Conversion Characteristics of Double-Layer Washcoat Tri-Metal Three-Way Catalyst Using High Cell Density Substrate*

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The research was conducted to evaluate conversion characteristics of three-way catalyst (TWC) with a double-layer washcoat to improve the light-off temperature and the thermal durability. The evaluations considered factors such as the PM loading ratio and loading quantity of the tri-metal catalyst for Rh-Pd-Pt configuration, the washcoat composition, and the cell density. The higher cell density of TWC can improve the light-off temperature because of the lower heat capacity of the substrate and the increase of the surface area. Loading quantity and ratio of precious metals have appropriate value to light-off performance in each cell density of substrate. A proper selection of the bottom layer washcoat loaded with Pd can promote thermal stability and the upper layer washcoat with an excellent ability of oxygen storage can improve the light-off performance and the durability of the double-layer TWC. The best TWC with double-layer was 9Hy(0.6x11x3) with 140 cell/cm² substrate.

Key Words: Gasoline Engine, Catalyst, Emission, Three-Way Catalyst, Double-Layer Washcoat, Precious Metal (PM), Durability

1. Introduction

The three-way catalyst (TWC) applied in the gasoline fuelled vehicles uses Pd, Pt, Rh, and other metals on the γ-Al₂O₃ washcoat. The TWCs are expected to give light-off performance, high conversion efficiency, and improved thermal durability. To satisfy these expectations, researchers introduced various emission after-treatment techniques using catalysts such as the high cell density(1) based substrate on the thin wall, the hybrid catalyst(2)–(4), and the plasma photo-catalyst(5), (6).

The catalyst with high cell density substrate demonstrates a high exhaust emission conversion efficiency during the warm-up driving period. Such high conversion efficiency could be achieved because of the low thermal capacity of the catalyst substrate, and moreover the reaction frequency increased by the wide catalyst surface. The high cell density substrate and the wash coating method regulate the loading quantity of the PMs, and this regulation increases catalytic activity and the selectively catalytic reaction reaction for exhaust. In relation, researches on the selection and loading quantity of proper PMs are on-going(7), (8). Furthermore, there have been studied on the selection of the pertinent catalyst additives to optimally design the catalyst for automobiles. However, it has been difficult to find the performance evaluations on the loading quantity of the PMs, on the washing coating types, and on the relative reactions between the PMs when the cell density is the main variable of catalyst efficiency under identical experimental conditions. Since Pd is more lucrative than Pt, Pd is selected as the catalyst in the composition of Pd/Rh(9) or only Pd. Pd was successfully used in the past, but due to recent price changes in PMs, the development of Pt as the catalyst has been studied(10) since it has excellent durability and selective response. However, no research has been done to optimize the introduction of the new materials for the washcoat, to optimize the minimum installation expenses, and to optimize loading of Pd-Pt-Rh catalysts with respect to the coating development.

The TWC with a double-layer as its structure can suppress the deactivation derived from the negative interaction between Pd and Rh as well as block the catalyst poisoning of Pd(11). These outcomes improve the durability of the catalyst and promote prominent catalytic activity. Once the price competition of Pt is secured, the Pd-Pt-Rh tri-metal catalyst is composed of Pt and Pd, a con-
firmed as confirmed active catalytic metal in a low temperature\textsuperscript{(12),(13)}, will be preferred as the general TWC.

We propose a concept to design the TWC for gasoline fuelled vehicles by obtaining the result of light-off performance on the catalytic activity with respect to the composition ratio of the PM, the loading quantity within the Pd-Pt-Rh tri-metal catalyst, the combination of the washcoats, and the cell density of the substrate.

2. The Experimental Apparatus and Test Procedure

2.1 Catalysts preparation

The substrate of catalyst is based on the honeycomb monolith cordierite with cell densities of 63(0.165), 93(0.102), 140(0.064) cell/cm\(^2\) (wall thickness, mm). The \(\gamma\)-Al\(_2\)O\(_3\) was employed as a washcoat impregnated with Pd, Pt, and Rh.

Each double layered washcoat is composed of different catalyst additives(Ce, Zr, La, Ba etc.), and each layer has a about 60–110\(\mu\)m coating thickness. The upper layer washcoat is impregnated with Pt and Rh, whereas the bottom layer washcoat is with Pd.

After the deterioration of the catalyst by laboratory hydrothermal aging process, the thermal durability of the catalyst was evaluated. Laboratory hydrothermal aging can be defined as a cycle process that initiates from the preparatory temperature to 900\(^\circ\)C with a gradual heat implementation for 90 minutes and maintains its temperature consistently for 2 hours. Then the content undergoing this process is allowed to cool to 300\(^\circ\)C. The content is re-heated back to 900\(^\circ\)C, maintained at 900\(^\circ\)C for 2 hours, and then cooled to the preparatory temperature, thus completing one full cycle. The air supplied during the hydrothermal process consists of 19\% of water. One cycle of the laboratory hydrothermal aging is thought to be equivalent to 64,000 km of the UCC (under-body catalytic converter).

An inscription identifying the type of the designed and manufactured catalyst is required in the format showing the substrate cell density, the washcoat structure, and the impregnation ratio of PM, as shown in the case 6Hx(0.35x11x3), where 6H indicates the cell density (H: \(\times\)100 cell/in\(^2\)), x is a kind of combinations of double-layered washcoat additive (washcoat additive 1(upper) + washcoat additive 2(bottom), 0.35 for the Rh loading quantity (g/litter), 11 for the ratio of Pd/Rh and lastly 3 for the ratio of Pt/Rh.

2.2 Catalytic reaction test

The catalytic efficiency evaluation was conducted by using the model gas reaction device and the single cylinder engine. Initially, the model gas catalytic reaction device seemed similar to the static-catalytic reactor at atmospheric pressure of the previous research\textsuperscript{(12),(13)}.

The catalytic reaction test specified 20,000 h\(^{-1}\) as the space velocity(SV). The catalyst was heated at 10\(^\circ\)C/min. The model gas supplied to the catalytic reaction was composed of 1100 ppm of propane (C\(_3\)H\(_8\)), 2800 ppm of NO, 8400 ppm of CO and 10\% of H\(_2\)O. The appropriate oxygen concentration that sustained the redox ratio = 1 was set by considering a specific condition within the individual reaction condition, and nitrogen was employed as a balance gas. There were TCP packed column and GC (gas-chromatography) installed with the FID (Flame Ionization Detector) to measure propane concentrations. The concentration of the propane was measured more than three times to corroborate ±1\% of the reproducibility.

The single cylinder engine that was used in the catalytic reaction test had specific configurations, including 0.5 L displacements, 25 kW of maximum output, and 4-stroke and port injection based engine (AVL-540)\textsuperscript{(13)}. The catalyst which was installed at 120 cm distance from the engine exhaust manifold was canned to 0.470 L. To control the engine temperature satisfactorily, a double-tube heat exchanger was installed at the inlet of the catalytic converter. The catalyst temperature was taken at the catalyst inlet and outlet as well as at the central position.

The precise control near the stoichiometry for the engine was supported by the ECU controller (Dasan Internet, DEC 500 K), specifically manufactured to control fuel injection. The excess air ratio was carefully monitored by the excess air ratio device (ECM, AFR-2400), which received the signals from the oxygen sensor installed in the exhaust manifold. The exhaust concentration was measured by the exhaust analyzer (Horiba, MEXA-9100DEGR) at the inlet and outlet of the catalytic converter.

3. Results and Discussion

3.1 Catalysts performances

The catalytic activity of the TWC with the double-layered washcoat structure had respect to the following factors such as the impregnation ratio and the loading quantity status in the tri-metal PM of the Rh-Pd-Pt as well as the structure of the washcoat and the substrate cell density. Figure 1 shows the conversion efficiency of the propane according to the temperature of the catalyst, which had the double-layered washcoat impregnated with Rh-Pd-Pt as the tri-metal on the substrate of 93 cell/cm\(^2\) (600 cpsi) as the cell density.

The 6Hx(Rh-Pd-Pt) catalysts have higher propane conversion efficiency even with a lesser PM loading quantity compared to the 4H(0.27x18) based Rh-Pd bi-metal catalysts, which gives the most effective conversion efficiency at the substrate where the cell density is 62 cell/cm\(^2\) (400 cpsi). In other words, the increase in cell density of the substrate could lead to the increase of the surface area of the catalyst and the increase in the PM dispersion as well as the effect of the low thermal capacity.

The 6Hx(Rh-Pd-Pt) series catalysts can demonstrate
Fig. 1 C$_3$H$_8$ conversion efficiency as a function of the temperature on the 6Hx(Rh-Pd-Pt) catalysts

the effect of Pt loading quantity on the conversion efficiency. The highest PM loading catalysts including 6Hx(0.35x9x3) and 6Hx(0.35x11x3) are activated at 300°C and reach 80% conversion efficiency at 350°C, which is considered to be an excellent conversion efficiency.

Even though the 6Hx(0.35x13x1) catalyst has the highest loading in Pd among the catalysts 6Hx(Rh-Pd-Pt), it shows lower light-off activation. Hence, we found a catalyst, among the catalyst group of 6Hx(Rh-Pd-Pt), with a specific PM loading ratio that yields a superior light-off performance. The catalytic activity in low temperature according to the appropriate loading of Pd and Pt promotes the overall catalyst reaction. It is found that the optimum PM loading ratio is Rh/Pd/Pt = 1/11/3 as catalyst 6Hx(0.35x11x3) composition. Compared to the catalyst 6Hx(Rh-Pd-Pt), the catalyst 6Hy(Rh-Pd-Pt) had a modified washcoat composition and increased overall PM loading quantity. Figure 2 demonstrates the conversion efficiency of the catalyst 6Hy(Rh-Pd-Pt) in accordance with the catalyst temperature changes due to the adjustments mentioned in the previous paragraph.

The conversion efficiency of 6Hy(Rh-Pd-Pt) series catalysts are lower than that of the catalyst 6Hx(0.35x11x3), which had the optimum PM composition with respect to the light-off activity of the catalyst shown in Fig.1. The catalyst 6Hy(Rh-Pd-Pt) has a washcoat different in composition to that of the 6Hx(0.35x11x3), but the catalyst 6Hy(Rh-Pd-Pt) has a PM loading ratio similar to that of catalyst 6Hx(0.35x11x3). Even with more PM loading quantity, the catalyst 6Hy(Rh-Pd-Pt) represents 80% of the propane conversion efficiency at 385°C temperature, which was 35°C higher than that of 6Hx(0.35x11x3).

Figure 3 shows the conversion efficiency relative to the temperature of the TWC that applies a tri-metal of a double-layered washcoat into the high cell density substrate of 140 cell/cm² (900 cpsi). The catalyst 9H(Rh-Pd-Pt) was applied with washcoat having the identical composition to the washcoat of catalyst 6Hy(Rh-Pd-Pt) and the PM loading quantity was twice that of the 6Hx(Rh-Pd-Pt) of Fig.1. The catalyst 9Hy(0.6x11x3) activity initiated at 275°C and gave more than 80% propane conversion efficiency around the catalyst temperature of 350°C. This result implies that catalyst 9Hy(0.6x11x3) had the conversion efficiency similar to that of the catalyst 6Hx(0.35x11x3) which has an impressive light-off performance. However, the other catalysts, except the catalyst 9Hy(0.6x11x3), exhibited low conservation efficiency even with more abundant PM loading quantity than the catalyst 6Hx(0.35x11x3). The catalyst 9Hy(0.6x14x3)
displays relatively low conversion efficiency, although its catalyst is composed of the most abundant PM loading quantity. It may be due to its PM dispersion and its PM loading technique.

The catalyst 9Hy(0.6x11x3) has a catalyst PM loading ratio and loading quantity equal to that of the catalyst 9Hx(0.6x11x3), and showed 80% conversion efficiency at 350°C, which is 30°C lowered than that of the catalyst 9Hx(0.6x11x3). The different conversion efficiency may be due to the difference of the washcoat composition between the two catalysts. Because the catalyst 9Hy(Rh-Pd-Pt) was loaded with Rh-Pt on the upper washcoat, which provided more efficient oxygen storage compared to the 9Hy(Rh-Pd-Pt) upper layer, the catalyst 9Hy(Rh-Pd-Pt) would have a significant advantage over the light-off activity. Therefore, catalyst 9Hy(0.6x11x3) may provide superior light-off performance, which amplifies the washcoat capability and provides an optimum PM loading ratio. The evaluation of the conversion efficiency is based on the light-off performance due to the deactivation of the catalyst, which is thermochemically affected by the moisture. The oxidant is maintained by laboratory hydrothermal aging at high temperatures.

Figure 4 shows the results of the model gas reaction test, which measures the conversion efficiency of propane for the catalyst 9Hy(Rh-Pd-Pt), which is thermochemically deactivated from the oxidant atmosphere at a high temperature. The catalyst 9Hy(0.6x11x3) activates near 325°C and gives 50% conversion efficiency around 400°C, which is a relatively good conversion efficiency compared to those of the aged catalysts. After the hydrothermal aging process, the LOT80 (that the catalyst temperature shows 80% conversion efficiency) of the 9Hy(0.6x11x3) catalyst, which exhibited the most impressive conversion efficiency among the fresh catalysts, was close to 450°C, approximately 100°C higher than those of the fresh catalysts. Moreover, the conversion efficiency of the catalyst 9Hy(0.6x11x3) was higher than that of the catalyst 9Hx(0.6x11x3), which has an identical PM composition as the 9Hy(0.6x11x3) but a different washcoat composition. This result means that the 9Hy has better durability than the 9Hx because the 9Hy was constructed with components that induce oxygen storage on the upper layer washcoat and thermal stability on the bottom layer washcoat.

Even with the most abundant Pd loading quantity, the aged catalyst 9Hy(0.6x14x1) has a relatively low conversion efficiency possibly because the hydrothermal aging process that decreased the PM dispersion by the agglomeration of PM, followed by reducing the catalytic activity. To improve the light-off performance and durability of the TWC, the TWC should be optimally designed by considering the PM loading with respect to the surface area of the substrate, the PM dispersion, and the optimum PM composition ratio according to the PM coating techniques.

3.2 Results of engine test

Figures 5 and 6 show the experimental results of the gasoline engine catalysts 6Hx(Rh-Pd-Pt), which was treated by 2 cycles of the laboratory hydrothermal aging. They gave similar conversion efficiencies of THC and CO but the overall higher conversion efficiency of CO than that of THC. The catalyst 6Hx(0.35x9x3) exhibited the highest efficiency among catalysts of 93 cell/cm² substrate.

After the hydrothermal process, the LOT50 (the light-off temperature indicating 50% of THC conversion efficiency) of this catalyst 6Hx(0.35x9x3) was 280°C, which
was 30°C higher than the temperature of the fresh catalyst. Also, the maximum level of conversion efficiency of the aged catalyst was approximately 80%. The LOT$_{80}$ of the fresh 6Hx(0.35x9x3) catalyst was 290°C but the LOT$_{80}$ of the aged catalyst was 400°C, which indicates a considerable decrease in the conversion efficiency.

The LOT$_{50}$ of the catalyst 6Hx(0.35x11x3) was 230, which was 50°C lower than that of 6Hx(0.35x9x3). The catalyst 6Hx(0.35x11x3) demonstrated the most effective light-off performance among the aged catalysts. Catalyst 6Hx displayed this light-off performance because the active sites of catalyst were reduced by the agglomeration and sintering effect of PM resulted from the hydrothermal aging process. Thus, the aged catalyst 6Hx(0.35x11x3) produces the high conversion efficiency of THC since the catalysts are composed of more loading quantity of Pd which has advantages over the light-off activity of the catalyst oxidation reaction.

Figure 7 shows the NOx conversion efficiency of the 6Hx(Rh-Pd-Pt) catalyst that was deteriorated by 2 cycles of laboratory hydrothermal aging. In the case of the THC conversion efficiency, the 6Hx(0.35x11x3) aged catalyst is more efficient than the 6Hx(0.35x9x3) hydrothermal catalyst. However, in case of the NOx conversion efficiency, the 6Hx(0.35x9x3) catalyst composed of a smaller quantity of the Pd loading proved to be more efficient. The catalyst 6Hx(0.35x9x3) exhibited the most effective light-off activity since its LOT$_{50}$ was 240°C, which was approximately 20°C lower than that of the catalyst 6Hx(0.35x11x3).

It was supposed that there happened an negative interaction between Pd and Rh by the hydrothermal aging process, which interfered the reduction reaction on Rh because it formed an alloy such as PdRhO$_2$ at the interface in between the upper and bottom layer of the washcoat. Therefore, the catalyst loaded with the more Pd could be expected to encourage the frequency of Pd with Rh interaction, which hinders the reduction reaction on Rh.

The conversion efficiency of NOx of the aged catalyst 6Hx(0.35x9x3) with different loading quantities of Pt is significantly different from that of the catalyst 6Hx(0.35x9x1). The LOT$_{50}$ of the aged catalyst 6Hx(0.35x9x3) is 230°C, which is 70°C lower than the 6Hx(0.35x9x1) has. NOx is further reduced by the interactions between Rh and Pt, which are loaded at the upper layer of the washcoat.

Figure 8 describes the evaluation results of the light-off activity for the THC of 6 cycle aged catalysts.
catalyst 9Hy(Rh-Pd-Pt). The catalyst 9Hy(0.6x11x3) activated around 225°C and demonstrates 80% conversion efficiency around 350°C. The catalyst 9Hy(0.54x14x3) with the lowest PM loading composite demonstrated the lowest THC conversion efficiency. In the catalyst 9Hy(0.54x14x3), these effects were due to the decrease in the PM activity site with respect to the low loading quantity and the hydrothermal aging process.

The catalyst 9Hx(0.6x11x3) that consists of the identical PM composition with a different washcoat structure to that of 9Hy(0.6x11x3) displayed relatively similar conversion efficiency that was below 50% of the typical THC conversion efficiency. However, 9Hx(0.6x11x0.3) exhibited lower conversion efficiency above 300°C than the Hy(0.6x11x0.3) did. The bottom layer washcoat loaded with Pd of the catalyst 9Hx(0.6x11x3) showed low durability in the catalyst hydrothermal aging process. The catalyst 9Hy(0.6x11x3) improved the light-off activity and the durability for the TWC since its bottom layer loaded with the Pd strengthened the thermal stabilization and its upper layer reinforced the catalyst with a washcoat that features an excellent oxygen storage ability.

Figures 9 and 10 demonstrate the conversion characteristics of CO and NOx of the 6 cycle aged catalyst 9Hy(Rh-Pd-Pt). The conversion efficiencies of CO and NOx of the aged catalyst showed trends similar to those of the THC results.

The conversion efficiencies for the catalyst 9Hy(0.6x11x3) for CO and NOx reached approximately 80% around 300°C, thus it is regarded as the most effective catalyst in this condition. More specifically, conversion efficiencies for the aged catalysts 9Hy(0.54x14x1) and 9Hy(0.6x14x1) were seemingly lower since they have the smallest Pt loading quantity.

Based on these results, the performance of the trimetal TWC is heavily shown to be influenced by a double-layer washcoat and also can be enhanced by increasing the thermal stabilization according to the Pt increase and by improving the interactions of Rh-Pt for oxidation and reduction of CO and NOx, respectively.

Figure 11 shows the conversion efficiency according to the excess air ratio within the catalyst 6Hx(0.35x11x3), which gave the most efficient light-off activity and durability among 93 cell/cm² substrate catalysts. The λ-window is defined as the range of the excess air ratio that displays the conversion efficiencies of THC, CO and NOx exceeding 80% under the stoichiometric atmosphere and catalytic temperature of 500°C. The 4 cycle-aged

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**Fig. 9** CO conversion efficiencies as a function of the temperature on the 6 cycle aged 9Hy(Rh-Pd-Pt) catalysts

**Fig. 10** NOx conversion efficiencies as a function of the temperature on the 6 cycle aged 9Hy(Rh-Pd-Pt) catalysts

**Fig. 11** Sweep test result over the 4 cycle aged 6Hx(0.35x11x3) catalyst
catalyst 6Hx(0.35x11x3) exhibits 0.01 width of the $\lambda$-window. The highest conversion efficiencies of THC and CO were reserved at the stoichiometry but the conversion efficiency of NOx continuously decreased after the stoichiometry and displayed 50% conversion efficiency around $\lambda = 1.01$. The catalyst 6Hy(0.35x13x5) showed approximately 0.002 depth of the $\lambda$-window.

Figure 12 demonstrated 0.007 width of the $\lambda$-window for the catalyst 6Hy(0.54x13x3).

Figures 13 and 14 represent the conversion efficiencies according to the excess air ratio for catalysts 9Hx(0.6x11x3) and 9Hy(0.6x11x3), which were composed of the identical PM composition but different washcoat structures within the substrate of the high density cell 140 cell/cm$^2$. The catalyst 9Hy(0.6x11x3) had the higher maximum conversion efficiency within the stoichiometry than the catalyst 9Hx(0.6x11x3). The widths of the $\lambda$-windows were 0.0086 and 0.01 for the 9Hy(0.6x11x3) and the 9Hx(0.6x11x3), respectively.

By considering the evaluation of the light-off performance, the catalyst durability and the $\lambda$-windows characteristics, the catalyst 9Hy(0.6x11x3) was selected as the best TWC of the cell density 140 cell/cm$^2$ loaded with the PM ratio of Rh/Pd/Pt = 1/11/3 into the double-layered washcoat.

4. Conclusions

The conversion efficiency evaluation of the TWC for the gasoline fuelled vehicles confirmed the following conclusions. The evaluations considered factors such as the PM loading ratio and loading quantity of the tri-metal catalyst for Rh-Pd-Pt configuration, the washcoat composition, and the cell density.

(1) The catalyst 6Hx(Rh-Pd-Pt) of 93 cell/cm$^2$ substrate initiates propane conversion from 300°C, which was 50 lower than that of the 62 cell/cm$^2$ substrate-based catalyst having a low PM loading. Thus, the high density substrate had the superior conversion efficiency due to the high catalytic activity of the Pt and the effect of the low thermal capacity.

(2) The catalyst 6Hx(0.35x9x3) had the most efficient propane LOT$_{50}$ value of 350°C among the catalysts of 93 cell/cm$^2$ substrate. Moreover, the catalyst 6Hx(Rh-Pd-Pt) had lower conversion efficiency than the catalyst 6Hx(Rh-Pd-Pt) did, even though it had 70% more PM loading quantity, a result indicates an optimum value of PM loading for a specific cell density.

(3) The catalyst 6Hx(0.35x9x3) has LOT$_{50} = 240$°C, which is 20°C lower than that of the catalyst 6Hx(0.35x11x3). This lower value is due to the interaction of the Pd and the Rh such as the PdRhO$_2$ alloy
formation in the interface between the upper and the bottom washcoat, where the high Pd loading quantity demonstrates high frequency of impediments in the Rh reduction in catalysts.

(4) The 9Hy(0.6x11x3) of 6 cycle aged catalyst displayed the highest conversion efficiencies of THC, CO and NOx. This result implies that a proper selection of the bottom layer washcoat loaded with Pd can promote thermal stability and that the upper layer washcoat with an excellent ability of oxygen storage can improve the light-off performance and the durability of the TWC.

(5) The outcome of the conversion efficiency according to the excess air ratio shows that the width of the $\lambda$-window increases as the PM loading increases, and that the width of the $\lambda$-window is slightly wider in the catalyst 9Hx(Rh-Pd-Pt) than the catalyst 9Hy(Rh-Pd-Pt). However, the catalyst 9Hy(Rh-Pd-Pt) has advantages over the good light-off performance and the durability.

(6) The catalyst 9Hy(0.6x11x3) is selected as the best TWC of the cell density 140 cell/cm$^2$ loaded with the PM ratio of Rh/Pd/Pt = 1/11/3 into the double-layered washcoat. This catalyst is composed of the upper layer washcoat that can efficiently store oxygen and the bottom layer, which was highly stable against thermal effect.

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