

Sulfur Control for NOx Sorbate Catalysts: Sulfur Sorbate Catalysts and Desulfation

Jim Parks, Aaron Watson, Greg Campbell, and Greg Wagner
Goal Line Environmental Technologies LLC

Mike Cunningham, Neal Currier, Tom Gallant, and George Muntean
Cummins Engine Company

Copyright © 2001 Society of Automotive Engineers, Inc.

ABSTRACT

NOx sorbate, or "trap", catalysts have achieved >90% reduction of NOx from lean exhaust streams over a broad range of temperatures. Since diesel can be used as the reductant for NOx sorbate catalysts, the sorbate catalyst technology offers great potential for NOx control in a broad range of mobile diesel applications. Traditionally, the longevity of NOx sorbate catalysts in diesel exhaust applications has been limited by sulfur masking of NOx sorption sites. Two methods to control sulfur compounds and their associated effects will be presented here. Upstream sulfur sorbate, or "trap", catalysts are used to control the rate of sulfur masking by diverting sulfur away from the NOx sorbate catalyst. Desulfation of NOx sorbate catalysts can lead to the removal of sulfur compounds from the catalyst and reactivation of NOx sorption sites. Data demonstrating sulfur control with both of these methods will be presented here. The effect of temperature on sulfur control and thereby NOx sorbate catalyst longevity will be discussed.

INTRODUCTION

Lean burn engines offer the benefits of greater fuel economy and reduced CO₂ emissions, a greenhouse gas. However, the excess O₂ in the lean burn exhaust complicates the catalytic control of NOx emissions. One technology that has been demonstrated to control NOx in lean burn exhaust is the NOx sorbate catalyst.¹⁻⁷ This technology is also referred to as a NOx adsorber catalyst or a NOx "trap". Here the term "sorbate" is used since, in theory, NOx absorption is preferred to NOx adsorption.

The NOx sorbate catalyst offers great potential for NOx control in diesel applications since NOx reduction levels >90% can be achieved under steady-state conditions

using diesel fuel as the reductant.³ Traditionally, the longevity of NOx sorbate catalysts has been limited by sulfur masking of NOx sorption sites.⁴⁻⁷ Although lower sulfur levels in diesel fuel are anticipated with recent proposed standards, some control over the adverse effects of sulfur on NOx sorbate catalysts will be required for successful implementation of the technology.

Two methods to control sulfur compounds and their associated effects will be presented here. The two methods are: (1) diversion of sulfur from the NOx sorbate catalyst with an upstream sulfur sorbate, or "trap", catalyst^{3,8,9} and (2) recovery of masked NOx sorption sites by desulfation of the NOx sorbate catalyst^{5-7,10}. Engine testing of an aftertreatment system containing both sulfur and NOx sorbate catalysts was used to demonstrate both sulfur control techniques. The engine tests included an aging study under light-duty loads to demonstrate the sulfur sorbate catalyst and a subsequent heavy-duty load test to demonstrate desulfation of the NOx catalyst in the diesel engine temperature range of operation. The effect of temperature on both sulfur control techniques will be discussed.

CATALYST SYSTEM

A two-chamber catalyst system was used for the engine tests; the system has been described previously^{3,8,10} and will be reviewed here. The two chambers will be referred to as reactor 1 (R1) and reactor 2 (R2). Each chamber of the device contains a sulfur sorbate catalyst upstream of a NOx sorbate catalyst. Both catalysts are of sorbate type and periodically need to be regenerated. Typically, one chamber is "on-line" treating the main exhaust flow while the other chamber is regenerated "off-line"; however, both chambers may be "on-line" simultaneously to increase system efficiency. Valves control the flow of exhaust and regeneration gases.

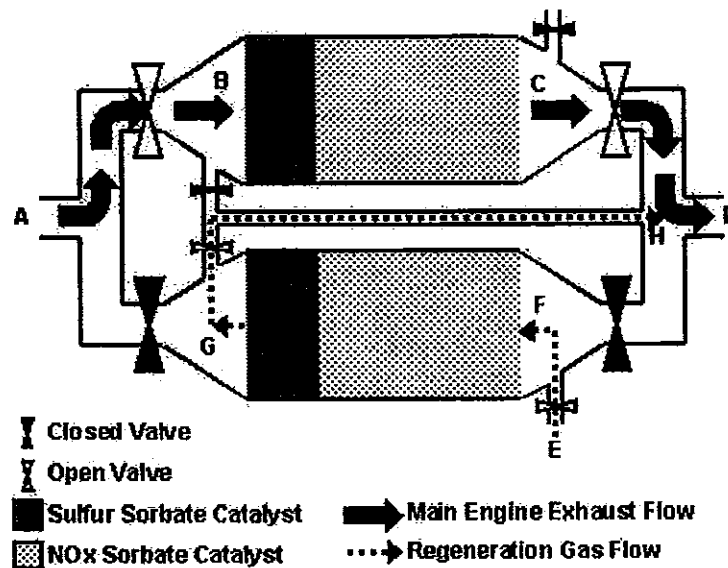


Figure 1. Dual-chamber system used for engine tests. The upstream sulfur sorbate catalyst diverts SO_2 from the downstream NOx sorbate catalyst in each chamber. Regeneration of the catalysts occurs in a direction reversed from the main exhaust flow.

A diagram of the system showing the flow of gases is shown in **Figure 1**. The exhaust from the engine enters the system at point **A** and is diverted to the catalysts in one chamber (**B**). The sulfur sorbate catalyst is upstream of the NOx sorbate catalyst and removes SO_2 from the exhaust. NOx is sorbed on the NOx sorbate catalyst, and both catalysts oxidize CO and hydrocarbons. The treated exhaust (**C**) mixes with the regeneration exhaust (**H**) before leaving the system (**D**). Regeneration is accomplished by closing off one chamber of the system, injecting a low flow of net-reducing gas into the chamber (**E**), and passing the gas over the catalysts in a direction reversed from the main exhaust flow (**F**). The regeneration exhaust containing the desorbed SO_2 (**G**) is carried via a bypass line back to a point downstream of the dual-chambers where the regeneration exhaust is mixed back into the main exhaust stream (**H**). A downstream oxidation catalyst (not shown in **Fig. 1**) oxidizes CO and hydrocarbons remaining from the regeneration process.

The space velocity of the sulfur sorbate catalyst was 46,000/hr for each chamber. The space velocity of the NOx sorbate catalyst was 23,000/hr for each chamber. Both catalysts were supported on a 230 cpsi ceramic substrate. During regeneration, the space velocity of the net-reducing gas was typically 3,700/hr. The net-reducing gas was formed by injecting diesel fuel into the catalyst chamber with an air-assisted injector. The diesel-air mixture was combusted and reformed over the catalysts to create the reducing gas for regeneration.

CATALYST TEMPERATURE PERFORMANCE

Data demonstrating the performance of the catalysts used in this study as a function of temperature is presented here. The data was taken on a bench scale reactor with simulated exhaust gases.

SULFUR SORBATE CATALYST - The performance of the sulfur sorbate catalyst has been documented previously⁸ and is summarized in **Figure 2**. The space velocity for the data was 30,000/hr, and the inlet gas contained 100 ppm SO_2 and 8% O_2 . H_2 , in a N_2 carrier, was used as the reductant in the study. The data shows the SO_2 sorption efficiency over a 10-minute sorption period and the relative release rate of SO_2 measured during regeneration. The sorption efficiency was greater than 90% for all temperatures tested; however, the rate of SO_2 release during regeneration slowed greatly as catalyst temperatures dropped from 350 °C to 150 °C.

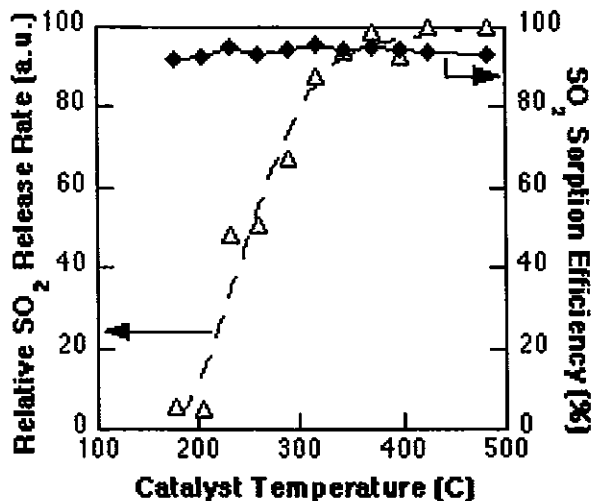


Figure 2. Performance of the sulfur sorbate catalyst as a function of temperature with H₂ as the reductant.

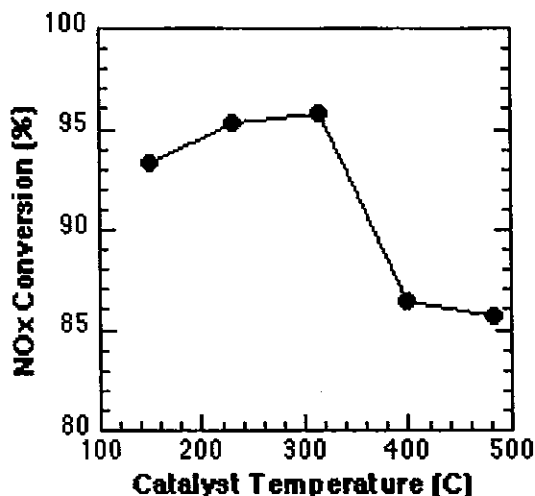


Figure 3. Performance of the NOx sorbate catalyst as a function of temperature with H₂ as the reductant.

NOx SORBATE CATALYST - The NOx sorbate catalyst used here is capable of desulfation at temperatures in the diesel engine exhaust range (<600°C) and has been described previously¹⁰. The NOx reduction performance of the catalyst vs. temperature is shown in Figure 3; the desulfation performance will be described below in the "Desulfation" section. The data in Fig. 3 was taken on a bench scale reactor. NOx conversion for a 5-minute sorption period as a function of temperature is shown. The space velocity for the NOx catalyst was 25,000/hr. The inlet gas contained 100 ppm NO, 100 ppm CO, 100 ppm propylene, 12% O₂, 8% CO₂, and 5% H₂O. H₂, in a N₂ carrier, was used as the reductant. The catalyst is effective at removing NOx over a broad range of temperatures with peak NOx removal occurring near 300°C.

ENGINE TEST DESCRIPTION

The catalyst system was tested on a light-duty platform with a 3.9-liter turbo-assisted diesel engine (Cummins 4B3.9T). The engine was attached to a generator as a gen-set, and load was applied to the engine with a resistive load bank (50 kW maximum load). The engine speed was held constant at 1870 rpm. All testing was performed with steady-state operation of the engine. No. 2 Diesel fuel was used for all tests; the average sulfur level in the fuel was 536.6 ppm.

The engine tests were conducted in three stages over a total of 170 hours: (I) the engine was operated with a light-duty test cycle for 150 hours, (II) heavy-duty engine loads were used to desulfate the NOx catalyst (10 hour time frame), and (III) the light-duty test cycle was repeated for 10 hours to compare with the fresh catalyst results. The light-duty test cycle (stages I and III) consisted of operation at four load points. The loads, in cycle order, were 0 kW, 15 kW ("15 kW up"), 25 kW, and 15 kW ("15 kW down"). The engine was operated at each load point for 15 minutes. 10 hours of operation were performed each day with cold starts occurring at the 0 kW load point without regeneration. The catalyst system was operated at constant 2.5-minute sorption-regeneration cycle periods; only one chamber was open to the main exhaust at one time, which allowed comparison between the performance of both chambers. The fuel penalty over the 150 hour stage I was 9.08%; No. 2 Diesel was also used as the catalyst reductant. Engine out NOx levels varied with engine load and are shown along with exhaust temperature in Figure 4.

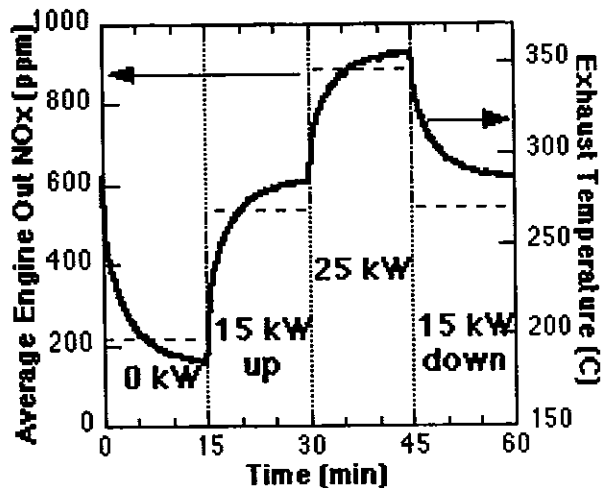


Figure 4. Average engine out NOx levels and typical exhaust temperatures for the light-duty steady-state load cycle.

The stage II desulfation test was performed by operating the engine at increasing engine loads from 25 kW to 50 kW in 5 kW increments. Each heavy-duty load was maintained for 30 minutes. Between operation at the

heavy-duty loads the light-duty test cycle was performed to monitor performance. Standard regeneration conditions were used during the desulfation process.

One set of analyzers was used to measure engine out and catalyst system out exhaust. During each 15-minute load point, engine out measurements were made during the first 5 minutes and catalyst system out measurements were made in the last 10 minutes. An ultraviolet adsorption analyzer was used for SO₂ measurement, and a chemiluminescent detector based instrument was used for NO_x measurement.

ENGINE TEST DATA

The results from the engine tests are summarized in Figure 5. NO_x conversions are shown for all four load points in the light-duty test cycle. During stage I of the tests, NO_x conversions declined from a range of 80-95% to a range of 20-50% as sulfur masking occurred. The average decay rate in NO_x conversion was 0.37% per hour; thus, decay rates with an upstream sulfur sorbate catalyst were less than typical decay rates of 3% per hour reported without an upstream sulfur catalyst.³ During desulfation (stage II), NO_x sorption sites on the catalyst were reactivated and NO_x conversion levels returned to a range of 55-89%. In stage III, the NO_x

conversion began to decline in similar fashion to the stage I data as the light-duty test cycle was resumed.

LIGHT-DUTY CYCLE AGING (STAGE I) - The capability of the sulfur sorbate catalyst to divert SO₂ past the downstream NO_x sorbate catalyst enabled a lower decay rate in NO_x conversion in the stage I light-duty cycle data. The variation in performance of the sulfur sorbate catalyst as a function of temperature (see Fig. 2) was observed in exhaust sampling during the engine tests. Figure 6 shows the engine out and catalyst system out data obtained from one hour of the light-duty test cycle. The engine out SO₂ levels are relatively constant as expected in steady-state engine operation. The profile of the catalyst system out SO₂ data varies between load points. During the 0 kW load point, the catalyst system out SO₂ level is low and relatively constant. However, during the 25 kW load point, SO₂ peaks (A and B) resulting from the release of SO₂ from the sulfur sorbate catalyst during regeneration occur. The magnitude of the peaks is larger than the engine out SO₂ level, and the frequency of the peaks (1 peak per 2.5 minutes) matches the frequency of regeneration as expected. The SO₂ peaks from regeneration of the R1 catalyst (A) are larger than from regeneration of the R2 catalyst (B); the difference suggests that more SO₂ is being diverted by the sulfur catalyst in R1.

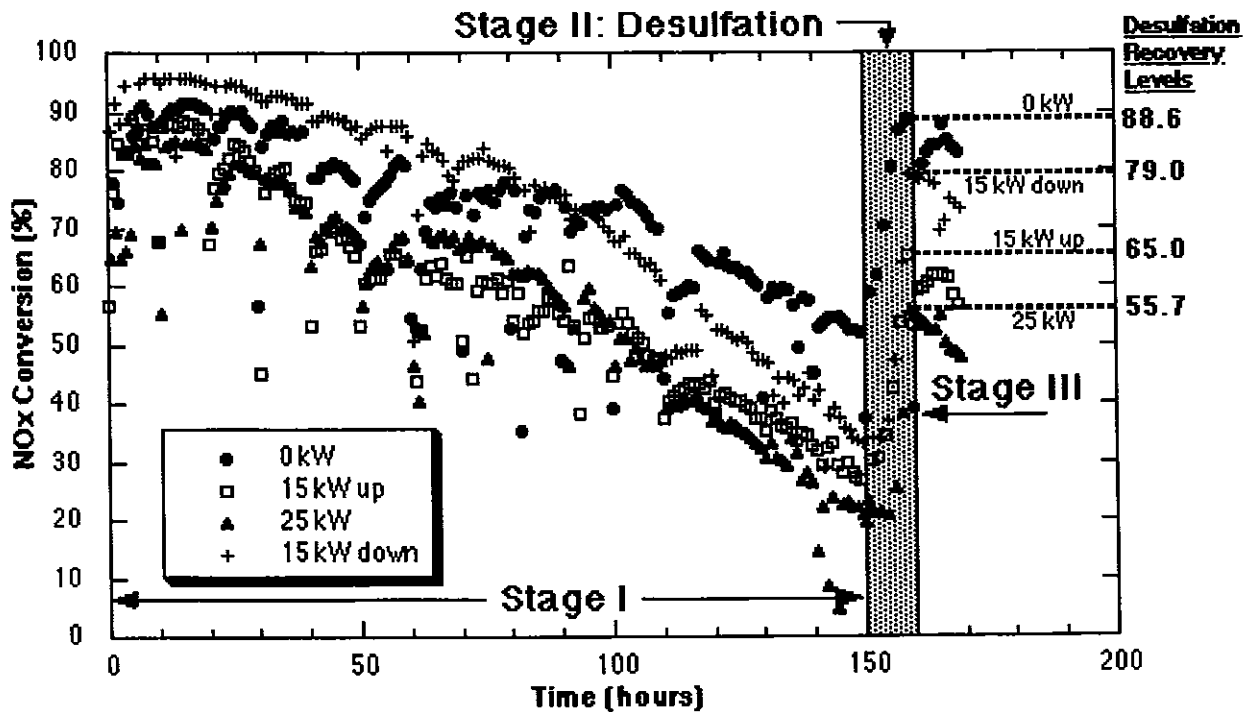


Figure 5. Summary of the results from the engine tests.

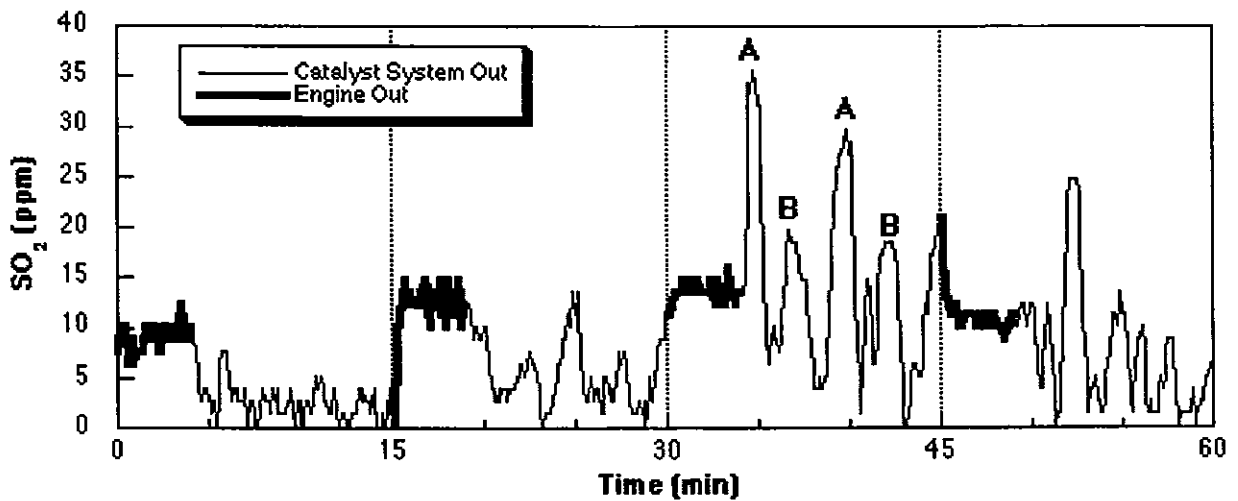


Figure 6. SO₂ measured at engine out and catalyst system out positions for one light-duty load cycle.

Load Point	Average Engine Out Exhaust Temperature (°C)	Average Engine Out SO ₂ (ppm)	Average Catalyst System Out SO ₂ (ppm)	SO ₂ Diversion Efficiency
0 kW	202	9.1	2.5	26.9 %
15 kW up	268	12.7	5.2	40.8 %
25 kW	343	13.9	13.5	97.3 %
15 kW down	298	10.6	7.1	67.5 %

Table 1. Efficiency of diverting SO₂ from the downstream NOx sorbate catalyst. Data shown for each load point and corresponding exhaust temperature

Table 1 summarizes the amount of SO₂ diverted past the downstream NOx sorbate catalyst by the sulfur sorbate catalyst (SO₂ diversion efficiency). Assuming that all SO₂ slip through the sulfur sorbate catalyst is trapped by the NOx sorbate catalyst, the diversion efficiency can be determined by comparing engine out and catalyst system out SO₂ levels. The data shows that SO₂ diversion efficiency increases with increasing exhaust temperature as expected by the data shown in Fig 2. Since efficient SO₂ sorption occurs at low temperatures (<200 °C), the SO₂ released at the 15 kW and 25 kW load points may be from SO₂ sorbed and stored during operation at the 0 kW load point; thus, the SO₂ diversion efficiency data for each load point may be affected by prior SO₂ sorption. Note that catalyst temperatures were generally lower than the engine out exhaust temperature due to cooling by the regeneration gas.

light-duty test cycle as a function of the exhaust temperature where desulfation occurred. Data was taken in the order of increasing temperature. The NOx conversion shown is the relative NOx conversion to the NOx conversion obtained with the fresh catalyst at hour 15 in the stage I data.

DESULFATION (STAGE II) - During the desulfation process, NOx conversion levels improved as the desulfation temperature increased. Figure 7 shows the NOx conversion performance for each load point in the

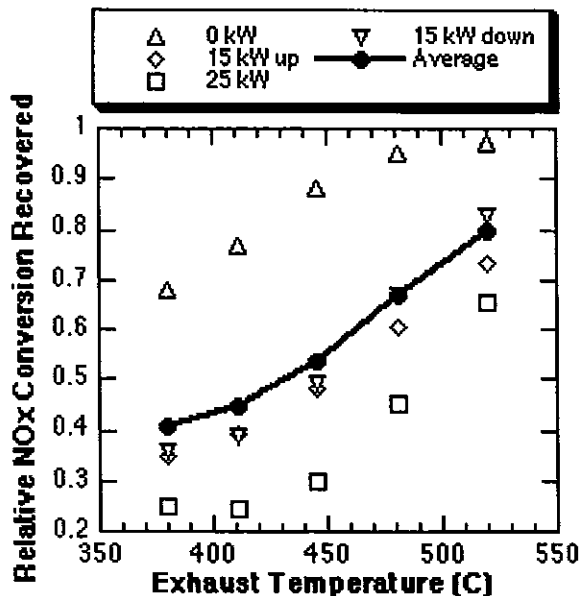


Figure 7. NOx conversion, shown relative to the NOx conversion obtained with a fresh catalyst, obtained after desulfation at the exhaust temperatures shown on the x-axis during heavy-duty load operation.

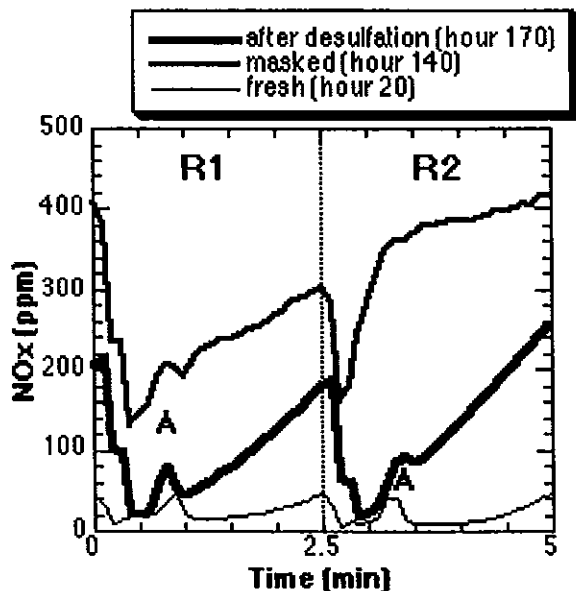


Figure 8. Catalyst system out NOx levels measured for "fresh" catalysts, "masked" catalysts, and catalysts "after desulfation". NOx peaks from the regeneration of the opposing reactor are noted at A.

A comparison of the performance of the NOx sorbate catalyst before and after desulfation can also be seen in the NOx sorption profile data shown in Figure 8. Three catalyst system out NOx signals are shown in Fig. 8; data during the 15 kW down load point is shown for a "fresh" catalyst (hour 20 in stage I), a sulfur "masked"

catalyst (hour 140 in stage II), and "after desulfation" (hour 170 of stage III). The NOx sorption performance of R1 and R2 are represented by the data in time frames 0-2.5 minutes and 2.5-5.0 minutes, respectively. The NOx performance for catalysts in R1 and R2 is comparable for the "fresh" condition; however, after sulfur masking the R2 data shows higher NOx levels indicating higher levels of sulfur on the catalyst. After desulfation the NOx levels are lower, but NOx levels for R2 are still slightly higher than for R1. Thus, the higher levels of NOx in the R2 data shown in Fig. 8 support the conclusion from Fig. 6 that less SO₂ was diverted from the R2 catalyst which resulted in more sulfur masking on the R2 NOx catalyst. The difference in the regeneration efficiency of the sulfur sorbate catalysts in R1 and R2 may be due to differences in the sealing effectiveness of the exhaust valves used for isolation of the reactors during regeneration. Data presented in the section "Catalyst Analysis" below adds further insight into the sulfur levels on the catalysts.

CATALYST ANALYSIS

The NOx sorbate catalysts used in the engine tests were analyzed for sulfur content after being sulfur "masked" (at hour 150 of stage I) and "desulfated" (at hour 170 of stage III). Four core samples were taken from each reactor from positions along the axis of the exhaust flow. The catalyst cores were ground and analyzed with an inductively coupled plasma technique for sulfur. The data is shown in Figure 9. The "fresh" sample level in Fig. 9 was obtained by analyzing a catalyst that had not been used in engine tests and represents the noise level of the analysis technique.

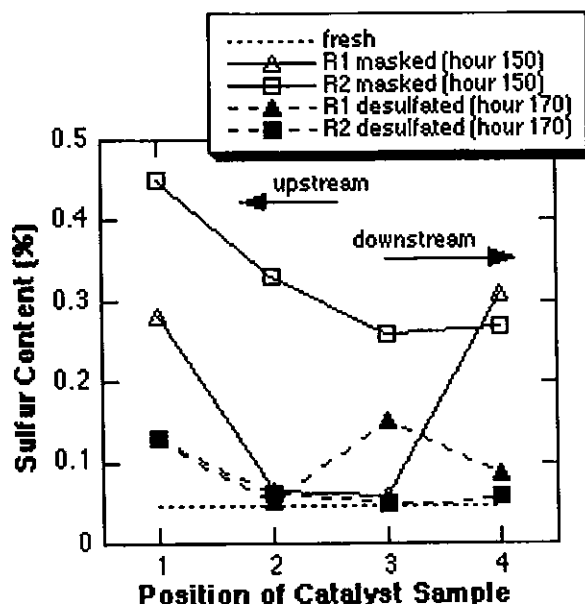


Figure 9. Sulfur levels on catalyst samples taken during the engine tests.

The "masked" data shows the presence of sulfur on the catalysts. Sulfur levels were highest for the most upstream (position 1) and most downstream (position 4) samples. The decreasing sulfur level observed with further downstream position in the R2 data is expected, since SO₂ will travel further into the catalyst after saturation of the upstream portion of the catalyst occurs. The amount of sulfur on the R2 catalyst samples was higher than for the R1 samples which confirms the conclusion from Figs. 6 and 8 that less SO₂ was diverted from the R2 NO_x catalyst than for R1. The most downstream sample (position 4) had high sulfur levels for R1 and R2 due to the sulfur in the diesel fuel used for the regeneration process; recall that the regeneration fuel is injected into the downstream side of the catalyst (See "Catalyst System" section above).

The "after desulfation" data shows significantly less sulfur levels on the catalysts. Some sulfur is measured at positions 1 and 4; however, the samples were removed at hour 170 after 10 hours of operation with the light-duty test cycle. The R1 data for position 3 is abnormally high and can not be explained with the current data especially since the sulfur level from that position is higher than the "masked" data. Some data points are close to the "fresh" sulfur level and appear to have minimal amounts of sulfur.

CONCLUSIONS

- Upstream sulfur sorbate catalysts can divert SO₂ around NO_x sorbate catalysts by storing and then releasing SO₂. The effectiveness of the sulfur sorbate catalyst in protecting NO_x sorbate catalysts from sulfur masking is largely dependent on exhaust temperature since the rate of SO₂ release slows at low temperatures. The sulfur sorbate catalyst consistently diverted SO₂ over a 150-hour light-duty cycle test.
- NO_x sorbate catalysts can be reactivated after sulfur masking in a process known as desulfation. During operation at high engine loads with no additional heat supplied to the catalysts, sulfur was removed from the catalysts using standard regeneration parameters. An average of 80% of the "fresh" NO_x conversion performance was recovered after desulfation for the engine loads tested.
- Analysis of the catalysts used in the engine tests confirmed that sulfur masking occurred during the 150-hour light-duty test. The results also confirmed the removal of sulfur from the catalysts during the desulfation process.

ACKNOWLEDGMENTS

This work was supported by Cummins Engine Company and Goal Line Environmental Technologies LLC. Goal Line Environmental Technologies is a partnership of

Advanced Catalyst Systems and Sunlaw Energy Corporation. Catalyst analysis was provided by Galbraith Laboratories, Inc.

REFERENCES

1. M. Kramer, J. Abthoff, F. Duvinage, N. Ruzicka, B. Krutzsch and T. Liebscher, "Possible Exhaust Gas Aftertreatment Concepts for Passenger Car Diesel Engines with Sulphur-free Fuel", SAE 1999-01-1328.
2. R. A. Marshall, D. Gregory, B. Eves, G. Pierce, T. Taylor, S. Cornish, M. Dearth, and J. Hepburn, "Optimising the Aftertreatment Configuration for NO_x Regeneration on a Lean-NO_x Trap", SAE 1999-01-3499.
3. J. E. Parks II, G. J. Wagner, W. S. Epling, M. W. Sanders, and L. E. Campbell, "NO_x Sorbate Catalyst System with Sulfur Catalyst Protection for the Aftertreatment of No. 2 Diesel Exhaust", SAE 1999-01-3557.
4. M. A. Dearth, J. S. Hepburn, E. Thanasiu, J. McKenzie, and G. S. Horne, "Sulfur Interaction with Lean NO_x Traps: Laboratory and Engine Dynamometer Studies", SAE 982595 (1998).
5. Takamitsu Asanuma, Shinichi Takeshima, Tetsuya Yamashita, Toshiaki Tanaka, Toshimi Murai and Satoshi Iguchi, "Influence of Sulfur Concentration in Gasoline on NO_x Storage - Reduction Catalyst", SAE 1999-01-3501.
6. Sara Erkfeldt, Mikael Larsson, Hakan Hedblom, and Magnus Skoglundh, "Sulphur Poisoning and Regeneration of NO_x Trap Catalyst for Direct Injected Gasoline Engines", SAE 1999-01-3504.
7. Sh. Hodjati, F. Semelle, N. Moral, C. Bert and M. Rigaud, "Impact of Sulphur on the NO_x Trap Catalyst Activity - Poisoning and Regeneration Behaviour", SAE 2000-01-1874.
8. J. E. Parks II, J. A. Watson, G. L. Campbell, G. J. Wagner, and L. E. Campbell, "Sulfur Sorbate Catalysts for Diesel Aftertreatment: Temperature Effects on the Release of Sulfur", SAE 2000-01-1932.
9. Owen Bailey, Danan Dou, and Michel Molinier, "Sulfur Traps for NO_x Adsorbers: Materials Development and Maintenance Strategies for Their Application", SAE 2000-01-1205.
10. J. E. Parks II, J. A. Watson, W. S. Epling, G. J. Wagner, M. W. Sanders, and L. E. Campbell, "Sulfur-Resistant NO_x Sorbate Catalyst for Increasing Longevity in Diesel Exhaust", SAE 2000-10-1012.

CONTACT

Jim Parks
Goal Line Environmental Technologies LLC
11141 Outlet Drive, Knoxville, TN 37932
jparks@glet.com