

Development of a Diesel Emission Catalyst System for Meeting US SULEV Standards

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ABSTRACT

In recent years, catalyst systems such as a lean NOx trap (LNT) catalyst system and a urea selective catalytic reduction (SCR) system have been developed to obtain cleaner diesel emissions. At Nissan, we developed an emission control system for meeting Tier 2 Bin 5 requirements in 2003. On the basis of that technology, a new HC-NOx trap catalyst system has now been developed that complies with the SULEV standards without increasing the catalyst volume and precious metal loading.

Compliance with the SULEV standards requires a further reduction of HC (NMHC) emissions by 84% and NOx by 60% compared with the emission performance Tier 2 Bin 5 compliant catalyst system. Consequently high conversion performance for both HCs and NOx is needed.

An investigation of HC emission behavior under the FTP75 mode showed that a reduction of cold-phase HCs was critical for meeting the standard. Large quantities of HCs above C4 are emitted in the cold state. Thus, a HC trap type three-way catalyst (HCT-TWC) which contains a relatively big pore size zeolite was selected for reducing cold-phase HCs corresponding to the size of HCs. This catalyst has the capability to convert not only HCs but also NOx effectively.

The possibility of integrating the HCT-TWC and a LNT catalyst was investigated with an eye toward downsizing the catalyst system. This catalyst combination was also investigated with the expectation of obtaining functional synergies. That led to the development of an HC-NOx trap catalyst.

The NOx reduction capability was improved by increasing the dispersion of precious metal and the NOx trapping agent in the LNT catalyst layer.

It was found that this HC-NOx trap catalyst system maintains good conversion performance even after aging equivalent to driving 120,000 miles. That confirmed

the possibility of meeting the SULEV standards without increasing the catalyst volume and precious metal loading over the Tier 2 Bin 5 compliant system.

1. INTRODUCTION

Expectations of clean diesel vehicles have been rising in recent years from the viewpoint of their low carbon dioxide (CO₂) emissions. In this regard, technologies for reducing the particulate matter (PM) and nitrogen oxide (NOx) emissions of diesel engines in particular are being investigated vigorously. Currently, much work is being devoted to the development of NOx conversion technologies such as lean NOx trap (LNT) systems and urea selective catalytic reduction (SCR) system for meeting the Tier2 Bin 5 standards to be phased in beginning in 2010. There are various reports about the possibility of these technologies being able to meeting the tougher standards.^{(1), (2), (3), (4), (5), (6)}

At Nissan, we previously developed an emission control system that complies with the Tier 2 Bin 5 requirements under an aged condition (50 Kmiles). The emission performance was verified in evaluations of a prototype vehicle supplied to the Environmental Protection Agency.⁽⁷⁾

In this study, a new HC-NOx trap catalyst system was developed for meeting the stricter SULEV (Tier 2 Bin 2) standards scheduled to be phased in beginning in near future.

2. ISSUES IN MEETING SULEV STANDARDS

2.1 POSITION OF SULEV STANDARDS AND NISSAN'S CONCEPT OF EMISSION CONTROL SYSTEMS

Our catalyst system for meeting the Tier 2 Bin 5 standards for diesel emissions is shown in Fig. 1. The PM and NOx emission levels obtained with this system are shown in Fig. 2. This system is based on an engine with the Modulated Kinetics (MK) combustion concept^{(8), (9), (10)}, to which an LNT catalyst was added. As shown in

Fig. 1, the system is composed of a diesel oxidation catalyst (DOC), a LNT catalyst and a catalyzed soot filter (CSF). The specifications of the catalyst and vehicle are shown in Table 1 and Table 2, respectively. The vehicle has the original operation system that was optimized to obtain maximum catalyst performance.^{(11), (12)} Fig. 2 shows that compliance with the SULEV standards requires a further reduction of HC (NMHC) emissions by 84% and NOx by 60% compared with the emission performance Tier 2 Bin 5 compliant catalyst system.

The functions of the LNT catalyst are to trap NOx in the lean phase and reduce NOx in the rich phase. This catalyst reduces NOx by using reductants such as unburned HCs, CO and H₂. Increasing the amount of reductants provided to the LNT catalyst in the rich phase can improve the NOx conversion. However, if the efficiency of reductant utilization is lower, an excess amount of reductants needs to be provided, with the result that surplus HCs are emitted. The efficiency of reductant utilization is not sufficient at present and there is trade-off between NOx and HC emissions. The concept of our new emission control system is to reduce HC and NOx emissions together by increasing the level of efficiency. One aim of this study was to achieve an internal reforming method for transforming HCs to CO and H₂ as one measure for improving reductant utilization efficiency.

Table 1: Catalyst specifications for Tier 2 Bin 5

Catalyst	Specification
DOC	Substrate: Cordierite, Pd/Rh type, 0.9L
LNT	Substrate: Cordierite, Pt/Rh type, 2.6L
CSF	Substrate: SiC, Pt type, 2.5L
Aging	Rapid Aging with engine dyno. Catalyst Temperature: From 600 to 750 deg.C Duration: 260hrs. totally

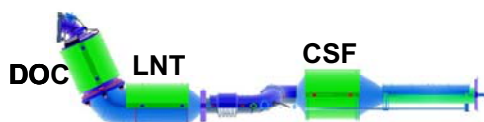


Fig. 1 Catalyst system for the diesel exhaust control for meeting Tier 2 Bin 5 standards

Table 2: Vehicle specifications and fuel used in this evaluation

Engine	2.8L DI diesel T/C (prototype)
Fuel system	HP common rail
Inertial weight	3750 lbs
Fuel	Sweden Class1 fuel Cetane number = 52.3 Sulfur content = 2 ppm

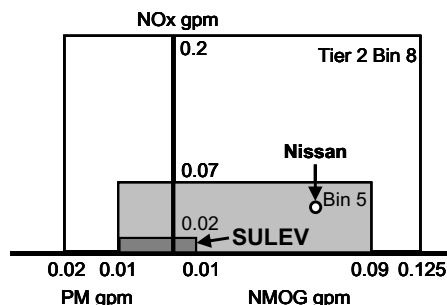


Fig. 2 Emission levels in Tier 2 Bin 5 system

2.2 DIVISION OF EMISSIONS IN THE TIER 2 BIN 5 COMPLIANT SYSTEM

To identify the emission targets for meeting the SULEV standards, an analysis was made of the HCs and NOx emitted from a Tier 2 Bin 5 compliant vehicle in the cold and hot phases of the FTP75 driving cycle. In this analysis, the cold phase was defined as the interval until the LNT bed temperature reached 250 deg.C. The results are shown in Fig. 3. As shown in this figure, HC and NOx emissions have to be reduced greatly to meet the SULEV standards. A reduction of HC emissions is especially necessary because the level exceeded the standard in the cold phase.

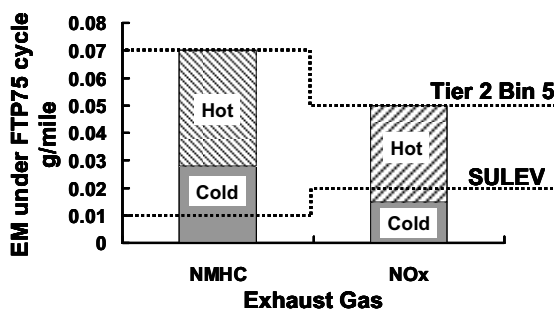


Fig. 3 Emission distribution of NMHC and NOx in Tier 2 Bin 5 compliant system (After rapid aging)

3. PROPOSED SOLUTION FOR SULEV STANDARDS AND ITS EFFECTS

3.1 REDUCTION OF COLD-PHASE HC EMISSIONS

HC species in cold phase

The HC species in the cold exhaust gas under the FTP75 driving cycle were analyzed by gas chromatography to determine the necessary catalyst capability for reducing cold-phase HCs. In this analysis, the cold phase was defined as the interval until the LNT bed temperature reached 250 deg. C. During that interval, the HC conversion with this system reached more than 90%.

A breakdown of HC emissions in the cold phase in terms of the carbon number is shown in Fig. 4. It was found

that HC species having a carbon number of 4 or higher accounted for 57% of all cold-phase HC emissions. This result indicates adding an HC trapping function like that of zeolite⁽¹³⁾ would be effective in reducing cold-phase HC emissions. Zeolite with its relatively big pore size would presumably be effective for cold-phase HC species.

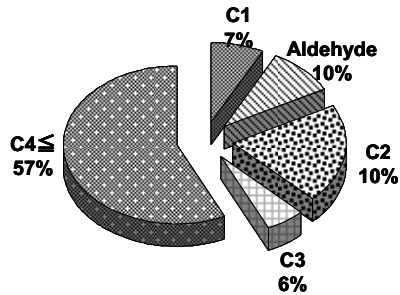


Fig. 4 Breakdown of HC species by carbon number in cold phase of FTP75 driving cycle

Comparison of HC trap performance with zeolite

Some HC trap type three-way catalysts (HCT-TWC) were prepared with HC trap agents having different pore sizes as shown in Fig. 5. Evaluations were made of their HC trapping and conversion in the cold phase of the FTP75 driving cycle. In this evaluation, each catalyst was rapidly aged equivalent to 120 Kmiles of driving.

The HC trapping and conversions were calculated with equations (1) and (2) below, respectively. Each catalyst was placed between the LNT and CSF shown in Fig. 1. The HC adsorption and conversions found for different zeolite species are shown in Fig. 6.

HC trapping rate:

$$\eta_{HC_ad} = \left(\frac{HC_trapped}{HC_cat_{in}} \right) \times 100 \cdots (1)$$

HC conversion:

$$\eta_{HC_des} = \left(\frac{HC_cat_{out}}{HC_trapped + HC_cat_{in}} \right) \times 100 \cdots (2)$$

With a small pore size like that of zeolite C, the amount of HCs trapped decreased. In contrast, good trapping performance was obtained with a larger pore size like that of zeolite A. The results confirmed that zeolite with a relatively large pore size can trap HCs effectively. All of the catalyst achieved approximately 100% HC conversion performance. Their conversion levels were higher than that seen for the gasoline vehicle. It is inferred that the O₂ concentration in diesel exhaust contributes to HC conversion because the concentration is higher when the trapped HCs are desorbed from the HCT agent.

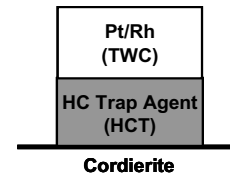


Fig. 5 Composition of HC trap type three way catalyst(HCT-TWC)

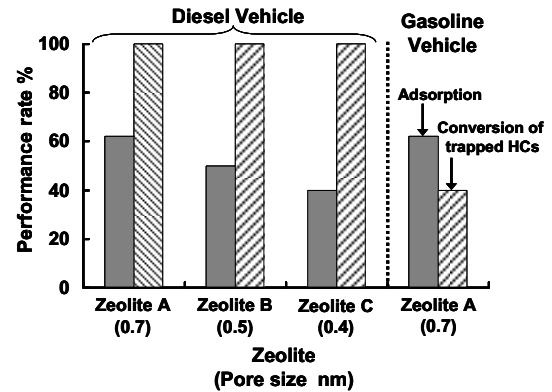


Fig. 6 Comparison of HC adsorption and conversion performance of HCT-TWCs contained zeolite species. (after rapid aging)

Effect of the position of HCT-TWC catalyst

In examining the possible combination of the HCT-TWC catalyst and the LNT catalyst, emissions under the FTP75 driving cycle were evaluated using two catalyst systems as shown in Fig. 7. The effects of the catalyst systems on HC emissions are shown in Fig. 8. In this evaluation, HC emissions were reduced greatly in comparison with the Tier 2 Bin 5 compliant system. Cold-phase HC emissions were reduced by about 60% with the HCT-TWC catalyst, and there was no difference between Systems A and B. On the other hand, it was found that System B with the HCT-TWC catalyst mounted in front of the LNT catalyst was more effective in reducing hot-phase HC emissions.

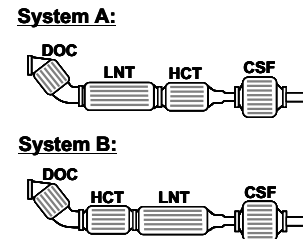


Fig. 7 Catalyst systems for reducing HC emissions