

Development of Clean Diesel NOx After-treatment System with Sulfur Trap Catalyst

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ABSTRACT

Diesel engines with relatively good fuel economy are known as an effective means of reducing CO₂ emissions. It is expected that diesel engines will continue to expand as efforts to slow global warming are intensified. Diesel particulate and NOx reduction system (DPNR), which was first developed in 2003 for introduction in the Japanese and European markets, shows high purification performance which can meet more stringent regulations in the future. However, it is poisoned by sulfur components in exhaust gas derived from fuel and lubricant. We then developed the sulfur trap DPNR with a sulfur trap catalyst that traps sulfur components in the exhaust gas. High purification performance could be achieved with a small amount of platinum group metal (PGM) due to prevention of sulfur poisoning and thermal deterioration. However, this required the exchange of the sulfur trap catalyst every 40,000 km to maintain a high NOx conversion efficiency, because the sulfur trap catalyst did not have enough sulfur trap capacity. In this paper, we investigated the sulfur trap mechanism, and it was found that the formation of potassium sulfate on the surface of the sulfur trap catalyst during the sulfur trap process inhibited gas diffusion into the surface of the catalyst. We then tried to improve this condition using an oxygen storage material, which could trap sulfur through adsorption without the formation of sulfates. Moreover, the sulfur trap capacity was greatly increased by controlling desorbed SO₂ and transporting it to the sulfur trap material by increasing the temperature. As a result, a system maintaining high NOx conversion efficiency of 80% after 80,000 km mileage accumulation was obtained with our new sulfur trap catalyst concept.

1. INTRODUCTION

Diesel engines with good fuel economy are an effective means of reducing CO₂ emissions and are recognized as an important technology for reducing global warming. However as diesel vehicles require expensive after-treatment systems to purify particulate matter (PM) and nitrogen oxides (NOx), the development of a low-cost compact after-treatment system is necessary. We have developed DPNR (Diesel Particulate and NOx Reduction system) that can reduce diesel NOx and particulate matter (PM) simultaneously which was introduced in 2003 for the Japanese and European markets⁽¹⁾, ⁽²⁾,⁽³⁾. In 2005, mass production of the Avensis began for the European market, which combined this system with a 2.2-liter direct injection common rail diesel engine and achieved both high power performance and low emissions. Although the DPNR system exhibits high purification performance to meet strict emissions standards in the future, it has issues with thermal deterioration and sulfur poisoning. In response, a new concept was proposed to prevent deterioration due to sulfur poisoning and to prevent thermal deterioration caused by SOx release⁽⁴⁾,⁽⁵⁾. In this concept, sulfur poisoning of downstream NSR (NOx Storage and Reduction) catalyst is prevented by trapping all sulfur components (SOx) in the exhaust gas using an upstream sulfur trap catalyst (see Fig.1). Thus, in this system SOx release control is unnecessary and high purification performance could be achieved with a smaller amount of platinum group metals due to reduced sulfur poisoning and thermal deterioration. However, it was discovered that the sulfur trap catalyst lacks sufficient capacity and had to be replaced every 40,000 km to maintain high NOx conversion efficiency. Therefore, in order to adapt to markets, the capacity of the sulfur trap catalyst must be doubled so that the catalyst does not require exchange for at least 80,000 km.

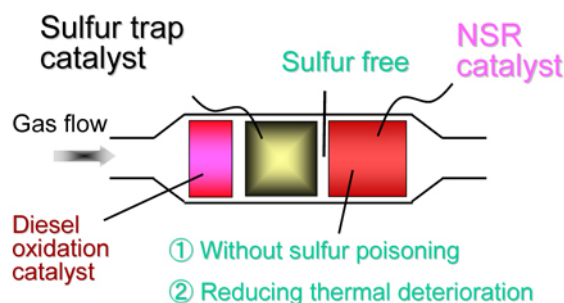


Figure 1. Sulfur Trap DPNR

To improve the sulfur trap performance, the following studies were performed as part of this research.

1. Analysis of insufficient sulfur trapping performance
2. Investigation of sulfur trap performance improvement
3. Verification of performance by vehicle durability testing

2. EXPERIMENTAL

CATALYST

Sulfur trap catalysts used in these studies were coated by Cataler Corporation on standard 400 cells per square inch (cpsi) cordierite substrates using conventional wash coating techniques, and contained sulfur trap materials such as barium (Ba) and potassium (K).

DOC (Diesel oxidation catalyst) and NSR were used in vehicle durability tests. The DOC and NSR were prototype catalysts provided by Cataler Corporation, with improved low-temperature performance.

MEASUREMENTS OF SULFUR TRAPPING PERFORMANCE

All experiments conducted in this study were carefully controlled and monitored online. The amount of trapped sulfur was investigated from both inlet and outlet SO_2 concentrations of the sulfur trap catalyst at flow reactor measurements. This reactor consisted of a quartz tube with a sample holder placed in a furnace. The catalyst used in this measurement was only the sulfur trap catalyst without the oxidation catalyst. The gas mixture at the reactor inlet consisted of SO_2 , NO , C_3H_6 , O_2 , CO_2 and H_2O .

FOURIER TRANSFORM INFRARED (FTIR) ANALYSIS

IR spectroscopic investigations were performed to analyze the sulfur trapping phenomena with JASCO 680 FT/IR. Self-supported wafers of sulfur trap catalyst diluted with KBr were prepared. The powders of the sulfur trap catalyst were collected by scraping away from the catalysts before and after experiments.

VEHICLE DURABILITY TEST

The prototype engine was a turbo-charged in-line 4-cylinder type, 2982 cm^3 displacement with a direct injection common rail system. The DOC, sulfur trap catalyst and NSR were installed in the under floor space. The prototype vehicle with 5-speed transmission was used for durability tests and emission tests, having an inertia weight of 2,000 kg.

3. RESULT AND DISCUSSION

3-1. ANALYSIS OF INSUFFICIENT SULFUR TRAPPING PERFORMANCE

Sulfur trap catalysts consist of precious metals and a sulfur trap material with strong basicity^{(6),(7)}. SO_x in exhaust gases are trapped through reactions with basic materials to generate sulfates (see Fig.2).

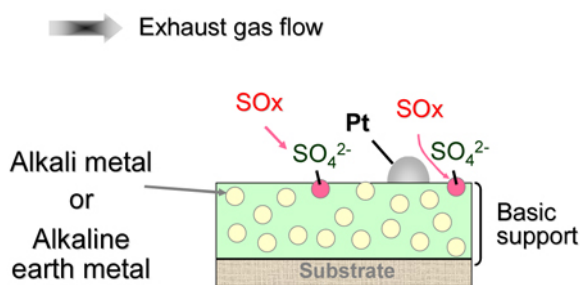


Figure 2. Sulfur Trap Mechanism

In a previous study, the trapping performances of the sulfur trap catalyst decreased as the amount of trapped sulfur increased, but the recovery of the performance were observed by controlling the temperature of sulfur trap catalyst. However, actual vehicle durability tests which Yoshida et al. had previously performed showed that the amount of trapped sulfur amounted to only 65% of the theoretical capacity of the sulfur trap material, indicating that the material was not being utilized to its full potential⁽⁶⁾.

Thus, we tried to analyze the same sulfur trap catalyst as Yoshida et al. had used (catalyst A shown in Table 1), which had been exposed to sufficient compound gases containing SO_x (see Table 2) until the sulfur trap efficiency began to decrease below 90 % at 400 °C. The distribution of sulfur and potassium, one of the sulfur trap materials, was investigated with EPMA. As shown in Figure 3, trapped sulfur was found to be disproportionately distributed on the surface of the catalyst, meaning the entire surface of the support could not be utilized. This indicates that, to achieve a substantial improvement in sulfur trapping performance, it is important to utilize the entire sulfur trap material to capture SO_x .

Table 1. Specifications of Sulfur Trap Catalyst

Sample	PGM	S-trap material (Ratio)	Size (cc)
A	Pt	Ba, K (1 : 2.3)	35
B	Pt	Ba (1)	35

Table 2. Feed Gas Components

Flow rate (L/min)	SO ₂ (ppm)	NO (ppm)	C ₃ H ₆ (ppm)	O ₂ (%)	CO ₂ (%)	H ₂ O (%)
15	100	200	200	10	10	5

Figure 3 shows the enrichment of sulfur on the surface of the catalyst may be caused by the characteristics of potassium. The melting point of potassium nitrate, which is used to store the NO_x in exhaust gas, is 333°C. At temperatures above this point, it enters a molten state and is attracted by the acidity of the SO_x on the surface of the catalyst. Consequently, the surface may be enriched, causing the formation of sulfates, which possibly inhibits the diffusion of gas into the support.

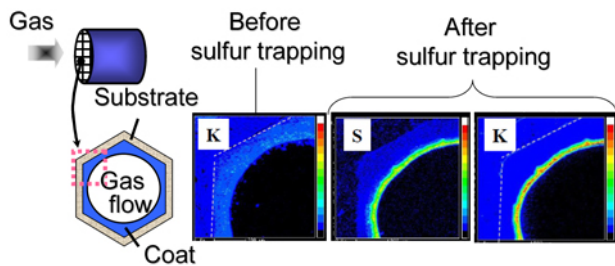


Figure 3. EPMA image of Sulfur Trap Catalyst A

In contrast, barium nitrate has a higher melting point at 592°C and barium enrichment of the catalyst surface may not occur at exhaust temperatures under normal driving conditions.

Therefore, to prevent the surface enrichment effect of potassium, sulfur trap catalyst B was fabricated with barium only and compared with a conventional sulfur trap catalyst A. A compound gas containing SO_x shown in Table 2 was passed over sulfur trap catalyst B and the amount of trapped sulfur was measured at high (400°C) and low (250°C) temperatures.

Figure 4 shows the amount of trapped sulfur. Compared with sulfur trap catalyst A, which contains both potassium and barium, the trapping performance of sulfur trap catalyst B, which contains only barium, was substantially higher than the target at high temperatures favorable for gas diffusion into the support, despite its lower amount of sulfur trap material. Moreover, it was also observed that the sulfur distribution within the sulfur trap catalyst could be utilized for trapping SO_x up to the sulfur trap material in the entire support (see Fig. 5).

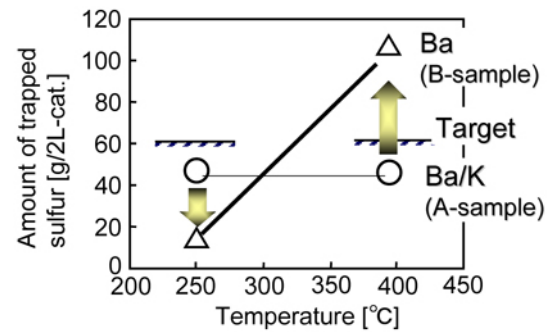


Figure 4. Sulfur Trap Capacity

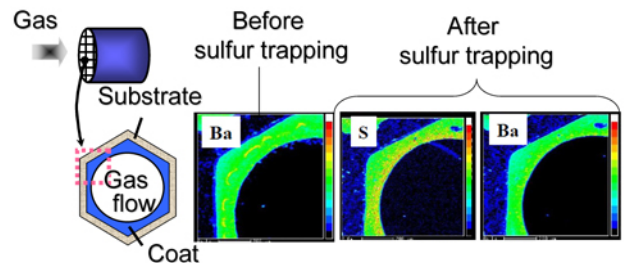


Figure 5. EPMA image of Sulfur Trap Catalyst B

These results show that it should be possible to greatly improve the amount of sulfur trapped at high temperatures by increasing utilization of the sulfur trap material over the entire support.

However, at low temperatures which are unfavorable for gas diffusion within the sulfur trap material, Figures 3 and 4 show that the properties of potassium, which has strong basicity and can exist in large quantities on the catalyst surface, may assist the trapping of sulfur.

Thus, the following two characteristics should be required to achieve an excellent sulfur trap capacity at all temperatures. One is the ability to trap sulfur on the catalyst surface at low temperatures, and another is no inhibition of gas diffusion into the support at high temperatures. The development then proceeded based on the following two policies.

1. The generation of a new mechanism for improving sulfur trapping performance at low temperatures
2. The design of an optimum system adaptable in all driving conditions