not available. The plot shows that there are impacts of the aging for all temperatures even if an extension of the duration of the aging does not lead to further deactivation like in the case of 650 and 750°C. Thermal aging primarily affects NO_x performance at lower temperatures, which is evident from the drop in activity at 150°C after 650°C aging. After aging 750°C there is also a reduction in NO_x conversion activity at 200 °C. For higher operating temperatures above 250°C however thermal aging causes an increase in the catalytic performance. This effect has already been described in the literature [7]. The reason is presumably linked to precious metal sites which have been shown to limit the stability of nitrates at high temperatures. After moderate aging those precious metal sites sinter which attenuates their activity in general and their destabilising impact on nitrate sites in particular. Lower precious metal activity allows some nitrates to exist at higher temperatures than their inherent thermodynamic stability would suggest thereby improving NO_x storage at higher temperatures.

For diesel applications the current emission legislation standards can be met without a catalytic aftertreatment solution in most parts of the world. As of 2007 the only exception were the new Tier II Bin 8 and Tier II Bin 5 standards in the US, which are virtually impossible to comply with without a catalytic aftertreatment device. For example the Daimler E320 Bluetec, launched at the end of 2006 in the US represented the first diesel vehicle certified to Tier II Bin 8 and is equipped with a NO_x-storage catalyst. Outside the US, changes to the engine calibration were enough to bring emissions into compliance with existing standards. However new legislation standards in Japan, Europe and North America will in many cases require dedicated catalytic aftertreatment solutions for diesel applications since adjustments to the engine calibration alone won't be sufficient (Fig. 1). While the upcoming Euro 5 standards which will come into effect in 2009 won't require catalytic aftertreatment, the more challenging Euro 6 standards will most certainly require both a further reduction in raw emissions and an active NO_x aftertreatment.

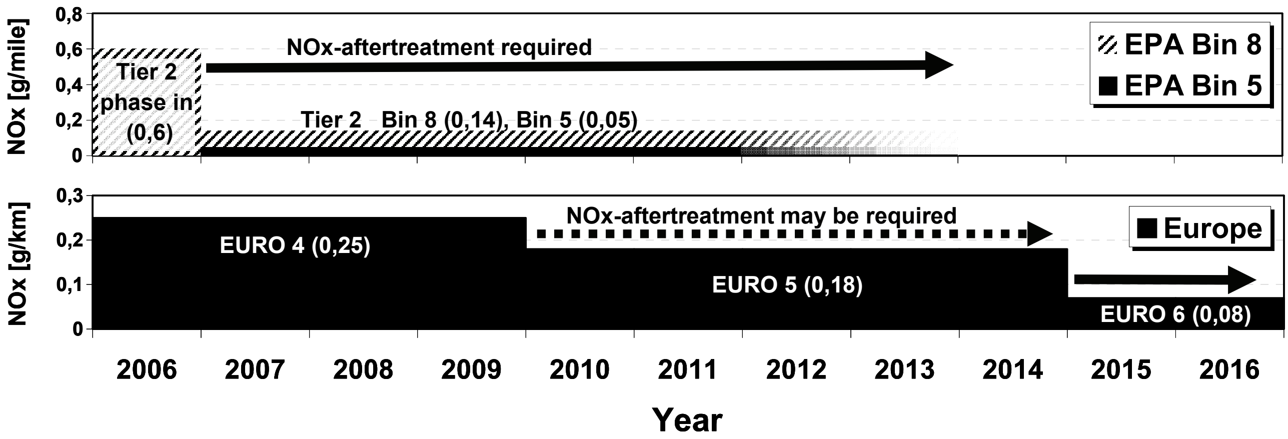

Figure 1: Emission legislation in North America and Europe

In Japan the market share of diesel passenger cars has always been relatively small in the past because of its particulate emissions and the higher noise levels than those found in gasoline engines. Improved driving characteristics as well as ever increasing fuel prices have led to an increased acceptance of the diesel in Japan as well. In Japan an active NO_x aftertreatment will most likely be widely required in 2009.

The first direct injection gasoline applications with stratified direct injection were introduced into the European market in 1999 and complied with the Euro 4 legislation standards. Like stoichiometric gasoline applications, gasoline DI applications have always required an active aftertreatment solution. LNTs are the key component for emission control. They function as a NO_x-control device under lean conditions as well as a regular three way catalyst under stoichiometric conditions [2].

The application of an LNT in a diesel vehicle poses some particular challenges compared to a gasoline DI case. In a diesel application the LNT must function properly in lean mode in the entire engine map since unlike in the gasoline DI case the diesel operates lean all the time. This puts high demands on the LNT's robustness. Another challenge is associated to the LNT's inherent vulnerability to sulfur poisoning which requires regular desulfations in order to restore the LNT's catalytic activity. The desulfation procedure involves quite harsh conditions of temperatures in the order of 600-750°C under rich, that is net reducing conditions. High temperatures are much harder to achieve in a diesel application compared to the gasoline DI case where desulfating conditions occur much more frequently. Furthermore an LNT requires brief intervals with rich exhaust gas, in order to provide NO_x control. Achieving rich exhaust gas in a diesel without adversely affecting driveability and sonic behaviour was a huge challenge that took some time to be solved.

In order to increase robustness and reduce cost, LNT systems are still being optimised and further improved. Especially for diesel applications one main approach in that regard is a reduction of the required desulfation temperature necessary to remove the sulphur adsorbed on the catalyst which causes deactivation over time. The desulfation procedure involves quite harsh conditions of temperatures in the order of 600-750°C which can cause unwanted thermal deactivation of the catalyst. A lower propensity to adsorb sulphur as well as a lower desulfation temperature required to remove the sulphur lead to a substantially improved durability of the LNT.

In this paper we focus on the ongoing development of diesel LNT formulations. We will present and discuss a detailed study into the effect of thermal aging at different temperatures and for various periods of time. These data allow to precisely define optimal operating conditions which in turn ensure maximum long term performance of the catalyst. The main subject of the remainder of the text is a formulation, denoted catalyst A, that exhibits improved sulphur release properties that allows for lower desulfation temperatures and hence result in improved long term performance as demonstrated in engine bench testing.

2. WORKING PRINCIPLE OF THE LNT

The basic mechanism of NO_x-reduction by an LNT involves storage of NO_x under lean engine operating conditions and subsequent reduction to nitrogen in brief pulses of net reducing gas composition. Substantial improvement in engine calibration of diesel engines has led to very smooth lean/rich transitions that go completely unnoticed by the driver. The NO_x storage process involves the oxidation of NO, which is the most abundant NO_x species, to NO_2. This step is crucial since NO_2 has a much higher adsorption rate than NO [3-6]. In the absorption process, NO_2 is stored as nitrate on basic sites on the catalyst, mainly oxides of alkali or earth alkaline elements such as barium or potassium. The transformation from NO_2 to nitrate involves another oxidation step which is believed to be assisted by precious metal present on the catalyst. The typical activity window of an LNT ranges from 150 to 500°C with a maximum NO_x conversion activity between 300 and 400°C.

In the temperature region below 300°C the activity is mainly limited by the kinetics of the NO-oxidation reaction. This reaction produces the precursor for the NO_x-storage, the NO_2, and the rate of this reaction decreases with temperature. In the high temperature regime the stability of the nitrates limits the conversion activity. Their thermodynamic stability decreases with increasing temperature and above 550°C Ba nitrates do not form anymore under lean gas atmosphere. The main storage materials comprise metal oxides that form stable nitrates in the relevant temperature range. Those are mainly oxides of alkali metals (Na, K, Rb, Cs), earth alkaline metals (Mg, Ca, Sr, Ba) and to some extend rare earth metals, like for instance La [7].

Two main mechanisms are responsible for the deactivation of an LNT catalyst in a diesel application [7,8]. Regular thermal regenerations of the particulate filter and desulfations of the LNT itself represent a substantial thermal load for the catalyst. Thermal aging impacts the NO_x conversion activity at moderate operating temperatures between 150-350°C first, while NO_x activity for higher operating temperatures is more resilient with respect to thermal exposure [8,9]. The second important deactivation mechanism involves the poisoning with sulphur contained in the exhaust gas. Sulfur forms very stable sulfates with the storage sites on the LNT and thereby reduces the number of sites available for NO_x-storage. Sulfur removal involves exposing the catalyst to reducing conditions at elevated temperatures of some 600-750°C for several minutes. Desulfation intervals can be anywhere in the region of one thousand to several thousand km. Sulfur contained in the fuel is the major source of the poisoning agent SO_2 which is why low sulfur fuel with less than 10 ppm of sulfur is recommended in

order to achieve realistic desulfation intervals. Low sulfur levels in the fuel reduce the numbers of desulfation events over the catalyst's lifetime and in turn reduce the thermal stress. Yet, even with 10ppm of sulfur in the fuel the catalyst still needs to be desulfated regularly, albeit with longer mileage between two events. Since lubricants also contain some sulfur components, sulfur poisoning will most likely still be an issue even with possible increased future use of synthetic fuels.
A delicate balance has to be struck in choosing the optimal desulfation temperatures. The desulfation represents thermal stress which can impact the NO_x conversion activity at moderate temperatures below 300°C. On the other hand inefficient desulfation due to insufficient temperature levels causes NO_x conversion at higher operating temperatures above 400°C to suffer. The desulfation temperature must therefore be defined depending on the type of application and the temperature window where NO_x conversion activity is mostly required.

3. AGING STUDY

The discussion in this paper will be mainly based on one LNT formulation, denoted catalyst A. If not stated otherwise the discussion pertains to this formulation. A systematic aging study has been conducted in order to assess the impact of high temperatures on catalyst aging. In particular the question regarding the relative importance of aging temperature and duration was being investigated. The sensitivity of catalyst aging to both parameters is crucial in order to define the optimal window for operating conditions which at least partly results from the trade-off between required desulfation temperature and maximum acceptable thermal exposure.

	1h	**2h**	**5h**	**10h**	**20h**	**50h**	**100h**
650°C			✓	✓	✓	✓	✓
750°C			✓	✓	✓	✓	✓
800°C			✓		✓		
850°C	✓		✓	✓			
900°C	✓	✓	✓				

Figure 2: Aging matrix for the LNT aging study

Cores with dimensions of one inch diameter and 3 inch length were being aged in a furnace at different temperatures and exposition times. The aging matrix is shown in Figure 2. It contains systematically varying temperatures and aging durations in order to derive quantitative trends and assess the relative impact of temperature and exposure time. The aging temperatures were chosen in order to reflect relevant conditions on the vehicle. Shorter durations were chosen for the higher aging temperatures since long expositions are not realistic on the vehicle. Furthermore, since aging processes are faster at elevated temperatures and therefore happen on a shorter timescale. The aged samples were tested on a synthetic gas bench with respect to their NO_xconversion activity.

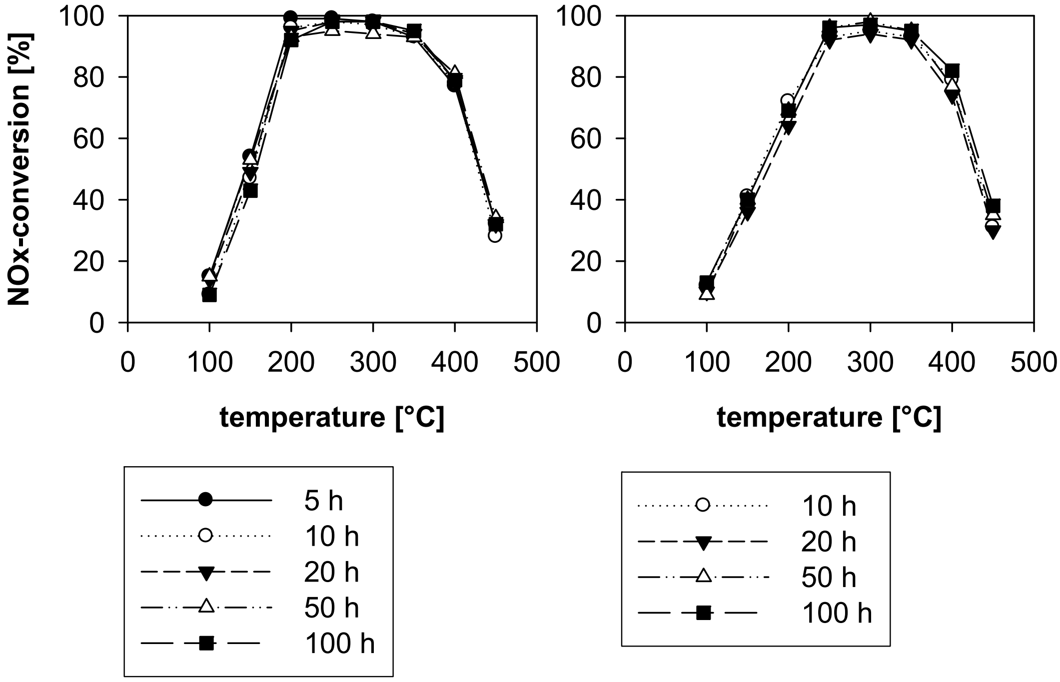

Figure 3: NO_x conversion for different times of aging and two aging temperatures; left T=650°C, right T=750°C

The activity test involves monitoring the exhaust species under lean/rich cycling conditions, typical of the operation on the vehicle. The NO_x conversion values represent average numbers calculated by averaging over both the lean and rich cycle. The duration of lean and rich cycles was 300 seconds and 20 seconds respectively at a space velocity of 35000 h^{-1}. The NO_x-concentration was 100ppm. Figures 2-5 show the NO_x conversion curve after aging for one given aging temperature and varying exposition time. The right plot in Figure 5 finally shows a comparison for a constant exposure time and varying temperature. For the lowest aging temperature (650°C) there is no noticeable deactivation for any time between 5h und 100h of exposition. The slight spread of results is most likely due to statistical variations in the aging and testing procedures. For aging at 750°C the same is being observed as for 650°C aging. The exposition time seems to have no impact on NO_x conversion activity for any duration between 5 and 100h (there are no data available for aging after 5h due to a malfunction of the analysis). For aging temperatures of 800, 850 and 900°C on the other hand there is a clear trend with exposition time. Longer thermal exposure leads to more severe deactivation of the catalyst.

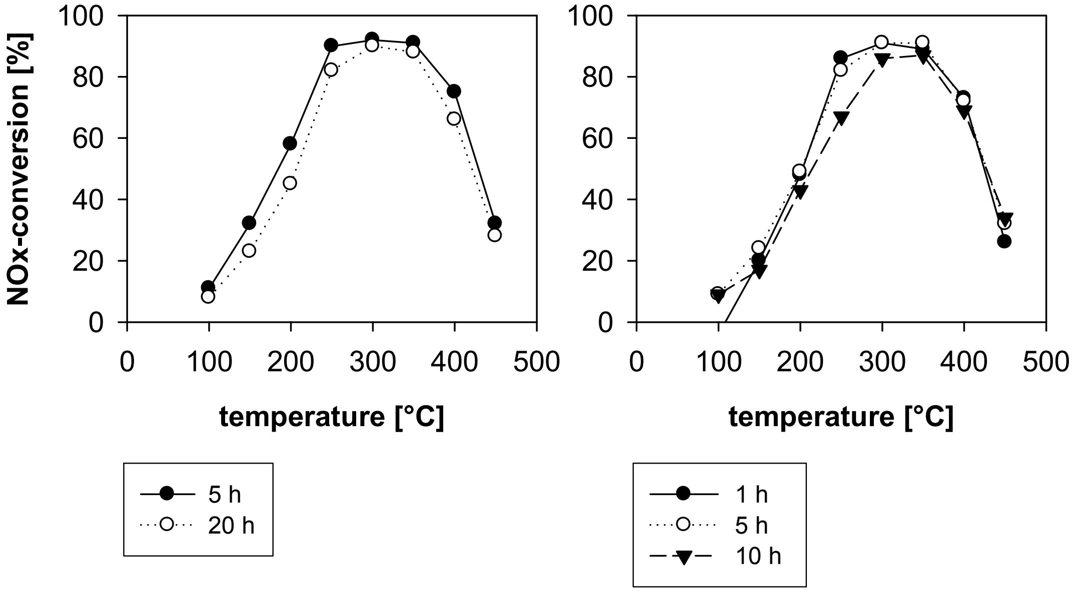

Figure 4: NO_x conversion for different times of aging and two aging temperatures; left T=800°C, right T=850°C

The right plot in Figure 5 compares the conversion curves for different aging temperatures with the fresh catalyst. Except for one case, the catalysts were aged for 5 hours; only in the case of the 750°C aging the data for 10 hours aging were used since data for the 5h aging were not available. The plot shows that there are impacts of the aging for all temperatures even if an extension of the duration of the aging does not lead to further deactivation like in the case of 650 and 750°C. Thermal aging primarily affects NO_x performance at lower temperatures, which is evident from the drop in activity at 150°C after 650°C aging. After aging 750°C there is also a reduction in NO_x conversion activity at 200 °C. For higher operating temperatures above 250°C however thermal aging causes an increase in the catalytic performance. This effect has already been described in the literature [7]. The reason is presumably linked to precious metal sites which have been shown to limit the stability of nitrates at high temperatures. After moderate aging those precious metal sites sinter which attenuates their activity in general and their destabilising impact on nitrate sites in particular. Lower precious metal activity allows some nitrates to exist at higher temperatures than their inherent thermodynamic stability would suggest thereby improving NO_x storage at higher temperatures.

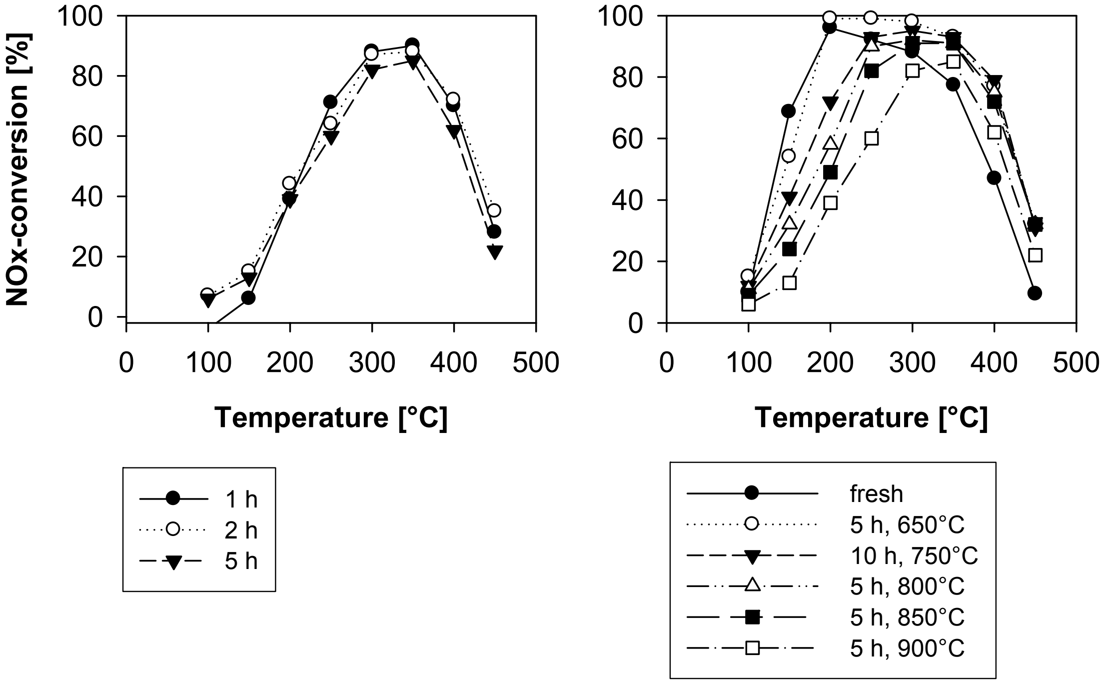

Figure 5: NO_x-conversion for different times of aging at T=900°C (left); NO_x-conversion for different aging temperatures and given time of aging (right)

One obvious strategy to protect low temperature NO_x activity as much as possible is therefore a reduction of thermal exposure during desulfation events by improving the sulfur release properties of the catalyst. The technology discussed in the aging study had been improved substantially with respect to the required desulfation temperature compared to its predecessor formulation (B). A reduction of the desulfation temperature by some 100°C allows to limit the peak thermal exposure during desulfation to 650°C and in turn to maintain good NO_x conversion activity at moderate temperatures. Figure 7 shows lab results for sulfur release tests performed on synthetic gas bench for catalysts A and B. The plot shows the rate of sulfur release as a function of temperature. The peak of maximum rate of sulfur release is occurring at clearly lower temperatures for catalyst A compared to formulation B.

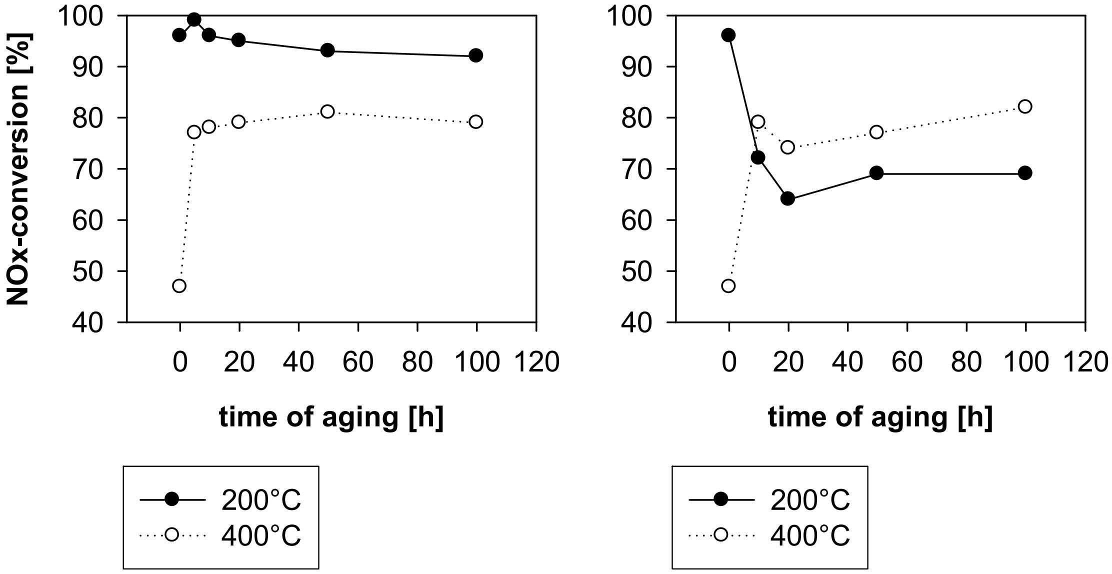

Figure 6: NO_x-conversions for two selected operating temperatures (200, 400°C) and two aging temperatures (left T=650°C, right T=750°C)

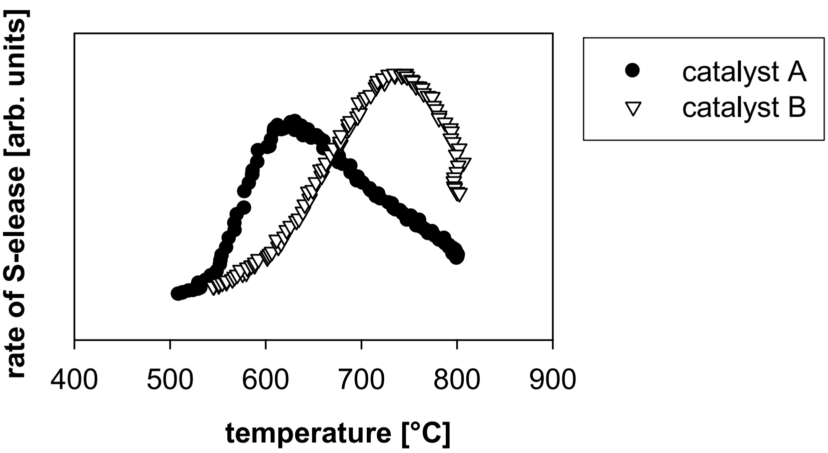

Figure 7: Sulfur release rate as a function of temperature for catalysts A and B

4. ENGINE AGING AND TESTING

In order to assess the long term stability under more realistic operating conditions catalysts were aged on the engine bench and evaluated in regular intervals in simulated NEDC (New European Driving Cycle) tests. This work was being conducted in cooperation with Bosch. The investigations were carried out with a catalyst volume of 2.5 L on a 2.2 L common rail diesel engine. Diesel fuel with 50 ppm sulfur content was being used throughout, so this aging also included aging effects due to sulfur poisoning. The catalyst was desulfated in regular intervals (after 1g per litre of catalyst exposure) and its performance in the NEDC cycle was evaluated after each desulfation. An aging sequence was being conducted with technologies A und B using a desulfation temperature of ~750°C and a desulfation strategy which had been optimised for technology A (Figure 8). The NO_x-performance as evaluated in the NEDC drops from 95% in the fresh state to some 60% after 450 hours of aging. Based on the sulfur exposure and assuming typical fuel consumptions of low sulfur fuel (10ppm) the entire aging corresponds to a mileage of some 200,000 km.
The trade off between the required desulfation temperature and the thermal aging linked to that is apparent in the test results. As Figure 7 shows the desulfation temperature for technology A is lower by some 100°C compared with catalyst B. The aging sequence was being repeated with catalyst A only and with a desulfation temperature of 650°C which is the optimal value for that technology. Furthermore the NO_x-regeneration strategy was being optimised. The results show an improved long term performance with a NO_x conversion of some 85% at the end of the aging.

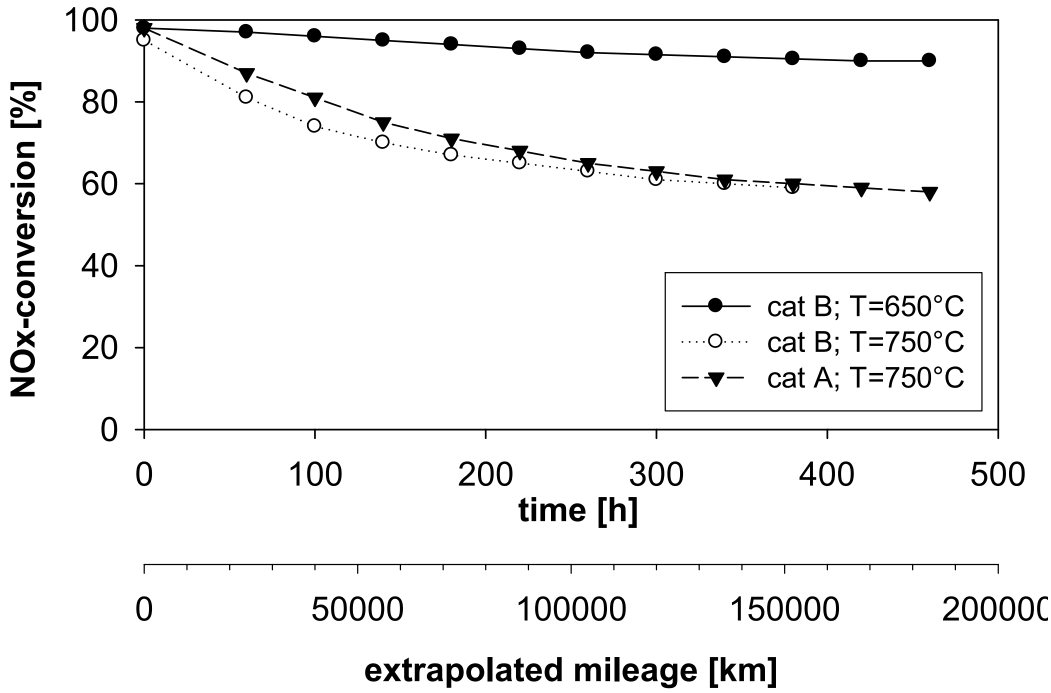

Figure 8: NO_x-conversions as recorded on the engine bench in simulated NEDC driving cycles as a function of aging time. Vehicle mileage was extrapolated assuming 15 ppm sulfur fuel

5. CONCLUSIONS

A detailed aging study has been conducted on synthetic gas bench in order to investigate the relative impact of aging temperature and time of exposure. Both parameters have an important influence on the catalytic performance. At increasing temperatures the rate of thermal deactivation accelerates so that a maximum temperature limit should be defined that the catalyst is not to exceed. In the case of technology A this limit is somewhere in the region of 650-700°C in order to protect and maintain good performance in the regime of moderate temperatures of 200-250°C. A reduction of the desulfation temperature by increasing the rate of sulfur release is the most important strategy to achieve this goal. The aging tests on the diesel engine demonstrated the improved robustness and durability of technology A once the desulfation temperature is adjusted to the technology’s optimal value. The present work shows that a holistic approach is crucial for a successful implementation of an LNT in a diesel application. Targeted design of the the chemistry of the LNT formulation as well as a good understanding of the importance and influences of application parameters are key in order to ensure long term stability and robustness of the LNT system.

6. ACKNOWLEDGEMENTS

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