Fast Regenerable Sulfur Dioxide Absorbents For Diesel Engine Emission Control

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Introduction

The emission of NO_x from on-road diesel trucks is an important environmental problem. One approach, based on NO_x trapping, stores NO_x as an alkali or alkaline earth nitrates during normal operation (lean conditions) and releases nitrogen as N_2 during a brief fuel-rich reduction step (rich conditions) [1]. Sulfur oxides contribute significantly and deleteriously to the overall performance of the NO_x trap system, mostly by reacting with alkali or alkaline earth oxides to form sulfates during the lean condition, which cannot easily be removed during the rich cycles and leads to the need for a high-temperature desulfurization ("desulfation") step [2]. This results in a gradual degradation of the NO_x trap over the course of many cycles. To protect the NO_x trap, a plausible approach is to include a separate sulfur oxide trap upstream. Dedicated, high capacity sulfur absorbents have been described [3]. However, due to its requirement for periodic replacement, an on-line regenerable sulfur trap is preferred, which can absorb SO_2 during the lean conditions and can be regenerated during the short rich conditions used during NOx trap operation. We have developed a non-precious metal-based regenerable SO_x trap materials that provide fast adsorption and desorption of SO_2 over the temperature range under which NO_x traps operate.

Materials and Methods

Adsorbents were prepared via incipient wetness impregnation using metal nitrate salts, followed by drying and calcination at 500°C. Typically a 50mg sample of 80-200 mesh adsorbent was employed using a small fixed bed reactor. Sulfation and desulfation tests and lean-rich cycling tests were carried out with an AMI-200R-HP unit (Altamira Instruments), which could automatically switch the feed to the heated reactor between lean and rich exhaust gas compositions at given time intervals. The compositions of the lean and rich exhaust simulants are given in Table 1. The gas composition downstream of the absorbent was measured using a mass spectrometer. The sulfur concentrations were measured by SCD. During an experimental run, the GC-SCD analytical system operated continuously, sampling the effluent once per minute.

Results and Discussion

A fast regenerable SOx absorbent must be able to adsorb SOx over a wide temperature range, and upon changing the gas feed, the sulfated absorbent should be rapidly regenerable at same temperature. We examined a series of materials based on supported non-precious metal compositions. In the first step, we measured their capacities. SO_2 uptake capacity was measured under continuous flow until 200 ppb in the effluent was reached ("breakthrough point") using the lean feed composition shown in Table 1. The sample was then exposed to the rich feed under a temperature ramp from 50-560°C, following which the sample was cooled and a new adsorption measurement made. Adsorption capacity vs. temperature for our preferred adsorber is shown in Figure 1. Over the temperature range of interest, 100-500°C, the capacity ranges from 0.15-0.45 wt%, which is sufficient for lean-rich cycling. After a small drop in capacity after the first cycle, the capacity is retained over three additional cycles. SO_2 appears to be fully removed during each rich cycle.

Table 1. Composition of lean and rich diesel emission simulants

Simulated Exhaust	CO	CO_2	C_3H_6	H_2	SO_2	O_2	NO_2	NO	N_2
Lean	--	5%	--	--	5.15 ppm	12%	20 ppm	180 ppm	Balance
Rich	2%	12.5%	333 ppm	2%	--	--	--	--	Balance

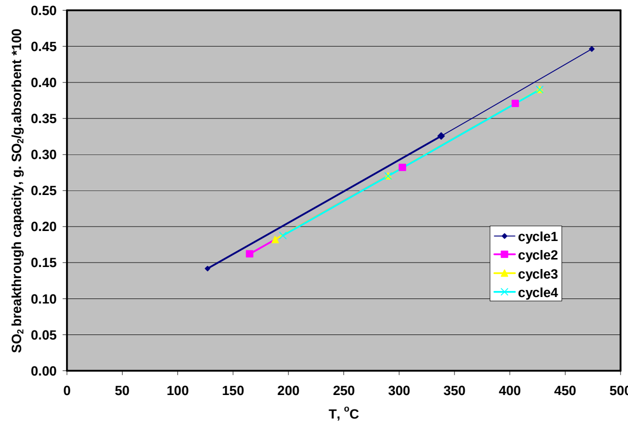

Figure 1. Temperature dependence of SO_2 breakthrough capacity over four sulfation cycles

A test was then carried out at 300°C, with cycling comprising a 20 sec rich feed at 10 hr^{-1} GHSV and 4 min lean feed at 50K hr^{-1} GHSV. Total test duration was 18.5 hr (258 cycles). The SO_2 evolved tracked very closely the reductant hydrogen signal, indicating that the evolution of SO_2 during the rich cycle is very rapid. During the lean cycles, more than 97% SO_2 was adsorbed, and during the rich gas cycle, the adsorbed SO_2 is rapidly released. No noticeable COS or other sulfur species were measured during the rich cycle.

Significance

A regenerable SOx trap material has been developed that has the capacity and the regeneration characteristics compatible with lean-rich cycling NOx traps. This development has important implications for improving the longevity of NOx traps.

References

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