

# Applicable Diesel Oxidation Catalyst for Multi-Diesel Exhaust System

Yosuke Goto  
Umicore Shokubai Japan Co., Ltd.

Naohiro Kato  
Umicore AG & Co. KG

Shota Kawashima, Yoshiyuki Hayashi, Hideki Goto, and Masao Hori  
Umicore Shokubai Japan Co., Ltd.

## ABSTRACT

The diesel oxidation catalysts (DOC) having high purification performance to the exhaust gas at low temperatures were investigated. In this paper two main technological improvements from conventional DOC are shown. First is forming Pt/Pd composite particles in order to suppress sintering of precious metal under high thermal aging condition. This generating Pt/Pd composite and the effect were exemplified by TEM-EDS and XRD analysis. Second is adjusting electric charge of Pt/Pd surface to reduce interaction between Pt/Pd and carbon monoxide (CO) by modifying the support material components. Adjusting electric charge of Pt/Pd surface by applying new support material could cancel CO poisoning at Pt/Pd surface. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) studies suggested that improved support material is more suitable for CO oxidation at a low temperature based on the concept.

In this study, the fundamental function of DOC such as oxidation activity at a low temperature and heat-up property by fuel injection were eventually evaluated using diesel engine. The new DOC achieved the performance competitive with conventional DOC applied for EU5 regulation, even if precious metal amount was reduced by more than 30 %, in terms of light off activity and fuel heat-up property after thermal aging at 800°C.

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## INTRODUCTION

In recent years, while emission gas regulation of vehicle has become severer worldwide, the temperature of exhaust gas from diesel engine has been lowered by downsizing engine from a viewpoint of the improvement in fuel consumption [1, 2]. And this tendency of lower temperature has become strong by introducing new EGR system concept for the reduction of NOx emission from diesel engine [3, 4]. On the other hand, this new EGR system has led to the result that CO emission increased from lower temperature. In addition to the above, much CO and hydrocarbon (HC) are emitted when the catalyst has not been activated sufficiently after engine start and low-load operation such as a drive in an urban area. Even if the previously mentioned trends in engine design or the emission controls are mainstream, it is not desirable, in the economical point of view, to increase the amount of precious metal on the catalyst in order to meet regulations, and that cannot be a fundamental solution if the catalyst does not have sufficient activity at a low

temperature and thermal durability. Therefore it is an important technical issue how to improve catalytic activity at a low temperature.

Currently, emission gas purification is controlled by catalyst system which consist of multiple catalysts. Especially DOC is the common application item for all catalyst system. Responsibility for generating heat is also expected to DOC as well as purifying CO, HC and soluble organic fraction (SOF). Heat generation activity is usually important for a system in which DOC is installed in front of the DPF or NH<sub>3</sub>-SCR catalyst. Raising gas temperature rapidly by combusting unburned substance comes from in-cylinder combustion or injected fuel into exhaust pipe is required for soot combustion, for hydrolysis of urea under any operating conditions, even at a low temperature.

DOC which has excellent CO, HC oxidation and injected fuel combustion performance will help reducing fuel consumption or saving the catalyst volume and precious metal loading. The effect would be greatly reflected in the catalyst system design.

In this study, key technological points aiming at the improvement of applicable DOC for multi-diesel exhaust systems are reported. Some analyses were conducted with the new catalyst which was designed with the objective of high thermal durability, dissolution negative mechanism of oxidation reaction at a low temperature and sulfur tolerance.

## EXPERIMENTAL

### Powders and Catalysts Preparation

Several powders and the catalysts were prepared for analysis and performance evaluation. The catalyst powders with precious metals were thermally treated at 700°C for 50 hours or 800°C for 20 hours in static furnace. Then the catalysts were coated onto standard cordierite monolith and aged under the same conditions. A summary of the differences between powders and catalysts are presented in [Table 1](#). The described Pt/Pd ratio in [Table 1](#) means weight ratio.

Table 1. DOC compositions

| Catalyst | Cat. Powder | Precious Metal | Support Material               | Composite Tech. |
|----------|-------------|----------------|--------------------------------|-----------------|
| A        | a           | Pt/Pd=2/1      | a'                             | with            |
| B        | b           | Pt/Pd=2/1      | b'                             | with            |
| C        | c           | Pt/Pd=2/1      | Al <sub>2</sub> O <sub>3</sub> | with            |
| D        | d           | Pt/Pd=2/1      | Al <sub>2</sub> O <sub>3</sub> | w/o             |

### Synthetic Gas Test

[Table 2](#) shows the synthetic gas test conditions under which oxidation performance was evaluated (24 mm diameter × 150 mm length; 30 cm<sup>3</sup> with 400 cpsi) with a conventional gas reactor system and analyzer bench.

Table 2. Synthetic Gas Test Conditions

|                                                                         |                        |
|-------------------------------------------------------------------------|------------------------|
| Space Velocity                                                          | 40,000 h <sup>-1</sup> |
| Temp. Ramp Rate                                                         | 20 °C / min            |
| NO                                                                      | 80 ppm                 |
| HC (C <sub>3</sub> H <sub>6</sub> :C <sub>3</sub> H <sub>8</sub> = 4:1) | 350 ppm                |
| CO                                                                      | 1,000 ppm              |
| O <sub>2</sub>                                                          | 12 %                   |
| CO <sub>2</sub>                                                         | 6 %                    |
| H <sub>2</sub> O                                                        | 6 %                    |
| N <sub>2</sub>                                                          | Balance                |

### Light Duty Diesel Engine Bench Test

A direct injection and turbo charged (DITC) diesel engine of 3.0 L displacement was used to evaluate the light-off performance and fuel combustion property. These evaluations are the test for DOC functions such as CO, HC oxidation activity and heat-up capability assumed DOC+ DPF system. Catalysts of 1.2 L volume (5.66" × 3") with 400cpsi were located downstream of the engine in the exhaust pipe as shown in [Fig. 1](#). And the engine bench tests were operated with fuel of which the specifications are listed in [Table 3](#). In the heat-up evaluation, diesel fuel was dosed directly into a section of 38 mm diameter exhaust pipe. The secondary fuel was delivered by dual plunger-type pumps and was injected with the assistance of compressed air. The temperatures were measured at inlet, 1/2 mid-bed and outlet position of the catalyst. And sulfur aging test was also conducted by using this engine with fuel contained 400 ppm sulfur. After the catalyst was exposed to 12 g sulfur at 350°C, adsorbed sulfur was purged at 700°C in the point of catalyst outlet by the fuel injected into the pipe. It was a simulation of active DPF regeneration, and its procedure was defined as sulfur treatment.

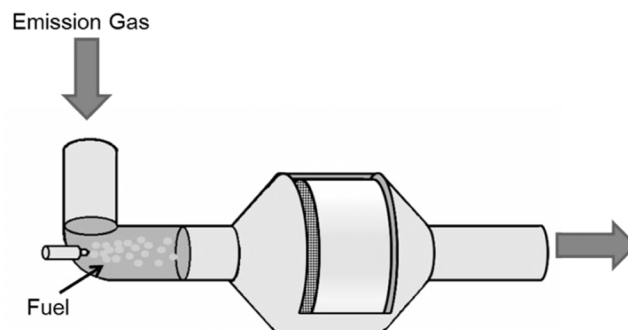


Figure 1. Schematic of Equipment Used for Heat-up Test (LD Diesel Engine)

Table 3. Diesel Fuel Specification

|                           |            |
|---------------------------|------------|
| Temp. at 90% distillation | 336.5 °C   |
| Cetane number             | 58.7       |
| S content                 | 6 ppm      |
| Total heat value          | 45,860 J/g |

### Characterization

Several catalyst powders were characterized by the following analytical instruments.

Powder X-ray Diffraction (XRD) : Spectris Co., Ltd. X-ray diffractometer X'Pert PRO MPD.

Transmission Electron Microscopy Energy Dispersive X-ray Spectroscopy (TEM-EDS) : JEOL FE-TEM JEM-2100F / JEOL EDS JED-2300F.

CO Pulse Measurement : Hemmi-inc Gas adsorption measuring equipment R6015.

BET Surface Area Measurement : Mountech Co., Ltd. Macsorb HM model-1210.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) : Infrared spectrophotometer Nicolet6700 Thermo Fisher Scientific K.K.

## RESULTS AND DISCUSSION

### *The Effect of Pt/Pd Composite Particles*

Pt is generally used for DOC as catalytic component and that has oxidation activity at a low temperature. However the cost is high, in addition to it, the thermal durability is not good. In case the Pt-containing DOC is installed upstream from DPF, the sintering of Pt particles would proceed significantly and the activity would be deteriorated because the particles are exposed to high thermal load which is necessary for soot regeneration.

Catalysts in which Pd is also added as an active component for the purpose of improving the performance in active regeneration system have been generally investigated. However, the thermal durability has not been sufficient. Upon this, it can be expected if the interaction between Pt and Pd becomes stronger, there would be a possibility to suppress Pt sintering based on the concept that Pd has higher thermal durability than Pt [14, 15]. Therefore, forming composite particles between Pt and Pd was investigated in this study.

Consequently, our attempt succeeded and it was confirmed that the Pt/Pd composite technique had suppressed sintering of Pt more than a conventional technique does, where Pt and Pd exist separately.

As shown in Fig. 2, the results of observation with catalyst powder c and d in TEM-EDS analysis after thermal aging at 700°C for 50 hours indicate that the effect of Pt/Pd composite technology was clear. Despite the fact that the catalyst powder c and d had the same catalyst formulation, their precious metals particle size were obviously different. The particle size with new technology, that was catalyst powder c, was about 20 nm, whereas the particles with conventional technology had grown to about 50 to 70 nm. And also the results of CO adsorption measurement presented in Fig. 3 supported the improvement. The values show the amount of CO absorbed in one gram of catalyst powder. Pt/Pd particles in the catalyst powder c had more CO adsorption capacity than those in

catalyst powder d. The result indicates that the catalyst powder c has smaller Pt/Pd particles at the macroscale as well as microscale in TEM-EDS observation.

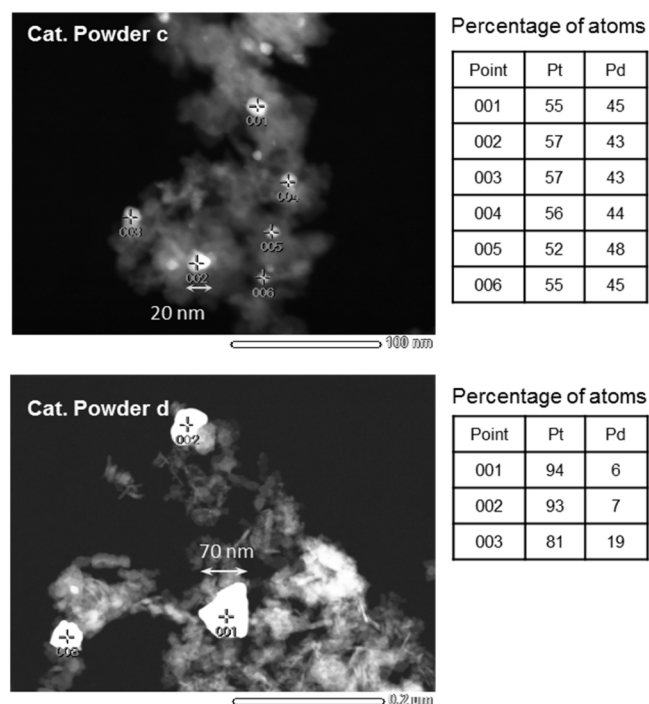


Figure 2. Observation of Pt/Pd Particles and Pt/Pd Atom Rate with TEM-EDS Analysis (700°C for 50 hours)

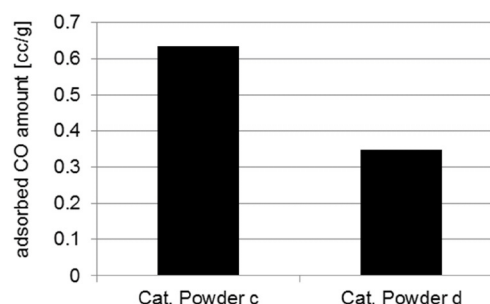


Figure 3. Measurement of CO Adsorption Capacity on Pt/Pd Particles (700°C for 50 hours)

In addition to this, the atomic ratio values of Pt and Pd in the irradiated point were almost equal to preparation ratio regarding new technology. On the other hand, Pt particles and Pd particles were supported individually by conventional technology which has not gone through the especial process. (Fig.2)

The probability of forming Pt/Pd composite particle was also confirmed by XRD analysis. Fig. 4 shows that the Pt-peak of new technology shifted to higher angle, that is to say the peak was closing Pd-peak. It suggests that the Pt-Pd bond is formed at least partly, and some interactions between Pt and Pd were presumably generated.