

Sulfur Poisoning of a NO_x Storage Catalyst - A Comprehensive Modelling Approach

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ABSTRACT

This paper describes the development of a 0-D-sulfur poisoning model for a NO_x storage catalyst (NSC). The model was developed and calibrated using findings and data obtained from a passenger car diesel engine used on testbed. Based on an empirical approach, the developed model is able to predict not only the lower sulfur adsorption with increasing temperature and therefore the higher SO_x (SO₂ and SO₃) slip after NSC, but also the sulfur saturation with increasing sulfur loading, resulting in a decrease of the sulfur adsorption rate with ongoing sulfation. Furthermore, the 0-D sulfur poisoning model was integrated into an existing 1-D NO_x storage catalyst kinetic model. The combination of the two models results in an "EAS Model" (exhaust aftertreatment system) able to predict the deterioration of NO_x-storage in a NSC with increasing sulfation level, exhibiting higher NO_x-emissions after the NSC once it is poisoned. Additionally, the so called "deterioration factors", used to reflect the lower NO_x-conversion and higher NO₂/NO_x-ratio with increasing sulfation, were determined for different sulfur levels. Finally, the impact of sulfur poisoning on the NSC performance was assessed in steady state operating conditions, as well as under dynamic conditions, such as the US06 and the Federal Test Procedure (FTP75). The latter was used to evaluate the quality of the model under transient operating conditions. Thereby, simulated deterioration of NO_x-emissions for a sulfured catalyst, compared to a desulfated one, differ only about 2% from the measurement results, representing the high accuracy of the developed model.

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INTRODUCTION

The low fuel consumption and the excellent high power performance of passenger car diesel engines leads to a significant market share in Europe [1, 2]. Their high efficiency is also advantageous in terms of a reduction of fleet-average CO₂-emissions. However, due to their lean combustion with locally high temperatures in the combustion chamber, NO_x-emissions are high [3, 4, 5]. As conforming future emissions regulations only by engine internal measures is not conceivable, NO_x aftertreatment devices are of special interest [6, 7].

Two common technologies are known to reduce NO_x in the exhaust gas: on the one hand there is the selective catalytic reduction (SCR) technology, in which urea is injected upstream the SCR-catalyst. The latter decomposes to NH₃ and then reacts with NO_x to form nitrogen [8, 9]. Beside the active SCR system, NH₃ needed for SCR can also be produced by catalytic components upstream the SCR catalyst, if sufficient reductants are available in the exhaust. This is referred to as passive SCR [10].

Another device to reduce nitrogen oxides in the exhaust gas is the NO_x storage catalyst (NSC). A NSC stores nitrogen oxides during lean-combustion. After a certain duration the catalyst gets saturated with NO_x and its DeNO_x-efficiency drops. Therefore the NSC needs to be regenerated after reaching the maximum allowable NO_x-slip. The regeneration of the storage catalyst (also called purging) is performed by short term rich-combustion of the engine, in which the engine generated CO, HC and H₂ are used as reductants for the released nitrogen oxides [11, 12, 13, 14, 15]. The advantages compared to the SCR-system with urea injection are: lower space requirement, lower costs and the elimination of an additional reducing agent with the associated tank and dosing system. On the other hand, rich combustion, i.e. an air-fuel-ratio richer than stoichiometric, is necessary to regenerate the NO_x-storage catalyst and is associated with higher fuel consumption and emissions during

this operating state. Furthermore, the operating range with high NO_x -conversion rate is limited in terms of temperature and mass flow. However, for the current EU6(b) regulation in Europe the combination of NSC and diesel particulate filter (DPF) is a widespread solution to fulfill the emission requirements, especially for light segment vehicles [16, 17, 18, 19, 20, 21].

Due to the fact that the NO_x storage component of a NSC stores not only nitrogen oxides but also sulfur components, a NO_x storage catalyst is sensitive to sulfur [11, 22, 23, 24, 25]. Sulfur components, present in the fuel and lube oil, react to sulfur dioxide (SO_2) in the combustion chamber. The latter either directly forms sulfates on barium, or is oxidized on platinum to SO_3 and then stored on the alkaline earth metal [11, 26, 27]. Therefore, the DeNO_x -efficiency drastically drops, due to the so called sulfur poisoning of the NSC. Sulfates formed during the poisoning have a higher thermal stability than nitrates and nitrites, and hence their decomposition requires high temperatures and an alternating lean/rich-combustion, called desulfation or DeSO_x [11, 28, 29, 30, 31, 32]. This engine mode does not only lead to higher CO_2 -emissions due to the rich combustion, but in many cases also to thermal aging of the catalyst. A detailed study of sulfation and desulfation mechanisms can be found in [33], which serves as a basis for the results that are presented here.

Sulfur poisoning does not only lead to deteriorations in emission results, but also causes higher fuel consumption due to the periodically requested desulfation-events. Therefore, knowledge regarding the sulfation status of the catalyst is of particular interest. This applies in particular for upcoming legislations such as the real driving emissions-legislation (RDE) in Europe or the LEVIII-legislation in the US, due to the fact that emission limits are very low and OBD-considerations are extremely strict [13, 35, 36, 37, 38, 39, 40].

In literature, a significant amount of NSC-models has been published, describing several characteristics such as CO -conversion or NO_x -storage behavior as a function of different variables. However, only a few models have focused on describing the sulfation processes [26, 41, 42, 43, 44]. Thereby, measurements of synthesis testbeds are often used to obtain new results, which leads - depending on the composition of the feed gas - to deviations compared to the real behavior. For example, by using feed gas without oxygen for the sulfation process, various effects can be analyzed in detail, but the behavior on the engine testbed shows significant differences. Therefore, measurements related to the sulfur poisoning were performed on an engine testbed in order to depict realistic behavior.

This study describes the development of an empirical model with the ability to predict the sulfur status of the NSC, which is based on experimental data obtained from a diesel engine testbed. Furthermore, the drop in NO_x -conversion and the consequently higher NO_2 -emissions can be described as a function of the sulfation status, which is of particular interest in order to support engineers in various development and application work.

EXPERIMENT

In order to evaluate the influence of sulfur on the NSC-performance, measurements were executed on a transient engine test bed. The obtained data and results were used as an input for the NSC-model.

Engine and Instrumentation

The engine used for the investigations is a passenger car common rail diesel engine, with an engine displacement of around 2 liters. It is single-stage turbo-charged and equipped with variable turbine geometry (VTG), as shown in Figure 1 and Table 1. Furthermore, a so called hybrid EGR-system was installed to achieve low NO_x -engine out emissions. The cooled low pressure EGR (LP-EGR) was used to obtain low NO_x -raw emissions in high load operating range, while the uncooled high pressure circuit (HP-EGR) was used for warm-up. The exhaust aftertreatment system (EAS) and the turbine outlet were close-coupled. The EAS consists of a NSC followed by a coated DPF (cDPF). The used NSC is characterized by a cell density of 600cps (cells per square inch) and a volume of 1.65 liters, as summarized in Table 2. Additionally, an exhaust gas analyzer (EGA) was installed upstream (AVL CEBII®) and downstream the NSC (AVL Sesam i60®), complemented by a mass spectrometer MSS (V&F AirSense®) downstream the NSC in order to measure sulfur components H_2S , SO_2 and COS [11, 33]. The two-point calibration procedure was performed at least daily.

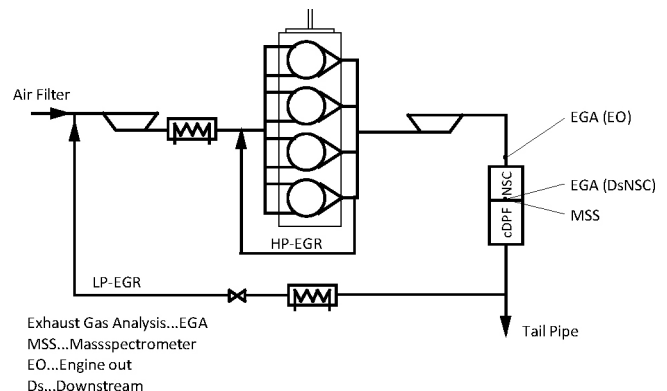


Figure 1. Engine configuration on test bed

Table 1. Engine info

Passenger car common rail diesel engine:	
Boosting system	Single-stage VTG turbocharger
EGR system	Hybrid (HP- and LP-EGR)
Engine displacement	2 liter class
Compression ratio	16.5
Emission family standard	Euro 6

Table 2. LNT substrate info

Substrate material	corderite
Volume	1.65 dm³
Substrate Length	10.16 cm (4 in)
Wall thickness	0.09 mm (3.5 mil)
Cell density	600 cps

Test Methodology

Due to the fact that - depending on fuel quality, engine power and vehicle weight - sulfur poisoning under real driving conditions takes several hundreds of kilometers, the sulfuring itself was done with a special fuel with 54ppm of sulfur. The special fuel was produced by adding sulfur to the special quality diesel in a volumetric way and the sulfur content of the blend was measured following DIN EN ISO 20884. Thereafter, measurements regarding NO_x-storage capacity or, for example, light-off-behavior were executed with sulfur free fuel in order to be objectively comparable. These tests were started with a regenerated NO_x-free NSC, i.e. no NO_x was stored at the beginning of the procedure. For the subsequent sulfuring the sulfured fuel was used again. Sulfuring itself was performed either without EGR (low CO- and HC-level) or with EGR (high CO- and HC-level). The fuel properties and the corresponding test methods can be found in Table 3.

Table 3. Fuel properties and applied standard test methods in brackets

Sulfur free fuel (Special quality diesel):	
Sulfur content	3 ppm _w (ASTM D-5453)
HC-ratio	1.89
FAME	0.0 Vol% (EN 14078)
Net Calorific Value	43216 kJ/kg (ASTMD-3338)
Density (at 288 K)	0.833 g/cm ³ (ISO 3675)
Viscosity (at 313 K)	3.08 mm ² /s
Cetane Number	52 (ISO 5165)
Sulfured fuel (based on special quality diesel as above):	
Sulfur content	54 ppm _w (DIN EN ISO 20884)

Emission results over FTP75 are only plotted as cumulated values and not weighted with any factors. Furthermore, the FTP75 was started as a cold test cycle, which means initial engine and aftertreatment temperatures of about 293K. Moreover, the NSC-regeneration events and durations were kept constant for various sulfur loadings due to comparability reasons [11, 33].

In order to detect irreversible damage of the catalyst by high-temperature desulfation, reference measurements were carried out after each desulfation. As shown in Figure 2, irreversible changes in NSC-performance could be avoided, so that the full NO_x-storage capacity was available again after desulfation.

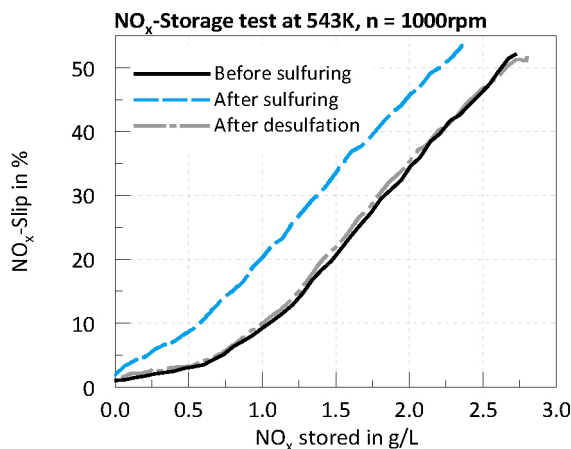


Figure 2. Elimination of irreversible changes in the NSC

For desulfation, the lean/rich-durations were chosen in a way to guarantee temperatures in the NSC between 810K and 970K. A detailed study on effective desulfation can be found in [11, 33].

Experimental Results

The impact of sulfation on the performance of the NSC in stationary operation mode is plotted in Figure 3. The amount of sulfur stored in the NSC was determined via the subsequent desulfation, where sulfur is mainly released as SO₂ and H₂S [33]. The NO_x-storage capacity decreases massively with increasing sulfur loading. In addition, the NSC is gradually saturated with ongoing sulfation. This effect can probably be explained by the reduction of available precious metals in case of higher sulfation levels, due to the fact that sulfur reacts with precious metals to form unreactive compounds [11, 45, 46, 47, 48]. Therefore, no more precious metal is available to oxidize SO₂ to SO₃. Since, compared to SO₂, SO₃ is preferably stored on barium, the catalyst becomes saturated. Moreover, impacts of sulfur poisoning on the NO_x-storage capacity are less at low temperatures. This is due to the partial NO_x-storage on cerium or on the washcoat at low temperatures, which runs unaffected by the sulfation [11, 33]. At these low temperatures, the storage of nitrogen oxides is based on physisorption or the connection with condensed water [11].

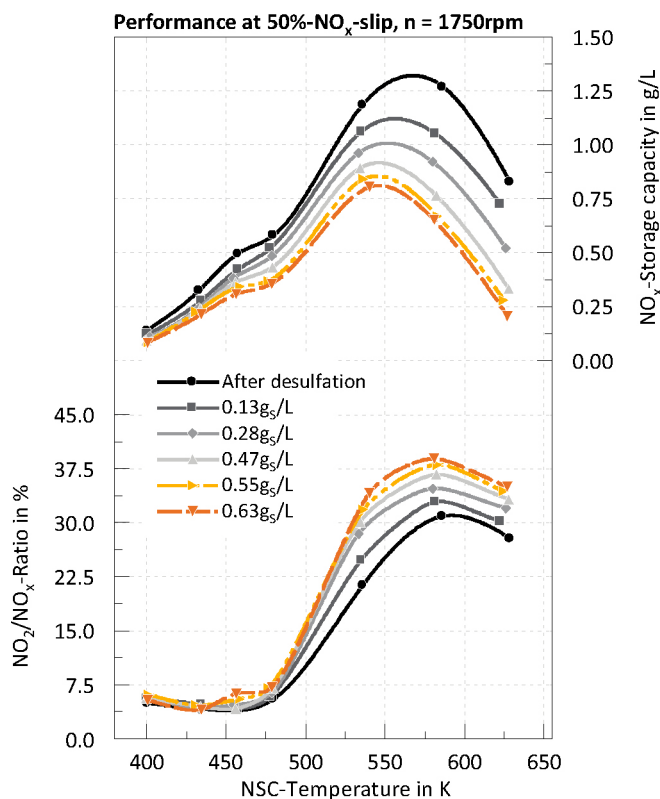
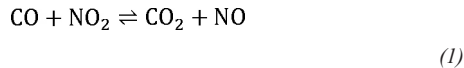


Figure 3. NSC-performance at various sulfation levels during NO_x-Storage-tests

In addition, the NO₂/NO_x-ratio increases with growing degree of sulfation. The oxidized NO can no longer be stored on barium, due to the fact that its storage-active sites are already blocked. Therefore,

NO_2 -emissions after NSC rise. Furthermore, the oxidation of carbon monoxide (CO) and hydrocarbons (HC) by the higher amounts of available NO_2 is conceivable, see Eq. (1). However, no clear trend regarding the CO- and HC-conversion could be figured out by the experimental data (not plotted here), presented in [11]. According to that, the latter effect is likely to play a minor role.



Transient operation mode also shows a significant decrease in NO_x -storage ability with increasing sulfur content, see Figure 4. During the first 200s of FTP75 only small emission deterioration is detected. On the one hand the NSC was empty at the cycle start, i.e. NO_x -free, and despite the sulfur loading, enough NO_x -storage active sites are available to adsorb NO_x . On the other hand, the NO_x cold-storage mainly takes place on the washcoat or on cerium, as mentioned before, and therefore the drop in NO_x -storage is significantly lower.

However, cumulated NO_x -results over the entire cycle show significantly higher NO_x -emissions with increasing degree of sulfation. Accordingly, this results in a deterioration of NO_x -emission of over 45% if the NSC is loaded with 0.63g/L sulfur, compared to the sulfur-free status.

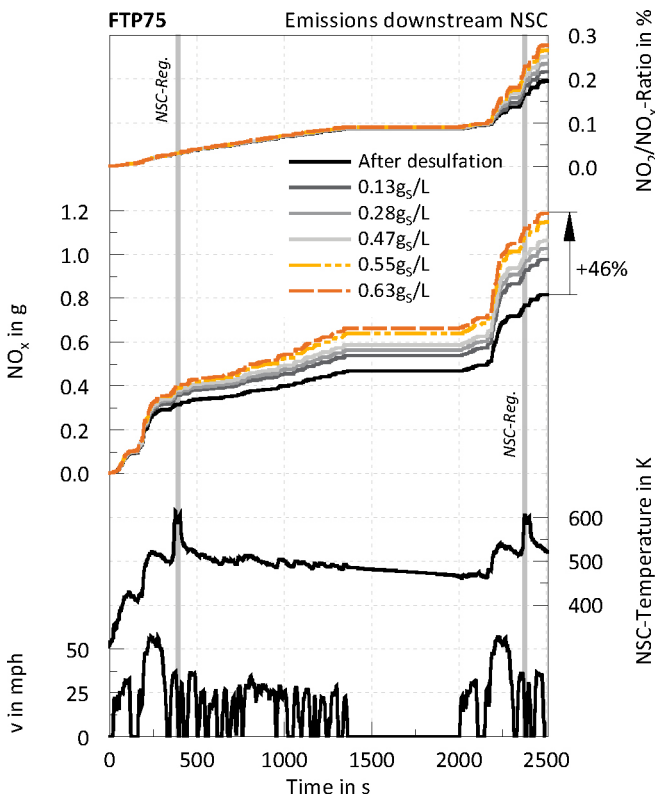


Figure 4. NSC-performance at various sulfation levels in the FTP75

Despite the lower NO_x -storage ability in the sulfated status, NO_2 -emissions initially remain approximately at the same level and rise only in the last part of the FTP75. This is likely to be related to the relatively low NSC-temperature, whereby NO_2 -formation occurs slowly compared to its formation at higher temperatures. Therefore, an increase in NO_2 -emissions is only visible if the NO_x -loading on the NSC is high. At the end of the FTP75 cycle and before the second purging event, the NSC gets full of NO_x and the oxidized NO leaves the NSC. This leads to an increase of the NO_2/NO_x -ratio, which is augmented in the sulfated state, as discussed in Figure 3. Again, an interaction of NO_2 with hydrocarbons or carbon monoxide is attainable, oxidizing the latter to CO_2 and reducing nitrogen dioxide to NO, although CO- and HC-emissions show no clear trend (not plotted here) [11, 33].

To gain further insights into the sulfur adsorption performance, a sulfur balance was performed. The amount of sulfur at the catalyst inlet (calculated based on fuel consumption, S_{inlet}), corresponds to the amount of sulfur stored in the NSC (determined via desulfation, S_{Stored}), plus the passed SO_2 (detected by mass spectrometer, $\text{SO}_2^{\text{Passed}}$) and SO_3 ($\text{SO}_3^{\text{Passed}}$). The latter was not detected by measurement and consequently determined by the mentioned sulfur balance in Eq. (2). Opposing the theoretically stored sulfur by using the fuel consumption and the real sulfation measured during the desulfation permits conclusions about the passed through SO_2 and SO_3 during sulfation.

$$S_{\text{inlet}} = S_{\text{Stored}} + \text{SO}_2^{\text{Passed}} + \text{SO}_3^{\text{Passed}} \quad (2)$$

In Figure 5, cumulated SO_x -storage is shown for a low load operation point with low CO- and HC-level. With increasing sulfation-time, less sulfur is stored in the NSC relative to the sulfur in the fuel, leading to a gradually saturation of the catalyst. After different sulfation times, desulfation-events were performed to evaluate the sulfur amount stored in the catalyst, whereby the concentration of SO_x after NSC was derived. Saturation behavior can be clearly seen, noticing that measured SO_2 -emissions after NSC during sulfation differ significantly from the balanced SO_x -trend. The latter indicates that at the present temperature of 473K, SO_2 is mainly oxidized to SO_3 in the catalyst before it is stored. With increasing sulfur loading SO_3 -adsorption drops, which leads to a higher SO_3 -slip after NSC, whereas SO_2 -breakthrough rises much less. Hence, the majority of sulfur is stored by prior oxidation of SO_2 to SO_3 in the illustrated case. Therefore, increasing sulfur loading predominantly leads to a higher SO_3 -slip after NSC.

Additionally, generated knowledge was extrapolated in fields with exorbitantly long sulfation times, taking into account that due to the cost-intensive test execution on a testbed no measurements were available. However, since sulfuring the catalyst is already virtually completed at the considered sulfation time, only minor deviations from real behavior are expected [11, 33].