

DOC Development Targeting Emerging High S Area Market

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ABSTRACT

Low cost and S(sulphur)-tolerant DOCs (Diesel Oxidation Catalysts) are being demanded in emerging countries such as China and India, where Euro 4 and 5 type emission standards are going to be implemented or are being implemented. However, fuel S content is different in the metros vis-à-vis non metros in many emerging countries. In such a scenario, DOCs need to maintain catalytic performance with high S fuel as well as standard low S fuel. This paper describes the development results of S tolerant Pt-Pd based DOCs.

A new washcoat technology (WT D) has been developed for EU 4 passive Pt-Pd DOC applications, in which PGM cost was thrifted by replacing part of Pt by Pd. Vehicle test results after thermal ageing and S poisoning demonstrated that the Pt-Pd DOC (Pt:Pd=4:1) prepared with WT D gave similar tailpipe CO (Carbon monoxide) and HC (Hydrocarbon) emission conversions as a commercially available EU 4 passive Pt-only DOC when 50ppm S diesel fuel was used. When 350ppm S fuel was used, the Pt-Pd DOC exhibits higher CO and THC emission conversions than the Pt DOC.

For EU 5 pre-DPF (Diesel Particulate Filter) DOC, a new washcoat technology (WT E) has been proposed. Engine bench test results show the DOC prepared with WT E has higher CO and HC oxidation activity than a commercially available EU 5 Pt-Pd DOC (WT B) after S poisoning and 40~50% PGM cost can be thrifted. Moreover, fuel combustion performance for downstream CSF (catalyzed soot filter) at forced regeneration has been proven, even with 500 ppm S fuel.

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INTRODUCTION

Diesel engines are used globally because of their energy efficiency compared to spark ignited gasoline engines. In addition, a diesel engine is preferred because of reduced greenhouse gases from the vehicles. On the other hand, regulations for HC, CO, PM (particulate matter) and NO_x (nitrogen oxides) emission from vehicles are becoming more and more stringent globally, especially for on-road vehicles, in order to reduce impact on human health and environment.

Table 1 shows movement of China and European regulations and it is known that China emission regulations are same to European ones. Regarding the implementation time, it may be started from 2015 for China 4 and from 2017 for China 5 in nationwide. Therefore we have to develop after-treatment systems for the coming markets. In order to treat diesel exhaust emissions, tremendous amounts of technical improvements are being made. Catalysts have been become essential devices amongst the technical countermeasures to reduce diesel emissions in after-treatment systems because their effectiveness has been successfully demonstrated in many applications [1, 2, 3, 4, 5].

Table 1. Vehicle emission regulations

	CO [g/km]	THC+NO _x [g/km]	NO _x [g/km]	PM [g/km]	PN [#/km]
EU 4	0.5	0.30	0.25	0.025	-
China 4	0.5	0.30	0.25	0.025	-
EU 5	0.5	0.23	0.18	0.0045	6×10^{11}
China 5	0.5	0.23	0.18	0.0045	6×10^{11}

DOCs are being used widely in LDD (light-duty diesel) applications, targeting EU 4 regulations, to oxidize CO and HC to CO₂ and H₂O. The combination of DOC and CSF is being applied in EU 5 applications because of stringent PM regulation. Considering rapid vehicle market growth in emerging countries, low cost DOCs with high S tolerance are being demanded. Here, WT D and WT E have been developed, targeting passive DOC for EU 4 and pre-DPF DOC for EU 5 regulations, respectively.

EXPERIMENTAL

Catalyst Preparation

In this paper, all catalysts utilized in vehicle and engine bench tests were prepared by coating slurries on extruded cordierite monolith substrates with cell density of 62 cell/cm². Core DOCs for simulated gas tests were taken from full size bricks. Coating slurries were dried and calcined for SO₂-TPD (temperature programmed desorption) and CO chemisorption testing.

Catalyst Evaluation

In washcoat technology screening, SO₂-TPD was used to evaluate desulphation temperature, in which SO₂ adsorption was conducted at 300°C with the mixture gas of SO₂ and O₂. SO₂ desorption was conducted in helium (He) with heating at a rate of 10°C/min. A mass spectrometer was used to record the desorbed SO₂. CO chemisorption was used to evaluate the PGM dispersion of washcoat powder.

In engine bench testing, a 2.5 liter EU 5 diesel engine was used for bench test and a 2.2 liter EU 4 vehicle was used in the vehicle test. A simulated gas reactor test was also used to evaluate with core DOCs.

RESULTS AND DISCUSSION

In this paper, the effect of Pt-Pd ratio on DOC oxidation activity, S-tolerance performance has been explored, firstly. It was found that Pt-Pd type DOCs have higher CO/HC oxidation, but poorer S-tolerance than Pt only DOC, based on our existing washcoat technologies. Hence, new washcoat technologies for Pt-Pd type DOCs have been developed targeting the improvement of S-tolerance. As a result, WT D and WT E have been proven efficiency for EU 4 and EU 5, respectively.

Effect of Replacing Pt by Pd on DOC Performance

Introducing Pd into DOC is one of approaches to reduce PGM cost, since Pd is historically cheaper than Pt. However, it is always reported that SO_x containing gas induces a strong deactivation of the catalytic activity by formation of stable inactive Pd sulfates when Pt-Pd type DOC are used [6, 7, 9]. Hence, the effect of Pd addition on DOC oxidation activity and S-tolerance has been investigated based on the existing washcoat technology.

Effect of Replacing Pt by Pd on DOC Oxidation Activity

In this study, all catalysts were prepared by coating the slurries with different Pt-Pd ratio on 1.3L cordierite monolith. The total PGM loading is 2.0 g/L for all DOCs and the Pt-Pd ratio was set to 1:0, 2:1, 1:1 and 0:1 to investigate its effect on CO and HC oxidation activity. Two washcoat technologies being applied

in commercial mass production parts were used in this test, in which WT A is used for EU 4 applications and WT B is used for EU 5 applications.

The oxidation activity was evaluated in simulated gas equipment with core DOCs (φ25.4 mm × 76 mm) taken from full size bricks. The gas condition is expressed in Table 2. Thermal ageing at 700°C was conducted for 20h in an electric furnace before the test.

A transient light-off program was applied in the test which started from 100°C to 400°C with a temperature ramp-up of 15°C/min.

T50 of CO and HC was utilized as the criterion of oxidation activity, in which T50 is the DOC inlet temperature when CO or HC conversion achieved to 50%. Hence, the higher T50 means lower oxidation activity.

Table 2. Gas condition of the activity test

C3H6	O ₂	NO	CO	CO ₂	H ₂ O	N ₂
[ppmC]	[%]	[ppm]	[ppm]	[%]	[%]	
1000	10	100	3000	8	8	balance

T50 of CO and HC are expressed in Figure 1. Pt only DOC shows the lowest CO oxidation activity and Pt-Pd type DOCs with Pt-Pd ratio of 2:1~1:1 exhibit the highest CO oxidation activity when WT A was used. The same tendency can be also found on WT B. For HC oxidation, it can be also found that the Pt-Pd type DOCs with Pt-Pd ratio of 2:1~1:1 exhibit the highest HC oxidation activity towards HC, both on WT A and on WT B.

Therefore, it can be concluded that Pt-Pd type DOCs have higher CO/HC oxidation activity than Pt only DOC, regardless of the washcoat technology. It has been reported that Pd addition into Pt type DOC improves thermal stability of Pt particles, since Pt particles suffer from poor durability, rapidly losing active metal surface area under high-temperature lean conditions [8]. In this study, CO chemisorption method was used to evaluate the PGM dispersion of prepared DOCs. The pre-treatment for CO-pulse was conducted at 400°C with H₂ reduction for 30 min. Then CO adsorption was carried out at 50°C. Here, CO adsorption amount was used as the criterion for PGM dispersion. The higher CO adsorption amount means higher PGM surface area indicating higher PGM dispersion. The relative CO adsorption capacity as the fresh Pt only DOC (WT A) is expressed in Figure 2. It shows that the Pt only DOC exhibits poor thermal durability and the CO adsorption capacity decreased greatly, even after 550°C ageing. On the contrary, the Pt-Pd DOC with Pt-Pd ratio of 2:1 shows lower CO adsorption capacity at fresh state, however it exhibits improved thermal durability since 40% CO adsorption capacity can be kept after 700°C ageing.

Hence, it can be concluded that Pd addition into Pt only DOC brings higher CO and HC oxidation activation by improving the thermal durability of Pt as well as catalytic performance advantage of Pd.

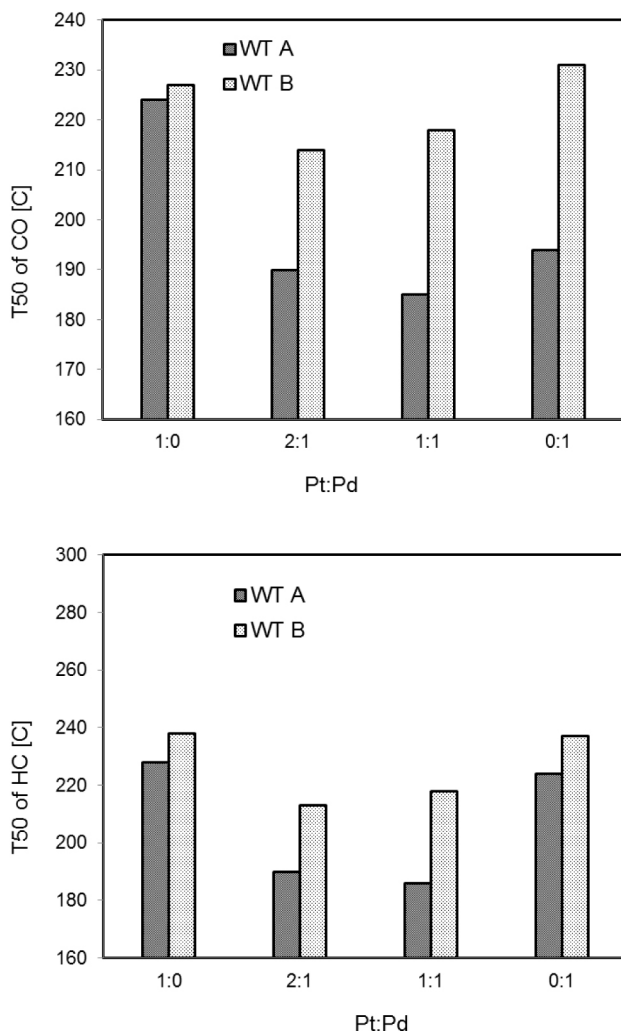


Figure 1. T50 of CO and HC of the DOCs with different Pt-Pd ratio

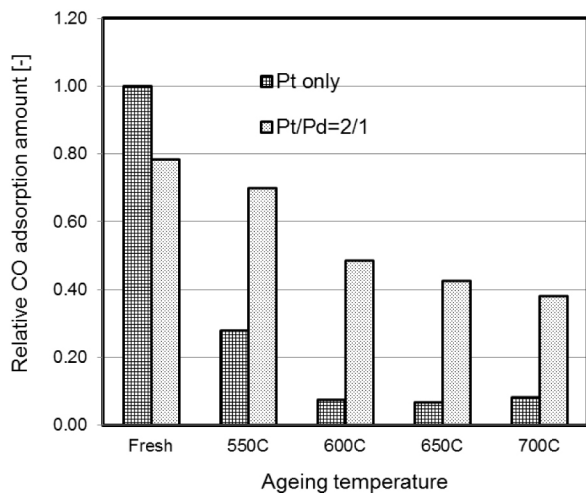


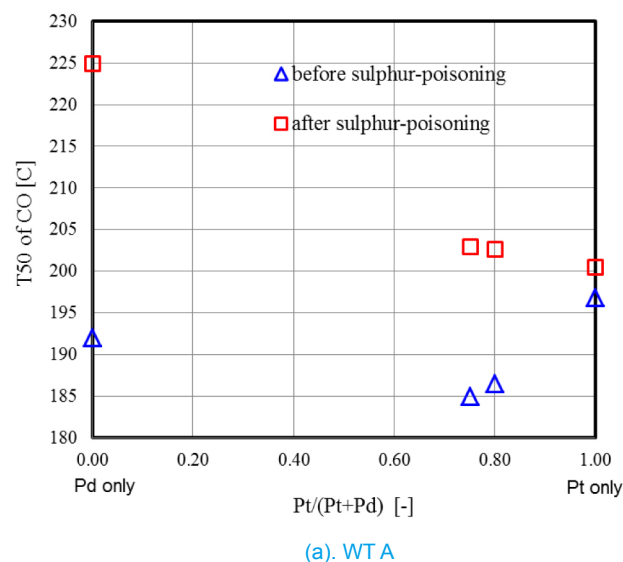
Figure 2. Relative CO adsorption capacity by CO-pulse at 50°C (WT A)

Effect of Replacing Pt by Pd on DOC S-Tolerance

S-poisoning is a risk where Pd replaces Pt in EU 4 applications, since $\text{Pt}(\text{SO}_4)_2$ with decomposition temperature $<400^\circ\text{C}$ is less stable than PdSO_4 ($\sim 650^\circ\text{C}$) and there is seldom opportunity for desulphation treatment of PdSO_4 in vehicle normal driving condition. For EU 5 system, there is a risk for our catalysts to be exposed to high S concentration exhaust gas due to the issue of formal diesel fuel supply, although DOCs have a chance of desulfation at CSF regeneration. Hence, the effect of S-poisoning has been investigated here.

In the S tolerance study, the oxidation activity towards CO and HC was evaluated with a transient light-off test mode on the 2.5 liters EU 5 diesel engine bench. Transient light-off tests were carried out after thermal ageing and then after S-poisoning on the engine bench. S-poisoning was conducted at different conditions for WT A and WT B, respectively. For WT A, the S-poisoning was conducted at 300°C (DOC inlet temperature) and the total fed S was 8 g/L catalyst with the diesel fuel containing 500 ppm S. The temperature was changed to 250°C for WT B. The S loading (8 g/L catalyst) corresponds to 5000~6000 km with the fuel economy efficiency assumption of 10 km/L with 500 ppm S fuel.

Here, T50 was also used as a criterion of oxidation activity and the results are expressed in Figure 3. Normally, CO oxidation reaction is more sensitive to S poisoning, rather than HC, since it was reported that S-poisoning has an improvement effect on oxidation of saturated hydrocarbon and an inhibiting effect on others [8], hence just T50 of CO are expressed here. Figure 3-(a) shows that Pd containing DOCs have higher CO oxidation activity than the Pt only DOC before S-poisoning. However, the Pd containing DOCs shows lower CO oxidation activity after the S-poisoning treatment.



(a). WT A