
NOx Sorbate Catalyst System with Sulfur Catalyst Protection for the Aftertreatment of No. 2 Diesel Exhaust

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ABSTRACT

A two-chamber catalyst system for the aftertreatment of No. 2 Diesel exhaust is demonstrated. NO_x conversion efficiencies greater than 90% were obtained over a broad range of operating temperatures and NO_x levels. The system incorporates a catalyst (SCONO_xTM) for the removal of CO, hydrocarbons, and NO_x from the exhaust stream and a sulfur catalyst (SCOSO_xTM) for the protection of the NO_x catalyst from sulfur poisoning. Both catalysts are of sorbate or "trap" type. No. 2 Diesel and hydrogen were used as reductants. Tests of the catalysts were performed with various loads, temperatures, and NO_x levels. A light-duty diesel engine with no particulate control was used for the tests. All tests were conducted using No. 2 Diesel fuel. NO_x conversion decay is compared with and without sulfur catalyst protection.

INTRODUCTION

The lean nature of combustion in diesel engines enables fuel-efficient operation. Increased use of diesel relative to stoichiometric gasoline engines would result in less CO₂ emissions, but upcoming regulations on NO_x and other pollutants deter the move to diesel engines. The future of the diesel engine will depend on how well NO_x and other pollutants can be controlled.

Research on aftertreatment control of NO_x has centered on lean NO_x catalysts, Selective Catalytic Reduction (SCR), and NO_x sorbate ("trap") catalysts.¹ Lean NO_x catalysts are similar to standard three-way catalysts but use hydrocarbon injection into the exhaust stream to supply sufficient reductant for operation. Even with hydrocarbon injection, lean NO_x catalysts suffer from the high oxygen content in diesel exhaust, and peak NO_x conversions are typically less than 50%.² Additionally, the temperature range of operation is typically narrow. SCR achieves higher NO_x conversion but requires urea for the reductant; any ammonia slip results in a pollutant added to the exhaust.³ NO_x sorbate catalysts enable much higher NO_x conversion and a broad temperature range of operation; however, typical NO_x sorbate catalysts are

poisoned by sulfur compounds in the exhaust.^{4,5} The susceptibility to sulfur poisoning results in short lifetimes when standard fuels are used.

This paper describes a sorbate catalyst system that reduces the effect of sulfur poisoning on a NO_x sorbate catalyst. The system uses a sulfur sorbate catalyst (SCOSO_xTM) and a NO_x sorbate catalyst (SCONO_xTM).^{6,7} Sulfur poisoning is diminished by the removal of SO₂ with the sulfur catalyst from the exhaust upstream of the NO_x sorbate catalyst. The catalysts are housed in a two-chamber system to allow efficient reduction. The lifetime of the NO_x catalyst in the diesel exhaust stream is increased by the sulfur catalyst protection.

DIESEL AFTERTREATMENT SYSTEM DESCRIPTION

The diesel aftertreatment system is a two-chamber device. Each chamber of the device contains a sulfur sorbate catalyst upstream of a NO_x 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. A diagram of the system is shown in Figure 1.

Aftertreatment of the exhaust begins with the sulfur catalyst where SO₂, SO₃, and H₂S are sorbed. The exhaust then flows over the NO_x catalyst where NO₂ is sorbed; NO is converted to NO₂ prior to sorption. Both catalysts convert CO to CO₂ and destruct hydrocarbons and volatile organic compounds. At some point the catalysts sites become saturated with SO₂ and NO_x and slippage of SO₂ and NO_x begins. At that point the catalysts require regeneration.

Regeneration occurs by passing a low flow of net-reducing gas over the catalysts; typical flow rates are 1-2% of the main exhaust flow rate. The low flow of regeneration gas results in less O₂. Thus, less fuel is required to obtain a net-reducing gas, and fuel penalty is minimized.

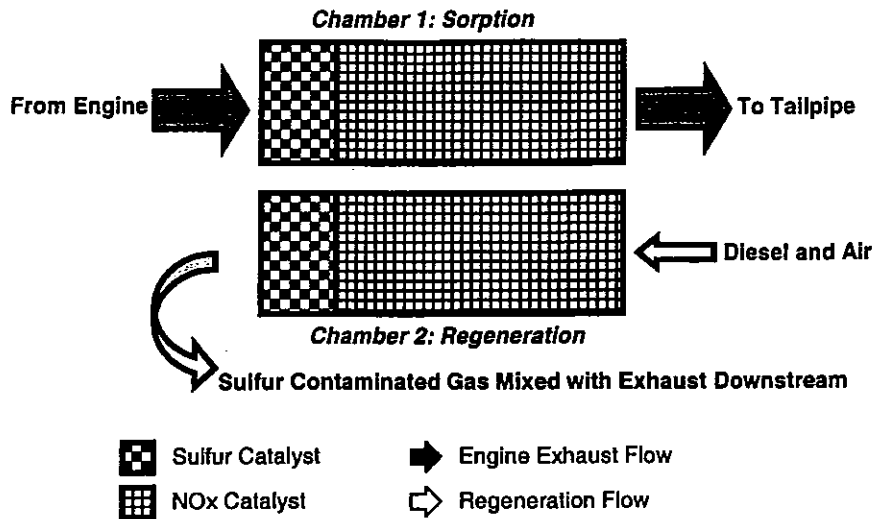
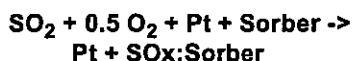


Figure 1. Diagram of the two-chamber aftertreatment system. Each chamber has a sulfur sorbate catalyst upstream of a NOx sorbate catalyst. The sorbate catalysts must be regenerated once saturation of the catalyst sites occurs. During regeneration, a low flow of reducing gas passes through the chamber in a reverse direction relative to the main exhaust flow. The sulfur compounds released by the sulfur sorbate catalyst during regeneration bypass the catalysts and are mixed in the exhaust downstream.

During regeneration, the NOx sorbed is reduced and released as N₂, and the SO₂ sorbed on the sulfur catalyst is released as SO₂. The direction of the regeneration gas flow is reversed from the main exhaust flow so that the SO₂ emitted from the sulfur catalyst will not come into contact with the NOx catalyst. The regeneration exhaust is bypassed around the catalyst chambers and reinserted into the exhaust line downstream. The use of an SO₂ sorbing cartridge in the bypass line would enable the removal of SO₂ from the exhaust; however, this technique has not yet been demonstrated.

Diesel fuel or hydrogen can be used as the reductant. When diesel fuel is used as the reductant, it is injected into the downstream side of the catalyst chamber and air or exhaust is used to push the diesel pulse through the catalysts. Regeneration with simulated reformer gases is also demonstrated.

SULFUR SORBATE CATALYST – The sulfur catalyst is a precious metal catalyst with a proprietary sorber. The formulation of the sulfur catalyst can be adjusted to release the sulfur as SO₂, H₂S, or a mixture of the two. The SO₂ releasing formulation is being used for this application. The chemistry of the sorption stage of operation is:



The chemistry of a typical regeneration reaction is:

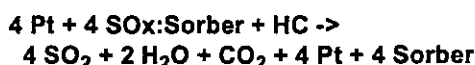


Figure 2 shows typical sorption and regeneration data obtained with the sulfur catalyst on a bench scale reactor. A stream with 60 ppm SO₂ was passed over the catalyst;

the data show the catalyst removing the SO₂ from the stream and then releasing the SO₂ during regeneration. The conditions for the experiment were 30,000/hr space velocity and 260°C. The 60 ppm SO₂ inlet level was reduced to 1 ppm SO₂ by the catalyst; thus, 98.3% of the SO₂ was removed from the stream.

Regeneration was accomplished with 4% H₂ gas at a space velocity of 8,000/hr. Since the flow rate during regeneration is relatively low and reduction occurs rapidly relative to sorption, the emission of SO₂ occurs as a concentrated peak; however, the net SO₂ sorbed and released is constant. The mass balance for the data shown is 99.3%.

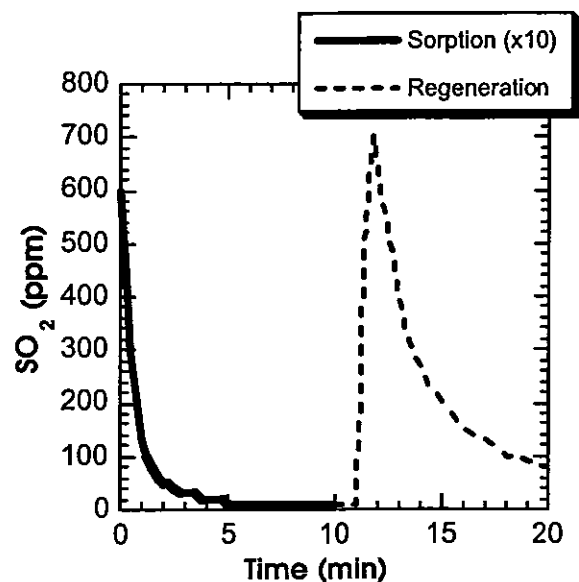
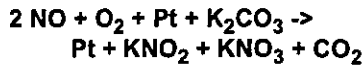


Figure 2. Typical data obtained with the sulfur catalyst on a bench flow reactor.

NOx SORBATE CATALYST – The NOx catalyst is also a precious metal catalyst. The standard sorber agent is K₂CO₃, but many other sorber components can be used. The K₂CO₃ forms KNO₃ and KNO₂ during sorption, and regeneration reduces the KNO₃ and KNO₂ to KOH. Sorption of CO₂ reverts the potassium back to carbonate form. The chemistry of the sorption stage of operation is:



The chemistry of a typical regeneration reaction is:

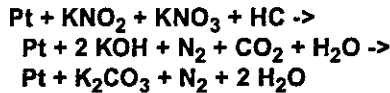


Figure 3 shows typical sorption and regeneration data obtained with the NOx catalyst on a bench scale reactor. A stream with 250 ppm NO was passed over the catalyst; the data show the catalyst removing the NO from the stream and then reducing the NO during regeneration. The conditions for the experiment were 10,000/hr space velocity and 150°C. The 250 ppm NO inlet level was reduced to a minimum level of 2 ppm NO by the catalyst; thus, the peak NOx conversion was 99.2%. During regeneration with 4% H₂ at 2,000/hr space velocity, a small amount of NOx was emitted; however, the vast majority of NOx was converted and emitted as N₂.

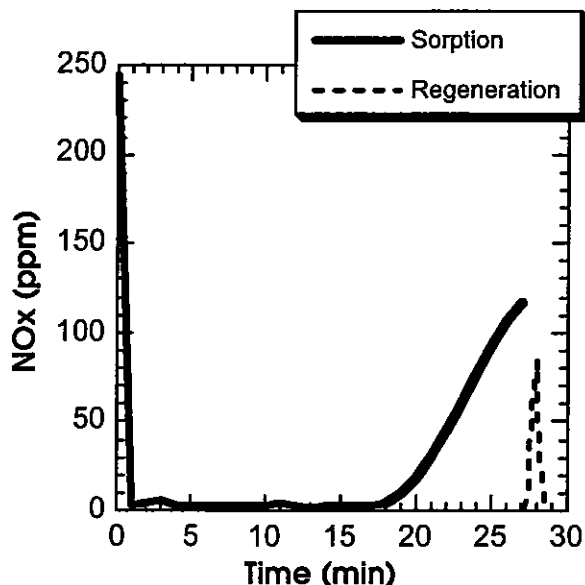


Figure 3. Typical data obtained with the NOx catalyst on a bench flow reactor.

EXPERIMENT DESIGN

The diesel aftertreatment system was tested on a light-duty platform. A 3.9-liter turbo-assisted diesel engine (Cummins 4B3.9T) produced the exhaust for testing. No particulate control or other exhaust treatment was used. The engine was attached to a generator as a gen-set, and load was applied to the engine with a resistive load bank. The engine speed was held constant at 1800 rpm.

The exhaust temperature and NOx level varied with engine load.

All testing was performed with steady-state operation of the engine. Cycle periods and thereby regeneration frequency were held constant; the typical cycle time was 2.5 minutes. The space velocity of the NOx catalyst was 23,000/hr (230 cpsi), and space velocities of 24,000/hr to 91,000/hr were used for the sulfur catalyst (230 cpsi). To reduce system size by increasing space velocity, reduced cycle times will be required. Catalyst regeneration is rapid with diesel vapor; so, potential for cycle time reduction exists. Frequency of regeneration could potentially be controlled by a downstream NOx sensor or by an engine map-based control scheme. These more advanced control schemes may be required for fuel penalty minimization and increased response control suitable for transient engine conditions.

The engine used No. 2 Diesel for all tests. The sulfur level in the fuel was 389 ppm; SO₂ levels in the exhaust were typically 12 to 30 ppm. Typical NOx levels ranged from 150 to 2400 ppm. CO levels were typically 100 to 800 ppm.

No. 2 Diesel fuel used for reduction was injected into the catalyst chamber on the downstream side. After the injection period (typically 0.3 to 0.5 minutes), the diesel vapor was slowly pushed through the catalyst with a low air flow. Regeneration with diesel vapor in air required low carrier flow; space velocities were 174/hr and 695/hr for the NOx and sulfur catalysts, respectively. Any oxygen mixing with the diesel pulse was consumed during diesel combustion on the catalyst surface. The high reductant to oxygen ratio resulted in a highly efficient reduction step; the fuel penalty was typically 1% per 1000 ppm of NOx. The simulated reformer gas used for regeneration was 4% H₂ in a N₂ carrier at a space velocity of 1,392/hr and 5,560/hr for the NOx and sulfur catalysts, respectively.

Exhaust gases were analyzed at standard conditions. Non-dispersive infrared analyzers were used for NOx and CO detection. SO₂ was measured with non-dispersive ultraviolet detection. All gases passed through a filter and chiller to remove the particulate matter and H₂O from the exhaust, respectively. One set of analyzers was used to test engine out and catalyst out exhaust. Engine out exhaust was typically analyzed every 20 minutes; NOx conversions shown were computed with the most recent engine out NOx measurement.

RESULTS

SULFUR CONTROL – The sulfur catalyst releases the sulfur captured during the regeneration stage. The sulfur is released as SO₂ and mixed into the exhaust downstream. Thus, the SO₂ levels observed downstream of the system show SO₂ emission peaks that correspond to the cyclic reduction of the sulfur catalyst (Figure 4). The cycle time used for the data in Figure 4 was 2.5 minutes; the NOx and sulfur catalyst space velocities were 23,000/

hr and 91,000/hr, respectively. The inlet SO₂ concentration during the experiment was 26 ppm; the exhaust temperature was 360°C. The reductant was No. 2 Diesel. The SO₂ shown represents the SO₂ that was prevented from poisoning the NOx catalyst.

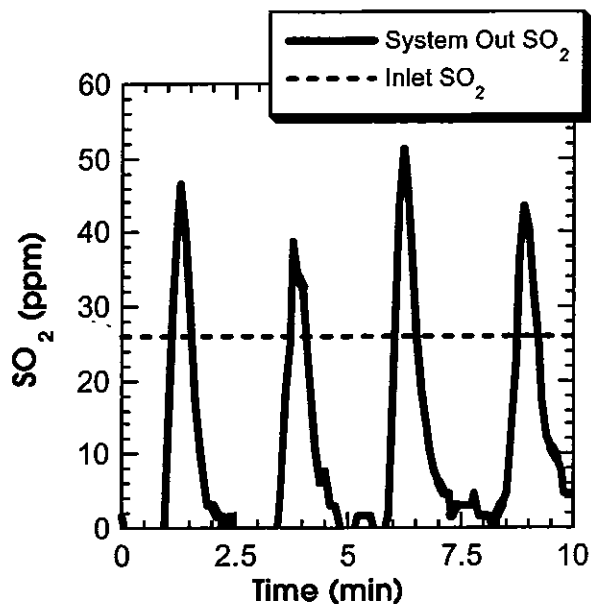


Figure 4. SO₂ measurement downstream of the catalyst system. Emission peaks occur due to the release of SO₂ during regeneration of the sulfur catalyst.

NOx CONTROL – The NOx catalyst stores NOx during the sorption stage and releases the NOx as N₂ during regeneration. Figure 5 shows typical NOx profiles downstream of the catalyst. Two plots obtained with inlet NOx levels of 778 ppm and 2326 ppm are shown; the exhaust temperatures for the data were 250°C and 360°C, respectively. The reductant used was No. 2 Diesel, and the NOx and sulfur catalyst space velocities were 23,000/hr and 91,000/hr, respectively. The engine speed was constant; the engine load was 25 kW and 50 kW, respectively. The cycle time was 2.5 minutes with only a 0.1-minute period when both chambers are open to the main exhaust stream. The data demonstrate the capacitive nature of the sorbate catalyst. For the 778 ppm inlet data, the outlet NOx level was mostly constant except for the brief moment when both chambers were open to the exhaust stream. However, the 2326 ppm inlet data shows saturation of the catalyst sites beginning where a rise in NOx slip through the catalyst occurs toward the end of each 2.5-minute cycle. Although some difference in catalyst performance exists between the demonstrated temperatures, catalyst performance from 250°C to 360°C is comparable, and the primary difference in the data is due to the total amount of NOx incident on the catalyst. The total amounts of NOx passing over the catalyst during the 10-minute test was 59.4 g and 177.6 g (as NO₂) for the 778 ppm and 2325 ppm levels, respectively. The NOx conversions obtained were 93.2% and 91.5%,

respectively; thus, the “breakthrough” of NOx after catalyst saturation did reduce NOx conversion a small amount.

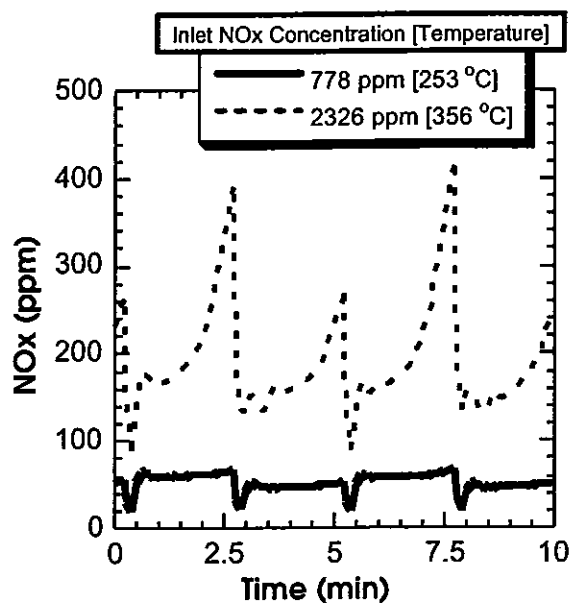


Figure 5. NOx measurement downstream of the catalyst system. Data for two different NOx inlet levels are shown. The exponentially rising peaks in the 2326 ppm data demonstrate saturation of the catalyst beginning.

The time required for saturation of the NOx sites on the catalyst depends on the NOx inlet level, space velocity, and temperature. If saturation does occur at a given set of operating conditions, the cycle time can be reduced to prevent saturation, and thereby loss of conversion, from occurring. Figure 6 shows data obtained with the same exhaust conditions but at different cycle periods. The inlet NOx concentration was 1441 ppm and the exhaust temperature was 285°C. The reductant was No. 2 Diesel; the NOx and sulfur catalyst space velocities were 23,000/hr and 91,000/hr, respectively. Cycle times of 1.5 minutes and 2.5 minutes obtained NOx conversions of 94.3% and 91.6%, respectively. During 1.5-minute cycle operation, the catalysts are regenerated just prior to the beginning of catalyst saturation.

Another method to increase NOx conversion is to increase the duty cycle of the system. Figure 7 shows three NOx outlet profiles obtained with the same exhaust conditions but different catalyst duty cycles. For the 70% duty cycle, both catalysts are treating the exhaust stream for a one-minute interval prior to the regeneration of one of the chambers. Thus, the catalyst volume is effectively doubled for one minute of the 2.5-minute cycle. The NOx conversion increases with duty cycle. The results were obtained at an exhaust temperature of 285°C and a NOx inlet level of 1441 ppm. The reductant was No. 2 Diesel; the NOx and sulfur catalyst space velocities were 23,000/hr and 91,000/hr, respectively. The rapid regeneration with diesel vapor enables higher duty cycle operation.

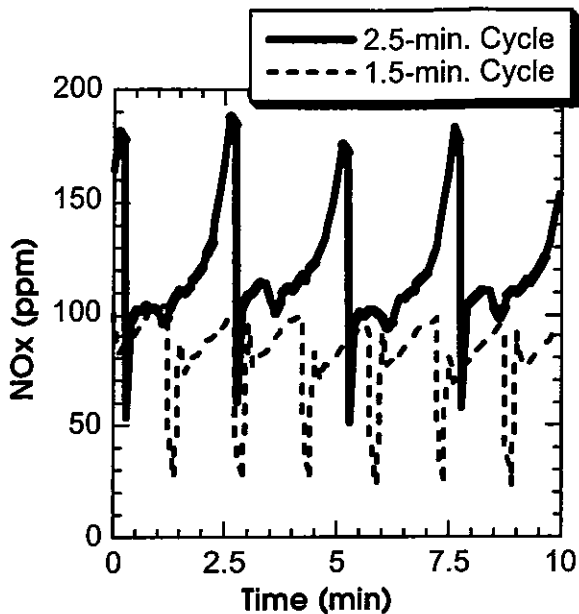


Figure 6. NOx measurement downstream of the catalyst system. Data for two different cycle periods is shown. NOx breakthrough due to catalyst saturation can be avoided by decreasing the cycle period.

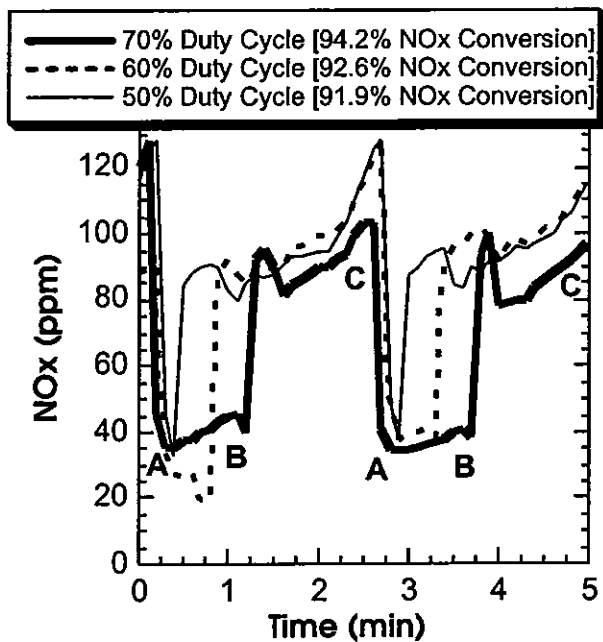


Figure 7. NOx measurement downstream of the catalyst system for three different duty cycles. NOx conversion and system efficiency are improved by increasing the duty cycle. For the 70% duty cycle data, both catalyst chambers treat the exhaust from point A to B; one chamber is regenerated from point B to C. For the 50% duty cycle, one chamber treats the exhaust while the other chamber is regenerated (point A to C).

NOx conversion as a function of temperature is shown in Figure 8. A cycle time of 2.5 minutes was used to collect the data; space velocity for NOx and sulfur catalysts was 23,000/hr and 91,000/hr, respectively. No. 2 Diesel was used as the reductant. The load on the engine was varied from 50 kW to 0 kW in 5 kW increments to control temperature. All data was obtained at steady-state operation and at steady-state temperature. The NOx levels varied dramatically during the experiment due to changing load; the minimum and maximum NOx levels were 175 ppm and 2326 ppm, respectively. The conversion is greater than 90% for most of the temperature range. The drop in conversion at the lower temperatures is due to a decrease in catalyst activity at those temperatures since NOx levels at low load were small.

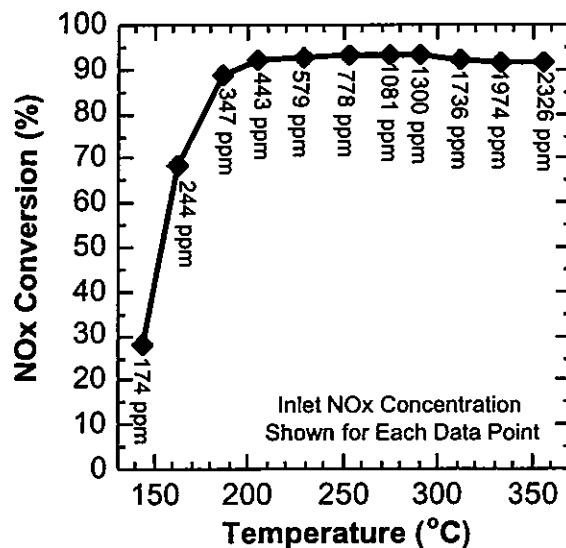


Figure 8. NOx conversion as a function of temperature for the system. The exhaust temperatures were obtained by varying the load of the engine; engine out NOx levels increased with engine load and exhaust temperature. The conversion is greater than 90% for all temperatures above 200°C. The conversion profile suits diesel exhaust well.

CO CONTROL – Both the sulfur and NOx catalysts are effective at oxidizing CO to CO₂. Figure 9 shows the CO conversion obtained by the system as a function of temperature. The conditions of operation were the same used for Figure 8. The CO conversion remains high across the temperature range. Measurements of CO concentration directly downstream of an individual catalyst chamber showed near zero CO emissions. The CO contributing to less than 99% conversion in the Figure 9 data resulted from rich diesel combustion during regeneration. Since the oxygen level in the regeneration gas was depleted, CO conversion to CO₂ did not occur efficiently during regeneration, and the resulting CO decreased system conversion when the regeneration gas exhaust was mixed with the main exhaust stream. One potential

method of recovering the loss of CO conversion is to use an oxidation catalyst to treat the regeneration exhaust.

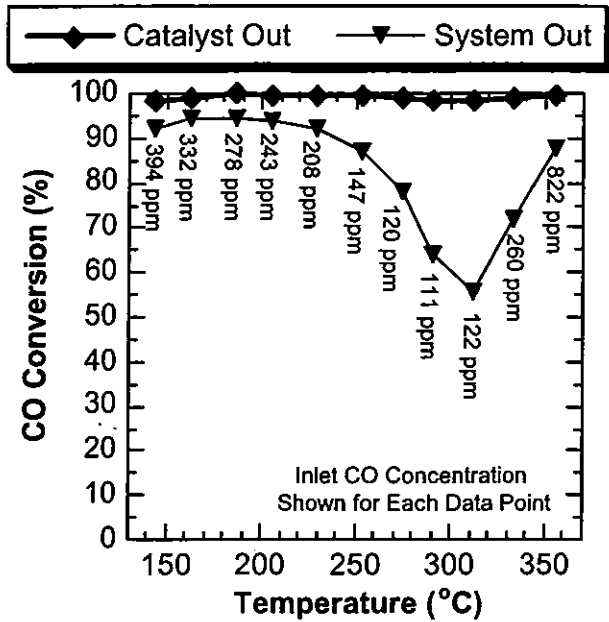


Figure 9. CO conversion as a function of temperature for the system. The exhaust temperatures were obtained by varying the load of the engine; engine out CO levels varied with engine load and exhaust temperature. The minimum and maximum engine out CO levels were 111 and 822 ppm, respectively. The catalysts convert greater than 98% of CO emitted from the engine as shown by the "Catalyst Out" curve. The "System Out" conversion is lower than the "Catalyst Out" conversion due to CO produced in the combustion of diesel during regeneration.

LIFETIME COMPARISON – A measurement of the effectiveness of the protection provided by the sulfur catalyst has been obtained by directly comparing the NOx conversion decay rate for NOx catalysts with and without an upstream sulfur catalyst (Figure 10). The comparison tests were done at steady-state conditions; actual conditions varied slightly over the course of the test in part due to test cell temperature variations. The average exhaust temperature was 278°C. The average engine out NOx and SO₂ levels were 855 ppm and 20 ppm, respectively. The space velocity of the NOx catalyst was 23,000/hr. For the case with the sulfur catalyst, the sulfur catalyst space velocity was 24,000/hr. A simulated reformer gas was used for regeneration (H₂ reductant) to isolate the sulfur poisoning effect due to engine out SO₂. Contributions to sulfur poisoning due to the sulfur in the diesel used for reduction may be significant but are not addressed here.

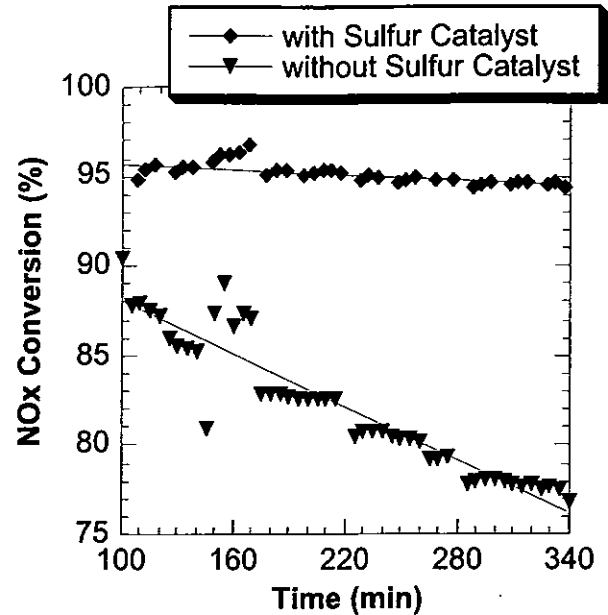


Figure 10. NOx conversion decay comparison between a NOx catalyst with and without sulfur catalyst protection. Data after a 100-minute warm-up period is shown. The NOx catalyst without sulfur protection decays rapidly relative to the NOx catalyst with sulfur catalyst protection.

The data in Figure 10 shows that performance of the NOx catalyst without sulfur catalyst protection decays more rapidly than the NOx catalyst with sulfur catalyst protection. The slope of the linear fit represents the decay rate, and the decay rates are summarized in Table 1. Also, shown in Table 1 is data obtained with a 91,000/hr space velocity sulfur catalyst under the same conditions as those used for the data in Figure 10. The "factor of improvement" in Table 1 is simply the ratio of the decay rate for the unprotected NOx catalyst to the decay rate with sulfur catalyst protection. The factor of improvement increases with decreasing sulfur catalyst space velocity; more SO₂ slip through the sulfur catalyst occurs at higher space velocities.

Table 1. NOx conversion decay rate for various levels of sulfur catalyst protection.

Sulfur Catalyst Space Velocity	NOx Conversion Decay Rate	Factor of Improvement
No Sulfur Catalyst	3.02 % / hour	—
91,000/hr	0.83 % / hour	3.6
24,000/hr	0.29 % / hour	10.4

CONCLUSION

A catalyst system for the aftertreatment of diesel exhaust has been demonstrated on a light-duty engine operating at steady-state conditions. The combination of a sulfur sorbate catalyst and a NO_x sorbate catalyst allows excellent NO_x conversion while reducing the poisoning effect of SO₂ on the NO_x catalyst. Measurement of cyclic SO₂ peaks corresponding to the regeneration of the sulfur catalyst demonstrated the protection from sulfur. The system utilized two catalyst chambers which maximized efficiency; reduction of the NO_x could be performed with low fuel penalties of 1% per 1000 ppm NO_x. The system demonstrated that NO_x sorbate catalysts can be used with No. 2 Diesel fuel, and that catalysts can be reduced efficiently in an exhaust stream with high oxygen content by using a two-chamber system design. The sulfur induced decay of the NO_x catalyst was reduced by a factor greater than 10 with the protection provided by the sulfur catalyst. Further testing will be required to determine the system performance for transient conditions and the sulfur protection provided over a wider range of operating conditions.

ACKNOWLEDGMENTS

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