54 Diesel Oxidation Catalyst System Development for a Diesel Passenger Vehicle *

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A diesel oxidation catalyst is required to remove hydrocarbons, carbon monoxide, and soluble organic fraction from the diesel engine exhaust gas stream. The emissions and the exhaust system of diesel light-duty diesel vehicles were analyzed with the intent of enhancing the low temperature catalytic activity and optimizing the aftertreatment system. The study reported hereunder was focused on the catalyst activity and durability, the thermal management of the system, and the enhancement in emission selectivity through via the precious metals. This paper describes the appropriate materials and their composition as a diesel oxidation catalyst. The paper also describes the optimum precious metal loading for the diesel oxidation catalyst. With the respect to the aftertreatment system, this paper proposes the overall oxidation catalyst system structure (i.e. substrate arrangement, substrate volumes, substrate cell densities, etc.). It also describes the modifications made to the system to improve emissions performance and to reduce the total system cost. The test results show that the proposed system exhibits an improvement in emission reduction performance compared to the previous standard baseline.

***Keywords*: Exhaust aftertreatment**, **Diesel oxidation catalyst**, **Emissions**

1. INTRODUCTION

The abatement of carbon dioxide (CO_2) and other air pollutant emissions into the atmosphere is one of the key global issues today. Light-duty diesel vehicles have been increasing in popularity because of their high fuel efficiencies. The light-duty diesel vehicle is also considered as a solution toward decreasing carbon dioxide emissions.

Through the EURO IV emissions standards the regulations for the four primary pollutants (PM, NOx, HC, CO) of light-duty diesel vehicles have been tightened from their current EURO III levels. As a result, the role of the diesel oxidation catalyst (DOC) is becoming more and more important. The primary function of the DOC is to oxidize the hydrocarbons (HC), the carbon monoxide (CO), and to some extent the particulate matter (PM) in the exhaust gas.

A significant amount of research has recently been focused on the performance enhancement specialization of the DOC, targeting its use for high or low temperatures and removal of hydrocarbon or soluble organic fraction as examples. In the aftertreatment system for light-duty diesel vehicles, a warm-up catalytic converter (WCC) is applied with a conventional underfloor catalytic converter (UCC) to reduce pollutants in the exhaust gas, especially for the cold start condition.

Therefore, the specialization and optimization of the aftertreatment system, including catalysts, is becoming more and more important relative to the performance and competitiveness of light-duty diesel vehicles.

In this study we improved the catalytic activity at low temperature and optimized the aftertreatment system on a 1.5L light-duty diesel vehicle which had a warm-up (WCC) catalyst and an underfloor (UCC) catalyst. This study was focused on the catalyst activity and durability, the system thermal management, and the emission selectivity via the precious metals. This paper describes the proper materials and their composition for a diesel oxidation catalyst and the optimum precious metal loading. In terms of an aftertreatment system, we also describe the converter structure (substrate arrangement, volume, cell density, etc) and a modified system which improves the performance (emission reduction performance) and reduces the overall cost.

2. PREPARATION AND EXPERIMENTS

Analysis of the emissions and the aftertreatment system

Recently developed diesel engine which incorporate improved control of injection timing and fuel injection rates, increased fuel pressure supply through common rail technology, and turbo charging, may well allow further reduction of NOx and PM. However, it is likely that further decreases in exhaust gas temperatures and increases in CO concentrations will result. Therefore, very effective low temperature oxidation catalysis will be necessary. Hence, there is a future need for catalysts with improved oxidation activity at low temperatures. Figure 1 shows a catalyst inlet temperature trace over the European test cycle.

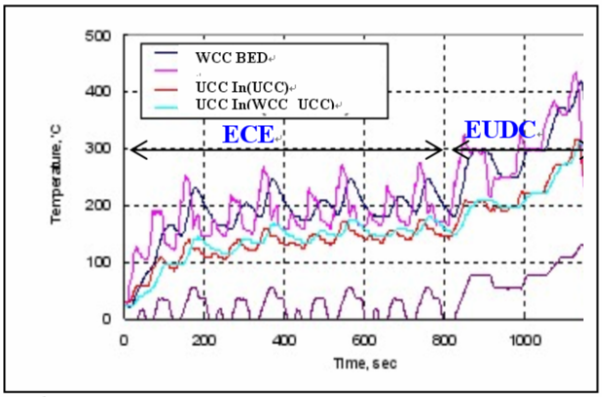

Fig.1 Catalyst Inlet Temperature Trace Over the European Test Cycle. (NEDC Mode)

For EURO Ⅲ/IV applications low temperature catalyst activity is required during the ECE portion of the test cycle. It can be seen that diesel catalysts are required to operate at low temperatures (typically below 200°C in the ECE portion of the European test cycle).

From the test results of the vehicle evaluation using a warm-up catalytic converter and catalysts with low temperature catalytic activity, a large amount of the four pollutants in exhaust gas are still discharged at low temperature. Results from the vehicle evaluation are given in Table 1.

Specification of catalyst	WCC: PGM 70g/ft3 UCC: PGM 40+20g/ft3
T_{50} CO light off data	CO: 150℃ HC: 170℃
Duration reaching T_{50}	140~160 sec
Emission level (vs. 2.0L diesel Engine)	HC: 70~90% CO: 150~170% NOx: 70~88%
* T_{50} CO light off performance is most important	

Table 1. Emission Data From EURO Ⅲ Light-Duty Diesel Vehicle (1.5L DI Engine with Warm-up and Underfloor Catalysts)

In terms of the catalyst system, the application of the warm-up catalyst close to the engine results in a quick increase in the bed temperature of the catalyst since exhaust gas temperature is high in WCC location near to engine. Furthermore, uniform distribution of the flow into the catalyst is one of the key factors toward improvement of the catalyst performance and durability. Accordingly, we investigated the potential for improvement of the flow uniformity in the warm-up catalytic converter.

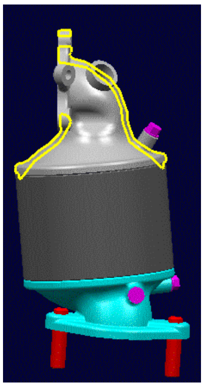

Fig.2 Schematic Drawing of Warm-up Catalytic Converter (WCC)

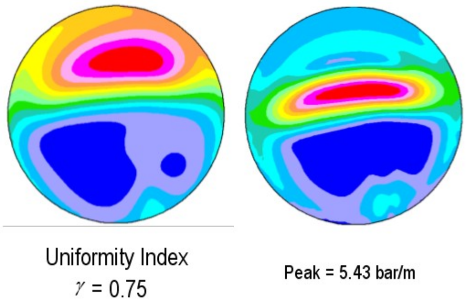

Fig.3 Analysis of the Exhaust Gas Flow and Pressure Distribution at the Catalyst Face (4000 RPM)

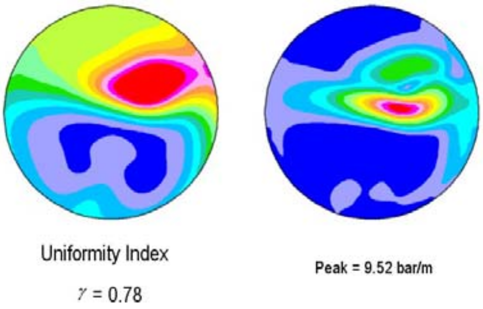

Fig.4 Analysis of the Exhaust Gas Flow and Pressure Distribution at the Catalyst Face (4000 RPM + Turbo Charger)

In Figure 3 the simulated catalyst performance will become worse as a result of poor inlet exhaust gas flow conditions (uniformity factor: 0.75). However, we observed an improvement of the exhaust gas flow uniformity due to the rotation effect of the turbocharger in front of the WCC. Figure 5 shows a favorable exhaust gas flow distribution at a low engine rpm region (the ECE portion of the European test cycle). This is important for emission certification.

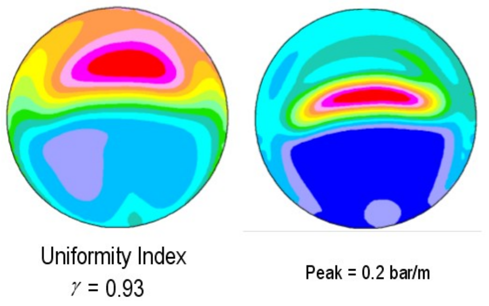

Fig.5. Analysis of Exhaust Gas Flow and Pressure Distribution at the Catalyst Face (1000 RPM)

Selection of optimum catalytic system
Characterization of diesel oxidation Catalyst

To improve the initial performance and durability of the DOC, we investigated different washcoats. Washcoats are important factors of the catalytic system. In this system, first Synthetic gas catalytic activity tests(SCAT) were performed on a rig.

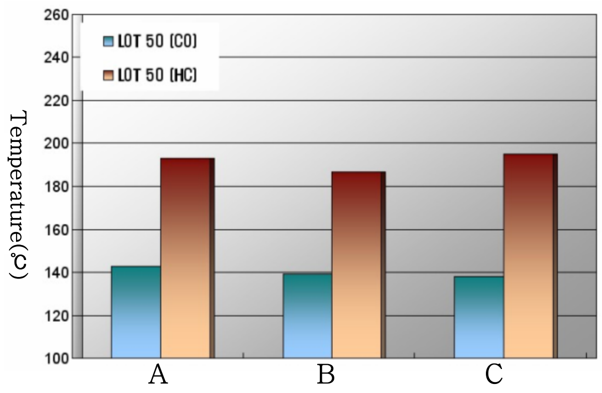

Fig.6. SCAT T_{50} CO/HC data for a conventional and a new washcoat.

In figure 6 it was observed that the CO light-off temperature is about 140℃ and the HC light-off temperature is more than 190℃. This result was consistent with that of the previous vehicle test. However, it was predicted that improvement of the catalyst performance by changing to conventional washcoat A is not possible.

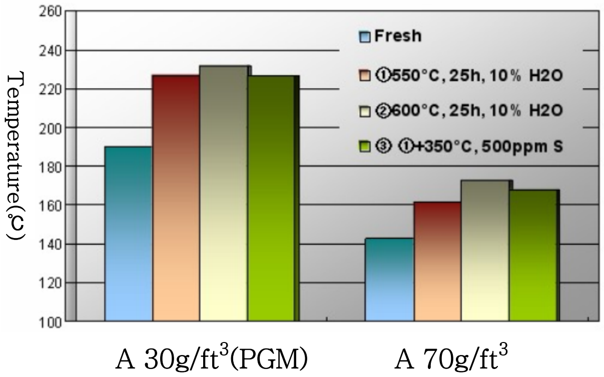

Fig.7. T_{50} CO Light-Off Data after Various Types of Aging for Conventional Catalyst A.

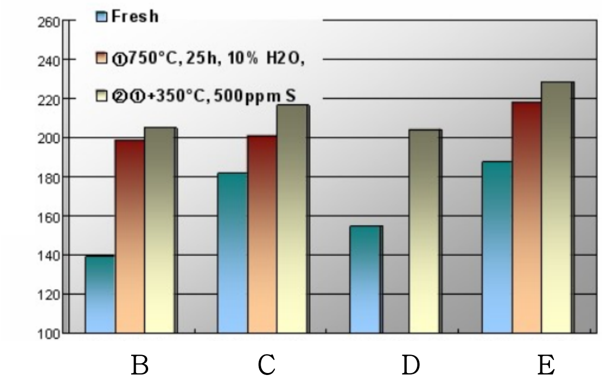

Fig.8. T_{50} CO Light-Off Data after Various Types of Aging for New Catalysts B, C, D, E.

The catalysts above were aged together with the conventional catalyst A for 10 hours with a tube furnace using 500ppm sulfur at 350℃. Hydrothermal aging was also performed on the catalysts at 550℃, 600℃, and 750℃. Figure 7 and 8 detail the CO and HC light-off performance after the aging cycles. The results show that conventional catalyst A has sufficient sulfur durability and but insufficient durability for thermal damage.

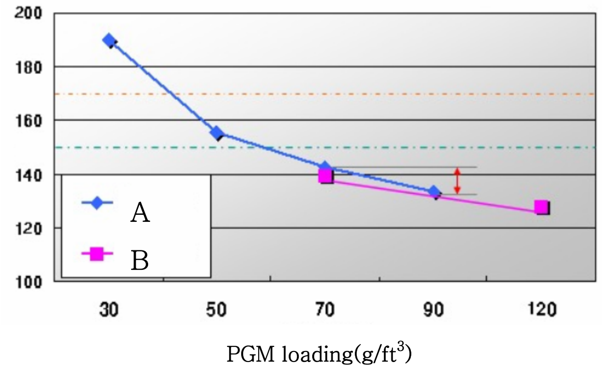

Fig.9. Effect of PGM loading on T_{50} CO Light-Off Performance of Catalysts in SCAT.

In order to investigate the improvement in catalytic activity as a function of precious medal loading increase, we evaluated the effect of the PGM loading on the light-off performance of catalyst in the SCAT (Fig.9). Changing the PGM loading from a conventional specification 70g/ft^3 (2.45g/L) to 90g/ft^3 (3.15g/L) lowered the T_{50} light-off temperature by 10^{o}C.

The Investigation of parameters which influenced the reaction

The reaction parameters which affect the catalyst activity in the aftertreatment system were investigated. First, the relationship between the conversion efficiency of the catalysts and the flow distribution was investigated. It is apparent that catalysts with better flow distributions (higher γ values) light-off at lower temperatures (Figure 10). Accordingly, it is possible that the conversion efficiency of the catalysts can be enhanced through the appropriate design of the catalytic converter.

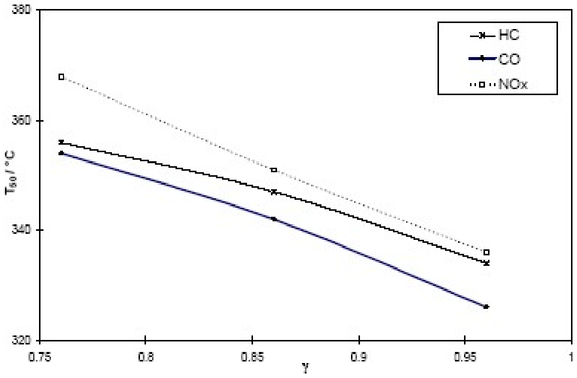

Fig.10. Effect of Flow Distribution on Light-Off

Second, the dependency of the catalyst's conversion efficiency on the catalyst's volume was investigated. In Figure 11 the dependence of the HC conversion efficiency on the catalyst's volume and on the exhaust gas mass flow is displayed. This shows there is an optimum catalyst volume for the warm-up catalytic converter which yields a maximum conversion rate.

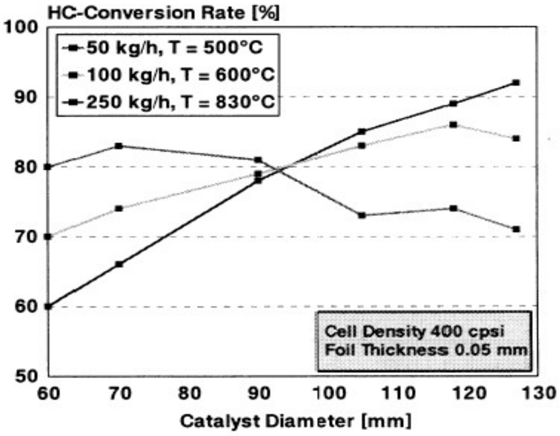

Fig.11. HC Conversion Rate as a Function of Catalyst Diameter and Mass Flow (cell density 400cpsi)

Third, the temperature profile at several different points of time in the warm-up catalyst was investigated (Figure 12). The aspect of cold start emissions can be rationalized in the following way. The light-off process is characterized by a heat front moving from the inlet towards the catalyst outlet. If light-off occurs, the catalyst volume upstream of the heat front contributes to the catalytic process while the downstream part of the catalyst remains cold and does not contribute to the reaction. Therefore, overall catalyst performance can be maximized by promoting the conversion efficiency at the front of the catalysts.

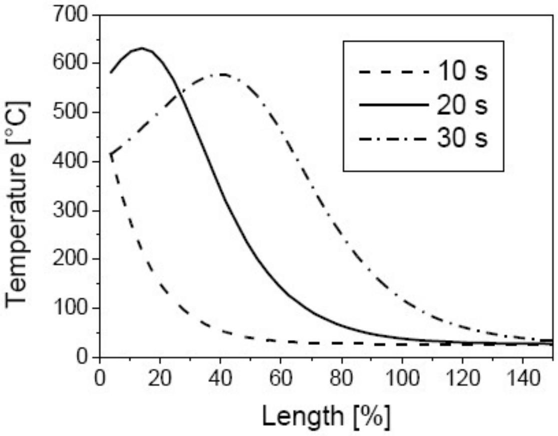

Fig.12. Temperature Profiles in the Warm-up Catalyst

Retaining the heat of the exhaust gas and quickly heating the catalyst to temperatures at which the catalyst can be activated is important for the emission performance of the vehicle. Furthermore, the surface area of the catalyst must be large in order to transfer the heat well; however, the catalyst's volume and heat capacity must be small in order to achieve rapid heating. When we design the aftertreatment system the following parameters must be considered: catalyst conversion efficiency, pressure drop, durability, cost. From the previous investigation, the reaction parameters which affect the catalyst activity of the aftertreatment system are arranged in Table 2.

Table 2. Parameters Which Affect Catalyst Performance.

Concept	Strategy	Check Point
Shape Optimization	·WCC/UCC Optimum Volume ·Catalyst Shape	·L/OUT Pressure Drop
Heat Capacity Minimization	·Minimize WCC Catalyst ·Change the Substrate ·Minimize Heat Emission	·Durability ·Cost
Catalyst Performance Enhancement	·Improve washcoat ·Zone coating	Durability

Selection of the improved system

As a result of the previous investigation, we made the following specification for an improved system (Table 3).

Table 3. Improved System.

Symbol	Contents	Effect
WCC-1	·Reduction of Catalyst Volume (29%↓) ·Thinwall Substrate (400→600cpsi)	·Optimization of Catalyst Shape ·Improvement in Flow Distribution
WCC-2	·Two brick catalyst (Aℓ→ 1/2Aℓ * 2) ·Zone Coating (70g→90/20g)	·Reduction of Catalyst Heat Capacity by Zone Coating
WCC-3	WCC-2 + Thinwall Substrate	Increase in Catalyst Efficiency
WCC-4	WCC-2 + Change the Washcoat (A→F)	Increase in Catalyst Durability
D-MF	Ahead of Muffler Double Wall Pipe	Keep Exhaust Gas Warm
UCC-1	·Reduction of Catalyst Volume ~ two brick (61%↓/28%↓) ·Zone Coating (40/20g→70/20g)	Reduction of Catalyst Heat Capacity by Zone Coating
UCC-2	·Reduction of Catalyst Volume ~ two brick (28%↓/28%↓) ·Zone Coating (40/20g→70/20g)	Reduction of Catalyst Heat Capacity by Zone Coating

Test Result

Comparison emission tests for the various configurations of the catalytic system were carried out on a vehicle (EURO III 1.5L light-duty diesel vehicle). The generated vehicle emissions were measured and the results are shown in Table 5.

Table 4. Various Configurations of the Catalytic System for the Vehicle Generated Emission Tests.

	WCC			UCC		
	Volume	PGM	cat.	Volume	PGM	cat.
	aℓ	70	A	bℓ+bℓ (b=1.3a)	40+20	A
①	↑	↑	↑	0.39b+0.72b	70+20	↑
②	↑	↑	↑	① + double wall pipe		↑
③	↑	↑	↑	0.72b+0.72b	↑	↑
④	1/2a + 1/2a	90+20	↑	↑	↑	↑
⑤	↑	100+20	F	↑	↑	↑

Table 5. Results of the Vehicle Generated Emission Tests (percentage improvement or decrease of performance compared with conventional catalytic system baseline)

	HC	CO	NOX	HC+ Nox	PM
	-	0.64	0.5	0.56	0.05
①	-24%	9%	-13%	-11%	-14%
②	-11%	25%	-10%	-8%	-3%
③	-20%	16%	-3%	-5%	3%
④	-2%	31%	-3%	0%	3%
⑤	44%	25%	0%	8%	-10%

From the results of previous baseline emission tests, we can obtain these results. First, as the PGM loading is increased at the front of catalyst, the removal of CO is clearly observed to be greater than that obtained for the conventional catalytic system. However, deterioration in removal of HC and PM is observed; this is especially the case where the underfloor catalytic converter volume is reduced. The removal of HC depends heavily on catalyst volume. The concentration of PGM loading at the front of catalyst and the reduction of catalyst volume has the advantage of improved CO removal rather than HC. Taking the aging pattern of the diesel oxidation catalyst into consideration, this design concept of catalyst system is desirable. Second, the higher concentration of PGM loading has more of an influence on the WCC compared to the UCC. This is due to the WCC being heated more quickly than the UCC. Third, the catalytic selectivity for a specific component in the exhaust gas can be controlled through the selection of proper materials and their composition. Removal of HC is improved when conventional catalyst A is to be replaced by catalyst B. Catalyst B has good thermal durability and is a zeolite material which is efficient for HC removal (Figure 13).

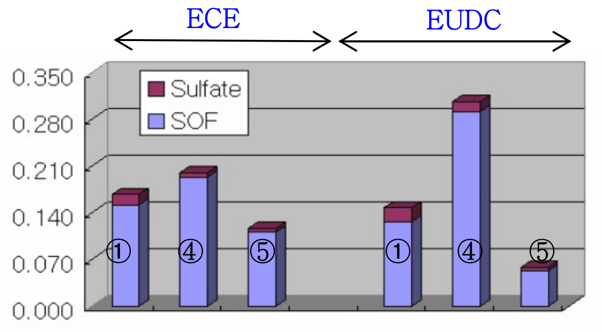

Fig. 13 PM (Particulate Matter) Emission Results for ①(Baseline System), ④ and ⑤ in Table 5.

In conclusion, the aftertreatment system has been optimized and shows significantly improved emission reduction results, as well as a reduction of overall cost. Through the selection of proper materials, a way to enhance the catalytic selectivity for a specific component in the exhaust gas was outlined.

3. CONCLUSION

Through this study we arrived results and conclusions which can be used as important data toward developing a diesel oxidation catalyst system. These conclusions are as follows:

(1) The reduction of the catalyst volume has the advantage of exhaust gas emission reduction at cold start due to reducing the heat capacity of the catalyst.

(2) Through concentration of the PGM loading in the WCC and UCC at the front of catalyst we can achieve improvement of the catalyst efficiency and an overall cost reduction.

(3) Through the development of catalyst, such as HC adsorbing functionality by the use of zeolite materials, we can enhance the catalytic selectivity for a specific component in the exhaust gas and improve the durability.

(4) In this study we describe proper materials and their compositions as diesel oxidation catalysts, as well as optimum precious metal loadings. In terms of the aftertreatment system, we also outlined the optimum converter system structure (i.e. substrate arrangement, volume, cell density, etc) and a modified system structure to improve the performance and reduce the overall cost.

4. ACKNOWLEDGMENTS

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