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J. E. Parks II, J. A. Watson, G. L. Campbell,
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Goal Line Environmental Technologies LLC

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ABSTRACT

Sulfur compounds in diesel exhaust diminish the performance of aftertreatment devices and contribute to particulate matter mass and composition. Sulfur sorbate catalysts that store and release sulfur compounds have been used in conjunction with NOx aftertreatment catalysts to decrease the negative effects of sulfur.[1] The temperature range of diesel exhaust is broad and may vary with application. The effect of temperature on the performance of sulfur catalysts will determine the usefulness of such catalysts for diesel applications. In this study bench reactor and engine testing of sulfur sorbate catalysts were performed to characterize the release of sulfur compounds as a function of temperature. Engine tests were performed on a light-duty platform with No. 2 Diesel fuel.

INTRODUCTION

Upcoming regulations on NOx emissions will most likely require aftertreatment devices on diesel engines. Since the diesel engine combustion process is lean, control of NOx with standard three-way catalysts is difficult. One potential aftertreatment device for diesel exhaust is the NOx sorbate catalyst, or "NOx trap". Although NOx trap catalysts have shown greater than 90% NOx reduction in the diesel exhaust stream, longevity of NOx traps has been poor due to sulfur poisoning of NOx sorbate sites.[2]

One method demonstrated to decrease the negative effects of sulfur in the exhaust stream on NOx trap catalysts is the sulfur sorbate, or "trap", catalyst.[1,3,4] The role of the sulfur trap catalyst in NOx trap protection is collection of the sulfur compounds in the exhaust upstream of the NOx catalyst. Subsequently, the trapped sulfur can be released from the sulfur trap and by-passed around the NOx catalyst during periodic regeneration of the sulfur catalyst.

The protection against sulfur poisoning attained by the sulfur trap catalyst will depend on a number of factors such as the sulfur level in fuel, catalyst space velocity, and exhaust temperature. In particular, the wide range of exhaust temperatures in conjunction with the relatively low temperatures found in diesel exhaust presents a challenge for sulfur catalysts.

Here the performance of a sulfur trap catalyst (tradename SCOSOx™) as a function of temperature will be presented. Experiments were conducted on a bench scale reactor and on a light-duty diesel engine. Catalyst characteristics measured were sulfur collection efficiency, regeneration efficiency, and sulfur capacity.

SULFUR TRAP CATALYST

The sulfur trap catalyst has been introduced in earlier work.[1,3] The sulfur trap catalyst is a precious metal catalyst with a proprietary sorber. The formulation of the sulfur catalyst can be adjusted to release the sulfur as SO_2, H_2S, or a mixture of the two. The SO_2 releasing formulation is being used for this application. The catalyst operates in a cyclic fashion. During the first stage of operation the catalyst sorbs SO_2. The chemistry of the sorption stage of operation is:

$$\mathrm{SO_2 + 0.5\ O_2 + Pt + Sorber \text{->}}$$
$$\mathrm{Pt + SOx{:}Sorber}$$

After the catalyst sites are filled with SO_2, the catalyst sites can be emptied, or regenerated, in the second stage of operation. The chemistry of a typical regeneration reaction is:

$$\mathrm{4\ Pt + 4\ SOx{:}Sorber + HC \text{->}}$$
$$\mathrm{4\ SO_2 + 2\ H_2O + CO_2 + 4\ Pt + 4\ Sorber}$$

Figure 1 shows typical sorption and regeneration data obtained with the sulfur catalyst on a bench scale reactor. A stream with 60 ppm SO_2 was passed over the catalyst; the data show the catalyst removing the SO_2 from the stream and then releasing the SO_2 during regeneration. The conditions for the experiment were 30,000/hr space velocity and 260 C. The 60 ppm SO_2 inlet level was reduced to 1 ppm SO_2 by the catalyst; thus, 98.3% of the SO_2 was removed from the stream.

Regeneration was accomplished with 4% H_2 in a N_2 carrier 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 SO_2 occurs as a concentrated peak; however, the net SO_2 sorbed and released is constant. The mass balance for the data shown is 99.3%.

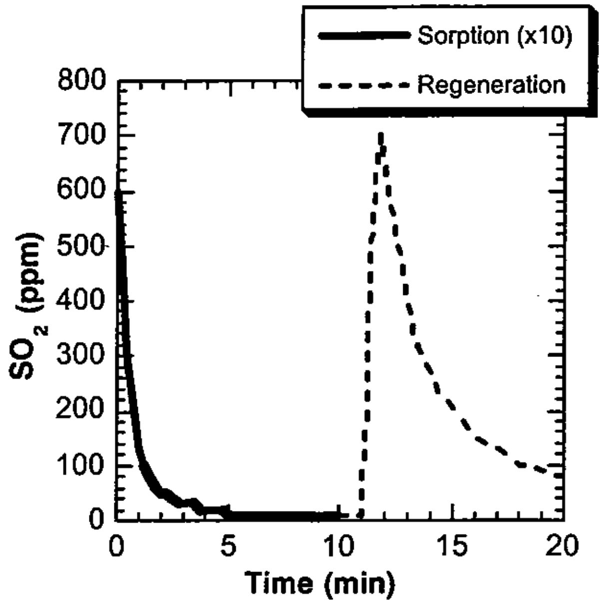

Figure 1. Typical data obtained with the sulfur trap catalyst on a bench flow reactor.

BENCH REACTOR EXPERIMENTS

The sulfur trap catalyst was tested in a bench flow reactor with simulated exhaust gases. The simulated exhaust gas contained 10.0% O_2, 6.75% CO_2, 7.0% H_2O, 100 ppm CO, and 100 ppm SO_2 in a N_2 carrier. The gas used for regeneration of the catalyst was 4% H_2, 7.0% H_2O, 1.0% CO_2, and 200 ppm CO in a N_2 carrier. The catalyst was applied to a ceramic substrate (230 cpsi). The space velocity was 30,000/hr during the sorption step and 5,000/hr during regeneration; samples were 7.5 mm long by 20 mm diameter cylindrical cores. An external furnace heated the reactor.

Tests were conducted at different catalyst temperatures. At each temperature, the sorption efficiency of the catalyst was characterized during the sorption stage of operation, and the amount of SO_2 released by the catalyst was analyzed as the catalyst was regenerated with the H_2 gas stream. SO_2 was measured with a pulsed UV analyzer.

BENCH REACTOR RESULTS

Figure 2 shows SO_2 removal by the sulfur trap catalyst at two different temperatures. For both catalyst temperatures, the 100 ppm SO_2 inlet level was reduced to less than a 1 ppm catalyst out level; however, saturation of SO_2 sorption sites begins earlier for the low temperature case resulting in SO_2 breakthrough at 7 minutes into the run. The available sites for SO_2 sorption, or capacity of the catalyst, is a function of temperature. The capacity of the sulfur catalyst is primarily determined by the amount of catalyst sites that are revitalized during the regeneration step.

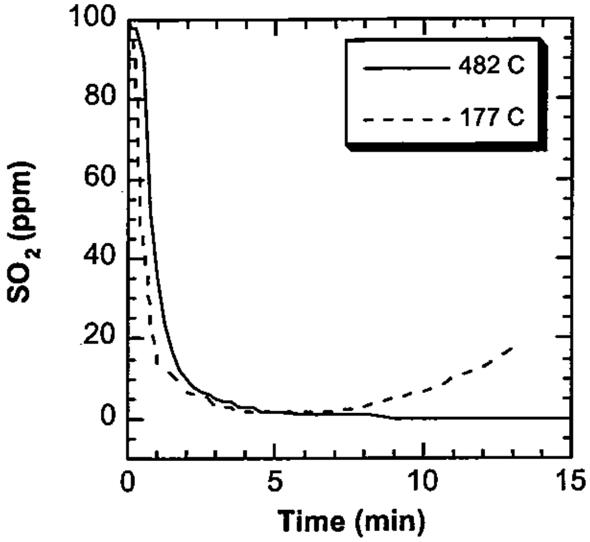

Figure 2. The sulfur trap catalyst sorbs >99% of SO_2 effectively over a wide temperature range (177 C and 482 C shown); however, the capacity of the catalyst for SO_2 sorption is lower for the 177 C data which demonstrates early breakthrough of SO_2.

Figure 3 shows the SO_2 emission profile in the regeneration gas exhaust as a function of catalyst temperature. In each case the catalyst was left in a 100 ppm SO_2 stream for 10 minutes prior to regeneration with H_2 containing gas. Note that the rate of SO_2 release also varies with temperature. **Figure 4** shows the time required to desorb 90% of the total SO_2 desorbed during regeneration. The required time above 300 C is constant and is dependent on reductant delivery. At temperatures below 300 C the rate of regeneration slows with a significant drop in regeneration speed below 250 C.

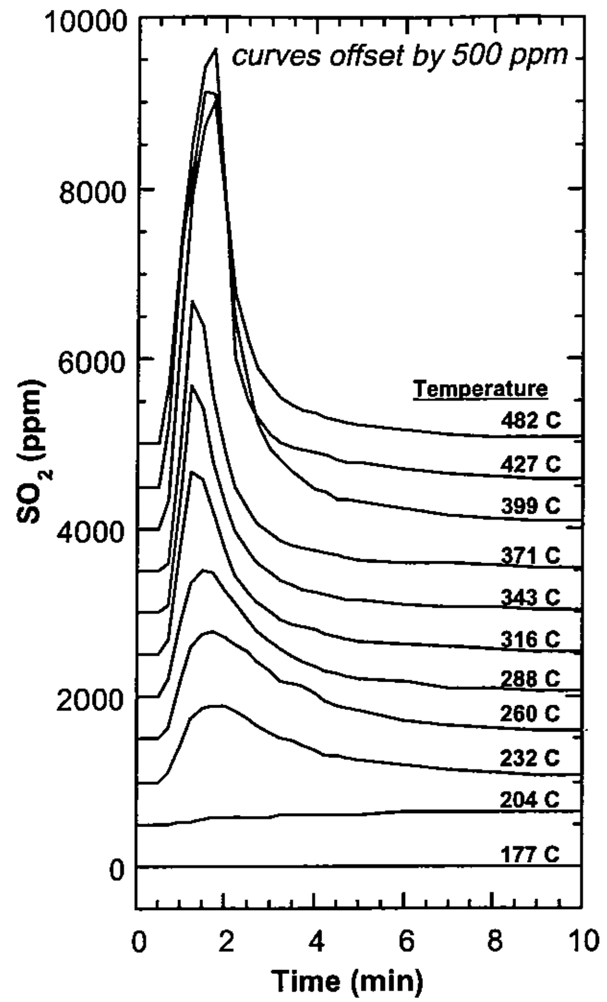

Figure 3. SO_2 concentration in the regeneration gas exhaust for regeneration performed at different catalyst temperatures. At low temperatures the release of SO_2 by the catalyst decreases in magnitude and speed.

The inefficient regeneration at low temperatures is observed in the sulfur mass balance data shown **Figure 5**. To compute the mass balance, the amount of sulfur desorbed from the catalyst during regeneration was compared with the amount of sulfur sorbed by the catalyst during the sorption stage of operation. The amount of sulfur sorbed by the catalyst during the sorption stage but not desorbed during regeneration was not measured or included in the calculation. For temperatures less than 250 C, the mass balance is low indicating the sulfur catalyst is trapping SO_2 but not releasing SO_2 during regeneration; thus, the sulfur is remaining on the catalyst. At temperatures greater than 250 C the mass balance shows a close relationship to SO_2 removal from the gas stream and SO_2 release during regeneration. During this experiment the regeneration step was done after the sorption process at each temperature point, and the temperature was decreased between data points.

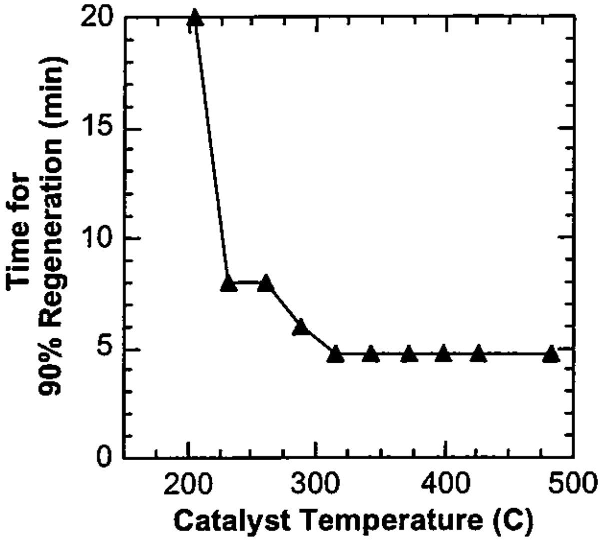

Figure 4. The speed of regeneration slows at low temperatures. At temperatures greater than 300 C the regeneration speed is a function of reductant delivery which is constant for these experiments.

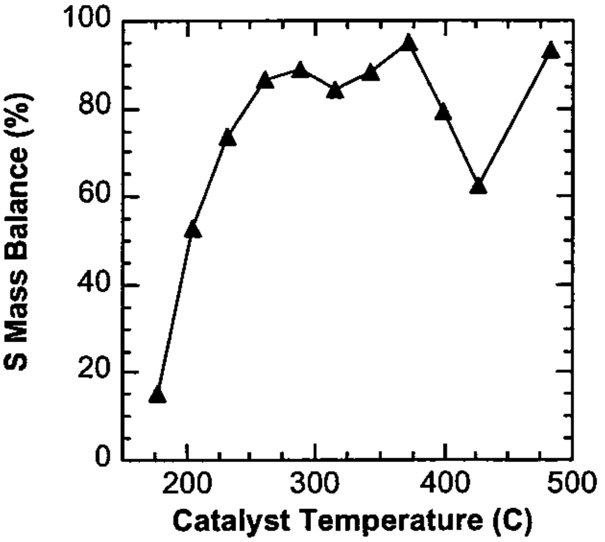

Figure 5. Sulfur mass balance for the data shown in **Fig. 3**. At low temperatures the catalyst is not releasing the same amount of sulfur that is being sorbed.

The sulfur catalyst sorbs SO_2 efficiently at all temperatures. **Figure 6** shows the SO_2 removal efficiency as a function of temperature. Peak SO_2 removal and total SO_2 removal over a 10-minute period are shown. The results indicate that if catalyst sites are available for SO_2 sorption, SO_2 sorption will occur efficiently at all temperatures tested. The freeing of catalyst sites during regeneration is strongly a function of temperature as shown in **Figs. 3-5**. For extended operation at low temperatures SO_2 sorption efficiency will eventually decline as catalyst sites are filled rapidly by SO_2 sorption while regeneration of the sites occurs at a slow rate.

ENGINE TEST DESIGN

The sulfur trap catalyst was tested on the full exhaust stream from a light-duty diesel engine (Cummins 4B3.9T). The catalyst was tested as part of a dual-chamber catalyst system, which was designed to efficiently provide regeneration capability for the catalysts. The dual-chamber system consists of two catalyst chambers that are isolated from the main exhaust by valves as shown in **Figure 7**. The exhaust from the engine enters the system at point **A** and is diverted to the sulfur trap catalyst in one of the chambers (**B**). The exhaust exiting the sulfur trap catalyst has reduced SO_2, CO, and hydrocarbon content (**C**), and the treated main exhaust leaves the system (**D**). Regeneration was accomplished by closing off one chamber of the system, injecting a low flow of net-reducing gas in to 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**).

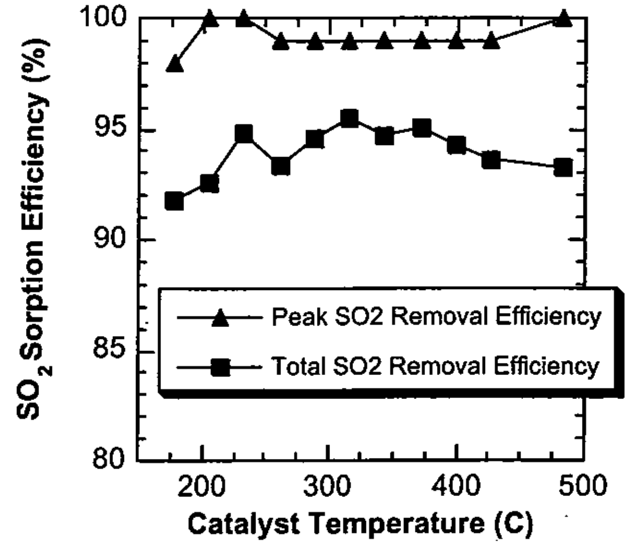

Figure 6. SO_2 sorption efficiency is relatively constant over all temperatures tested where the catalyst does not become saturated. The total SO_2 removal efficiency was taken over a 10-minute time frame and includes the SO_2 signal of the initial drop from the inlet SO_2 concentration.

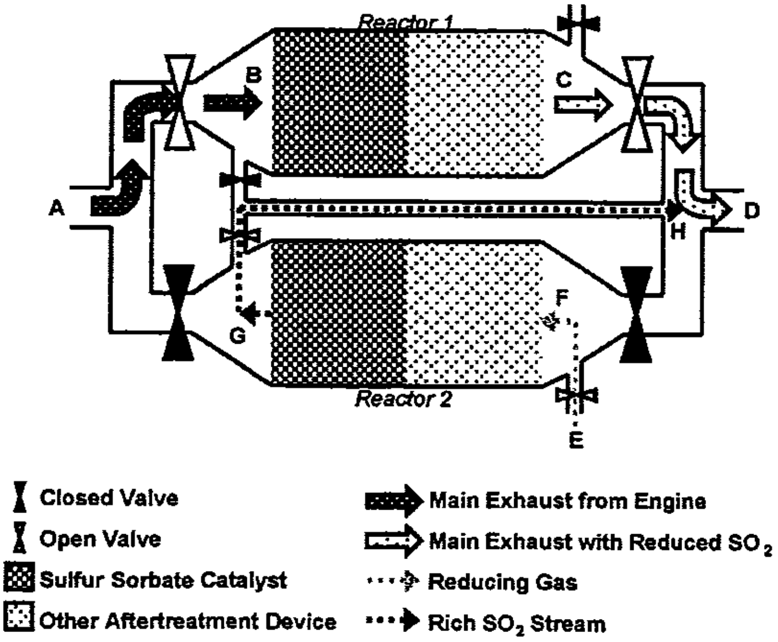

Figure 7. The dual-chamber system used for testing of the sulfur trap catalyst. The sulfur trap catalyst is designed to protect other aftertreatment devices (e.g. NOx trap catalysts) from sulfur compounds in the exhaust stream. The location of a protected "other aftertreatment device" is shown; however, tests were performed without any other aftertreatment device in place.

The sulfur trap catalyst was applied to a cylindrical ceramic substrate (200 cpsi). Each chamber of the system contained a 30-cm long and 15 cm diameter catalyst. The space velocity during SO_2 sorption was 48,000/hr for each chamber. The regeneration gas flow is typically a fraction of the main exhaust flow. The space velocity used for the regeneration step was 3,700/hr. For the experiments presented here, H_2 in a N_2 stream was used as the reductant to compare performance in the diesel exhaust to the simulated exhaust used in the bench flow reactor tests. H_2 is available from onboard fuel reformers.[5]

No. 2 Diesel fuel with a sulfur content of 389 ppm was used for the engine tests. The engine was coupled to a generator, which was connected to a resistive load bank. The engine was operated at constant speed (1900 rpm), and the load on the engine was varied with the resistive load bank to produce different exhaust temperatures. The SO_2 level in the exhaust varied with load also due to the varying A/F ratio. All testing was conducted at steady state conditions.

SO_2 was measured with a pulsed UV analyzer. SO_2 measurements were attempted in the main exhaust stream and in the bypass exhaust line. The concentration of SO_2 was largest in the bypass exhaust line due to the rapid release of SO_2 and the low flow of regeneration gas. Although SO_2 was measured effectively in the exhaust line upstream of the catalyst system, downstream measurements of SO_2 were difficult due to interference from NO_2 in the exhaust stream that was detected by the SO_2 detector. Correction for the detected NO_2 was difficult since the sulfur catalyst converted NO to NO_2 with an efficiency that was a function of temperature and potentially a function of the degree of sulfur saturation of the sulfur catalyst sites. Thus, quantitative measurement of SO_2 slip past the sulfur catalyst was not accurately obtained. Quantitative measurement of the mass of SO_2 in the bypass line was also difficult to obtain due to large leak rates in the valves used to isolate the catalyst chambers during regeneration. The analysis of SO_2 concentration in the bypass line did provide qualitative data describing the effectiveness of regeneration.

ENGINE TEST RESULTS

Figure 8 shows the SO_2 concentration measured in the bypass line during regeneration as a function of temperature. The temperature was varied by changing engine load; thus, the SO_2 inlet concentration varied with temperature. In all cases the sulfur catalyst in each chamber was left in the main exhaust stream for 2.5 minutes prior to the regeneration step. The data shows that the regeneration of the catalyst proceeds at a rapid rate for temperatures above 250 C, but the regeneration process slows at temperatures less than 250 C. At temperatures less than 200 C, virtually no SO_2 release was observed.

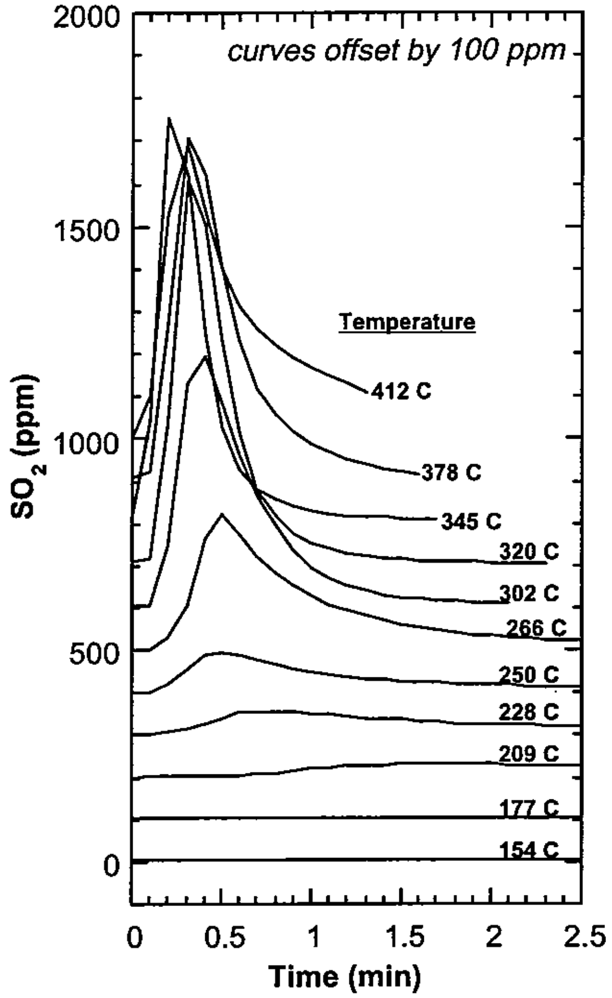

Figure 8. SO_2 concentration in the regeneration gas exhaust measured in the bypass line of the system. The exhaust temperature was varied by changing engine load; thus, the inlet SO_2 level increased with temperature. The amount and rate of SO_2 release decreases with decreasing temperature.

Figure 9 shows the relative sulfur mass balance obtained from the data shown in **Figure 8**. The relative mass balance was computed by comparing the SO_2 measured in the exhaust stream upstream of the catalyst system to the SO_2 measured in the bypass line during regeneration. The displacement and speed of the engine were used to calculate exhaust flow from the engine. The flow of gas used for regeneration was measured prior to addition to the system, and leaks in the valves prevented all of the gas from circulating through the bypass line where the SO_2 released during regeneration was measured. Therefore, the exhaust flow in the bypass line was not determined, and the mass balance shown is relative (expressed in arbitrary units). Actual numbers exceeded 100% due to the lower actual flow in the bypass line. The low mass balance at temperatures less than 200 C occurs since the sulfur trapped by the catalyst while on-line is not being released during the regeneration step.

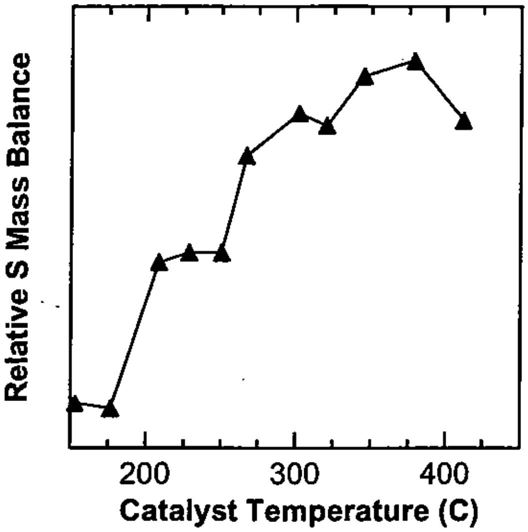

Figure 9. Sulfur mass balance for the engine tests. At low temperatures, the amount of SO_2 being trapped by the catalyst is greater than the amount of SO_2 released during regeneration.

CONCLUSION

A sulfur sorbate, or "trap", catalyst has been demonstrated on a bench scale reactor and on diesel engine exhaust. The catalyst sorbs SO_2 in lean exhaust and releases the sulfur as SO_2 in a net-reducing atmosphere; thus, the catalyst is used in a cyclic process to maintain active catalyst sites for SO_2 sorption. The SO_2 sorption efficiency of the catalyst does not vary significantly with temperature; however, the regeneration efficiency of the catalyst is a function of temperature. With H_2 as the primary reductant, the catalyst is regenerated rapidly and effectively at temperatures above 250 C. Continual removal of SO_2 from the exhaust stream will depend strongly on the catalyst temperatures experienced in driving cycles.

ACKNOWLEDGMENTS

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