Improvement of Performance and Durability of Three-Way Catalyst for Low-Emission Vehicles*

Jong-Woo JEONG** and Byung-Chul CHOI**

Research was conducted to develop an advanced three-way catalyst with better low-temperature activity and durability than those currently available. Honeycomb monolithic catalysts were designed with different Rh/Pd, Rh/Pd/Pt loading ratios in a double-layer washcoat. A single-cylinder gasoline engine was used to estimate the conversion efficiency of HC and CO. BET, SEM (scanning electron microscopy), and TEM (transmission electron microscope) analysis were performed to confirm the thermal aging process macroscopically. The characteristics of the catalytic reaction were also analyzed by TPR (temperature-programmed reduction) and TPD (temperature-programmed desorption). An Rh/Pd catalyst with a 1/18 loading ratio showed the best conversion efficiency and thermal stability in our study. The light-off temperature for 50% HC conversion of this catalyst was 260°C. The double-layer washcoat enhanced the thermal stability by inhibiting the negative interaction between Pd and Rh during the thermal aging process.

Key Words: Catalyzer, Gasoline Engine, Combustion Products, Chemical Reaction, Emission, After-Treatment

1. Introduction

Exhaust gases from automobiles lead to severe problems as they pollute the environment, which is quite contrary to the convenience offered by automobiles. Therefore, strict emission standards have been imposed on vehicles with respect to environmental preservation.

These regulations require that further upgrades be made on the after-treatment performed by the automotive emissions systems. To meet these requirements, the performance of catalysts must be improved in particular, lower the catalytic activation temperature and increase the conversion efficiency and durability. Furthermore development of an advanced three-way catalyst system involving superior catalytic reaction at low temperature, high durability and wider lambda window, are required to satisfy the

strict emission standards, for example, ULEV/SULEV⁽¹⁾⁻⁽⁶⁾.

Of the many approaches taken to satisfy these catalyst specifications, new catalytic techniques, such as the use of high-cell-density substrates using thin-walled substrates and plasma photocatalysts have been introduced^{(7),(8)}. These techniques yielded improvements in low-temperature activity via the lowering of the heat mass, increase of the precious metal content, and use of complementary devices. Thermal aging of the three-way catalyst (TWC) through a negative interaction between precious metals and sintering of metal particles causes the decrease in conversion efficiency. One of the effects of the thermal deactivation of the Pd-Rh impregnated catalyst is that the Pd, which is easily oxidized, prohibits the Rh from reducing NO_x through segregation and recombination into PdRhO₂⁽⁹⁾. Therefore, satisfactory improvements of the catalytic reaction by appropriate catalyst design have yet to be achieved. To improve the catalytic activity and durability, the research is to be focused on catalyst designs by improving the catalytic materials, by controlling the

* Received 15th February, 2001

** Department of Mechanical Engineering, Chonnam Nat. Univ., 300 Yongbon-dong buk-Gu, Kwangju, 500-757, Korea. E-mail: bcchoi@chonnam.ac.kr

catalytic components and the manufacturing processes and by optimizing the precious metal content.

In the present study, we examine the conversion characteristics and the thermal stabilities of newly designed three-way catalysts. The three-way catalysts, which consist of palladium, rhodium and platinum individually impregnated in a gamma alumina (γ -Al₂O₃) double-layer washcoat, are examined.

2. Experiments and Procedure

2.1 Catalyst preparation

In order to choose an advanced three-way catalyst, the composition and the amount of precious metals (PMs) were considered with the effects of additive catalysts (manufactured by Ordeg Co.). The PMs (palladium/rhodium and platinum) with nitrate salt, which is a solution of PM precursor (PM(NO₃)₂) were impregnated in a γ -Al₂O₃ washcoat. The washcoat had a double-layer with various additive catalysts (Ce, Zr, La etc.). The cell density of the honeycomb monolith was 62 cell/cm².

To investigate the thermal deactivation, the catalysts were aged under a laboratory thermal aging mode. The catalyst was heated at 900°C for 2 h and then cooled to 300°C once and then reheated and held at 900°C for 2 h in air atmosphere containing 19% H₂O. This procedure is one cycle of thermal aging. The prepared catalysts, their nomenclatures and compositions are presented in Table 1. The specific surface areas were measured using the multipoint BET method.

2.2 Engine test

The apparatus used for evaluating the catalytic conversion efficiency of exhaust gases from a gasoline engine as a function of the catalyst temperatures is shown in Fig. 1. The test engine for the experiment had an air-cooled single cylinder, of 197 cm³ displacement, and a four-stroke gasoline engine of 5 HP. By measuring the manifold temperature, the excess air/fuel ratio with an UEGO sensor and the engine speed, we monitored the operating states of the test engine.

Hydrocarbons and carbon monoxide were contin-

uously measured using a gas analyzer (Horiba, MEXA 554 JK). Simultaneously, light individual hydrocarbons (LIHCs), C1-C6, were measured using a gas chromatograph (Hewlett Packard, HP 6890) equipped with a flame ionization detector (FID). The engine was run at a speed of 1000 rpm with a stoichiometric air/fuel ratio. The exhaust gas during the test was constantly monitored after a 30 min engine warm-up period.

The catalyst used in these experiments had the diameter of 18 mm and the length of 20 mm externally. It was placed in a quartz reactor and used after pretreatment in a nitrogen atmosphere of 300°C for 2 h. The temperature was raised from 100°C to 500°C at 5°C/min using an electric furnace. The temperature of the catalyst was measured using a 0.5 mm K-sheath type thermocouple imbedded in the center of the catalyst. The flow rate of exhaust gas passing through the reactor was 1700 cm³/min and the SV (space velocity flow rate at STD/volume of catalyst) was 20 000 h⁻¹.

2.3 Characterization of catalysts

FE-SEM/EDX, BET and TEM measurements were performed in order to investigate the behavior of the catalyst surface and of the PM particles in the washcoat after thermal aging. TEM specimens were prepared, as described previously, by dimpling and ion milling to remove the cordierite supports⁽¹⁰⁾.

The reaction characteristics of the catalyst were evaluated by TPR (temperature-programmed reduction) and TPD (temperature-programmed desorption) using the catalyst characterization system (ZetonAltamira, AMI-90). TPR was performed in a conventional apparatus, as previously described^{(11),(12)}. Prior to reduction, the catalyst was heated for 0.5 h at 350°C in flowing argon. Oxidation was carried out in a stream of 10% O₂ in N₂ and then the sample was held at 400°C for 1 h. Reduction was carried out in a stream of 10% H₂ in argon at a flow rate of 30 cm³/min as the temperature was raised linearly from room

Table 1 Specification of catalysts

No.	PMs	Loading ratio	Total PMs weight (g/L)
A	Rh/Pd	1/9	2.744
B	Rh/Pd	1/13.5	3.98
C	Rh/Pd	1/18	5.214
D	Rh/Pd	1/22.5	6.45
E	Rh/Pd/Pt	1/9/3.5	3.706
F	Rh/Pd/Pt	1/3.5/9	3.706
G	Rh/Pd	0.83/12.5	3.55
H	Rh/Pd	1.25/12.5	3.67

Fig. 1 Experimental set up for exhaust gas measurement

temperature to 900°C at 15°C/min. Hydrogen consumption was measured using a thermal conductivity detector (TCD).

TPD experiments were performed in the apparatus used for the TPR experiments. The TPD of adsorbed H₂ was determined in order to analyze the characteristics of thermal deactivation. After purging the catalyst, the adsorption of H₂ was determined by supplying 30 cc/min of pure H₂ at 100°C for 0.5 h. After adsorption, the catalysts were heated at 15°C/min in stream of argon at a flow rate of 30 cc/min.

3. Results and Discussion

3.1 Catalyst performance

The conversion efficiency of the catalyst for HC emission from a gasoline engine is shown in Fig. 2. The C catalyst shows the best conversion efficiency for HC. The light-off temperature (LOT), at which a 50% conversion efficiency was attained, is about 260°C, and the conversion efficiency reaches 80% at 280°C. The D catalyst is less efficient than the C catalyst even though the D catalyst is loaded with a higher amount of Pd. This is presumed to be due to the poor dispersion of PMs in the washcoat of the D catalyst.

The CO conversion efficiency is shown in Fig. 3. The C catalyst exhibits higher conversion efficiency than other catalysts, and attains 80% conversion efficiency at 280°C. In addition, a fluctuation in the CO conversion efficiency appears below 200°C. This fluctuating behavior is attributed to the physisorption and the catalytic reaction of CO, which is more favorable than that of HC in the presence of oxygen on the surface of the catalyst. Even though the D catalyst has higher specific surface area and PM level, the C catalyst shows higher conversion efficiency than the D catalyst. Consequently, we can determine an optimum Rh/Pd weight ratio of oxidation of HC and CO. In this experiment, the best conversion efficiency for HC

and CO is obtained at the Rh/Pd ratio of 1/18.

The LIHC conversion efficiencies of the C catalyst are shown in Fig. 4. The conversion efficiency for methane, one of the C1 LIHCs, is the lowest. The conversion profiles for hydrocarbons of low carbon number, C1 and C2 LIHC, show a valley at 300 and 400°C, whereas under these conditions, hydrocarbons of high carbon number are amply converted by the catalytic reaction. It is believed that the catalytic reaction of HCs is initiated from the decomposition of the high LIHCs and then proceeds to the partial reconstitution of low LIHCs. Also, the species that are predominantly responsible for the valley are saturated hydrocarbons, methane and ethane. It is shown that the saturated hydrocarbons with low carbon numbers lag behind those with higher carbon numbers in the competitive catalytic reactions.

Figures 5 and 6 show the conversion efficiency of the thermally aged C catalyst for HC and CO from a gasoline engine. The 6-cycle-aged catalyst exhibits a conversion efficiency of 50% for HC and CO at 276 and 235°C, respectively. This is a higher conversion efficiency than those of the 2 or 4-cycle-aged catalysts. This result is supported by the results of FE-

Fig. 2 HC conversion efficiency of A-H catalysts

Fig. 3 CO conversion efficiency of A-H catalysts

Fig. 4 LIHC conversion efficiency of C catalyst

Fig. 5 HC conversion efficiency of the aged C catalysts

Fig. 6 CO conversion efficiency of the aged C Catalysts

SEM and BET measurements shown in Figs. 9 and 10. The specific surface area is renewed as the catalyst undergoes thermal aging. Accordingly, it is inferred that this feature affects the conversion efficiency of the catalyst and that the method of double-layer wash-coating maintains the interactions between the PMs despite aging.

Figure 7 shows the THC, CO and NO_x conversion efficiencies of the catalytic converter C (mounted downstream of the exhaust manifold) as a function of converter temperature. The catalytic converter C of 465 cc ($83\phi \times 86$ L) is wrapped in a thermal insulating mat and is canned. The exhaust gases from a single-cylinder gasoline engine (500 cc AVL research eng.) pass through the heat exchanger, which controls the converter temperature. The THC and CO conversion efficiencies show similar patterns to those in Figs. 5 and 6. The LOT of 50% NO_x conversion efficiency, appears to be at 320°C. The gradient of the NO_x conversion curve is steeper than those of THC and CO. Above 350°C, NO_x and CO conversion efficiencies are both higher than that of THC. Therefore, we suggest that NO_x reduction, using CO as a reducing

Fig. 7 Conversion efficiencies on the 2 cycle aged C catalyst for THC, CO and NO_x as a function of catalyst temperature. Engine speed, 1 000 rpm; partial load, 30%

Fig. 8 TPR profiles for A-H catalysts oxidized

agent, is vigorous occurs due to effectively maintained interactions among the precious metals.

3.2 Characterization of catalytic reaction

The TPR profiles of A-H catalysts oxidized by O_2 at 400°C are shown in Fig. 8. The TPR profiles representing the hydrogen consumption during the reduction of these catalysts show three features at around 100, 400 and above 700°C. The hydrogen consumption at around 100°C, represented by the sharp large peak, results from the reduction of the bulk or the crystalline PM oxides, which occurs because the PMs are in contact with CeO_2 , as an additive catalyst. In particular, Pd is known to strongly interact with the ceria of additive catalysts and to promote the partial reduction of CeO_2 in the catalyst, using the nitrate precursor as a Pd precursor solution. Therefore, Pd is converted to PdO, which is easily reduced in a reducing atmosphere. The broad peaks above 400°C are attributed to the reduction of CeO_2 and Al_2O_3 . In this case, CeO_2 is not in contact

Fig. 9 Surface characteristics of the fresh and aged C catalysts by FE-SEM ($\times 5K$)

with PMs^{(10),(12)}.

For E and F catalysts including Pt, the peak of H_2 consumption on the bulk or crystalline PM oxide sites is shifted to higher temperatures ($130^\circ C$) and increases in level. This shows that Pt does not initiate the catalytic reaction as fast as Pd on the temperature. Pt and Rh in the top washcoat layer enhance the catalytic reaction and the thermal stability of Pd in the bottom layer. Therefore, the appropriate Pd/Pt/Rh weight ratio is one of the major factors in designing a catalyst with PM on a double-layer washcoat. The catalyst designed with this consideration, therefore, shows potential in terms of thermal stability, high catalytic activity and antipoisoning effect against SO_2 or Pb^{(13),(14)}. As a result of TPR and LOT experiments, it is recognized that the initial activation temperature of the PMs is the dominant parameter of the conversion efficiency of the catalyst.

FE-SEM, BET and TEM are performed to observe the changes in the catalyst surface and the PM particles during the thermal aging process. Figure 9 shows the progression of the thermal aging of catalysts on the catalyst surface. First, the high temperature ($900^\circ C$) induces the migration and the agglomeration of the washcoat components. Cracks are formed and grow because of the cohesive force arising from the agglomeration of homogeneous catalytic components in the washcoat. Subsequently, the water-gas shift reaction regenerates pores in the washcoat during dehydration. Also, the specific surface area of the catalyst increases due to the microscopic cracks emanating from the large initial crack. This is supported by BET results shown in Fig. 10. The surface area of the 6-cycle-aged catalyst is larger than those of the 2- and 4-cycle-aged catalysts, but the mechanical strength decreases with thermal aging.

The behavior of the PM particles with thermal

Fig. 10 Specific surface areas by BET measurement

Fig. 11 TEM micrographs of both the fresh and aged C catalyst showing a PMs particles

aging is shown in Fig. 11. The dispersion of the PM particles deteriorates due to agglomeration and sintering. Agglomeration dominates the catalyst behavior over 2 and 4 cycles of aging, but sintering becomes predominant for the 6-cycle-aged catalyst.

The TPR profiles of the fresh and the aged C catalyst after oxidation at $400^\circ C$ are shown in Fig. 12. Three features are observed in the TPR profiles: TPR peaks representing the reductions on PdO or RhO (below $100^\circ C$), on CeO_2 that is partially reduced by PMs, with which it is in contact with PM (at around $110^\circ C$) and on CeO_2 and Al_2O_3 not in contact with PMs (above $400^\circ C$). Figure 12 for (a) for a catalyst that is not impregnated with PMs in the washcoat shows the reduction of CeO_2 (at around $400^\circ C$) and Al_2O_3 (above $500^\circ C$). In (b) for a catalyst impregnated with Pd, the reduction on PdO (at around $65^\circ C$) and on CeO_2 in contact with Pd (at around $110^\circ C$) are observed. In (c) for the fresh C catalyst, the reduction is increased in amount and

Fig. 12 TPR profiles for fresh and aged C catalysts oxidized at 400°C: (a) bottom-layer washcoat not impregnated Pd, (b) bottom-layer washcoat impregnated Pd, (c) fresh C catalyst, (d) 2 cycle-aged C catalyst, (e) 6 cycle-aged C catalyst

shifted to a high temperature (75°C) for PdO and RhO. The reduction on CeO₂ in contact with PMs is increased at the expense of the reduction of CeO₂ not in contact with PM (above 400°C). These results show that the double-layer washcoat improves the dispersion of the PMs and the interaction between PMs and the additives. In the cases of Fig. 12(d) and (e), the peaks originally shown at 75°C decrease in level and shift to higher temperatures due to the decreased amount of bulk or crystalline PM oxides such as PdO and RhO. The shoulder feature due to the reduction of CeO₂ in contact with PM at around 110°C decreases in level and shifts to higher temperatures upon thermal aging. The peak around 400°C, which is due to a reduction of CeO₂ not in contact with PMs, increases somewhat.

The negative peak is produced by desorption of weakly adsorbed hydrogen from the Pd surface or the decomposition of Pd hydride⁽¹⁵⁾. Also, the decomposition of the nitrate precursor as a PM solution accompanies the evolution of dimer N₂O₄ that has a higher thermal conductivity than that of H₂⁽¹⁶⁾.

From the above TPR profiles, it is realized that the thermal aging of these catalysts causes the PM to sinter via agglomeration and decreasing interactions between the PMs and the additive catalysts. Agglomeration and sintering are confirmed by TEM analysis.

The segregated Rh on the aged catalyst suppresses the oxidation on Pd and Pt, and causes a chemical shift towards higher binding energies, indicating it is being more deeply oxidized, presumably as Rh₂O₃⁽⁴⁾, which is probably one of reasons for the reduced catalytic deactivation of the aged catalysts.

Fig. 13 TPD profiles for fresh and aged C catalysts reduced by H₂ at 100°C: (a) bottom-layer washcoat not impregnated Pd, (b) bottom-layer washcoat impregnated Pd, (c) fresh C catalyst, (d) 2 cycle-aged C catalyst, (e) 6 cycle-aged C catalyst

The 6-cycle-aged catalyst maintains its oxidation state, as does the 2-cycle-aged catalyst, through PdO and CeO₂ in contact with PM. It is found that the catalytic deactivation of Pd due to the blockage of Rh upon thermal aging is inhibited by the effect of the double-layer washcoat.

The TPD profiles of adsorbed H₂ at 100°C are shown in Fig. 13. The features of TPD profiles following hydrogen adsorption are well defined at around 150°C and above 400°C. In the case of Fig. 13(a), the TPD curve does not appear at temperatures below 400°C. The TPD curve above 400°C may be due to the desorption of the bridge-bonded hydrogen on the washcoat and the decomposition of H₂O as described by the reaction $\text{Ce}_2\text{O}_3 + \text{H}_2\text{O} \longleftrightarrow 2\text{CeO}_2 + \text{H}_2$. Here, the water may have originated mainly from dehydroxylation in the support surface⁽¹⁷⁾.

The TPD profile in Fig. 13(b) exhibits only one peak at 120°C corresponding to desorption of the linearly bonded hydrogen on Pd. The curve initiates at 200°C, coinciding with the bridge-bonded hydrogen on Pd and the desorption of hydrogen adsorbed on partially reduced cerium oxides.

In Fig. 13(c), the TPD profile exhibits two peaks at 120 and 200°C. The peak attributed to the desorption of hydrogen on Pd at 120°C is considerably enhanced owing to the improvement of dispersion caused by the addition of Rh impregnated in the top washcoat layer. The peak at 200°C represents the desorption of linearly bonded hydrocarbon on Rh and the desorption of hydrogen adsorbed on CeO₂ partially reduced by the increased interaction between Pd and ceria.

In Fig. 13(d) and (e), the peak at around 150°C decreases in level as the thermal aging progresses. On the other hand, a broad peak appears at around 400°C. These results are attributed to the sintering of the PMs and the deterioration of PM dispersion during the thermal aging process. The effect of Rh appearing in the TPD profile of (c) decreases, but the effect of Pd is retained to some extent. It is confirmed that the double-layer washcoat composed of Rh in the top layer and Pd in the lower layer prevents the chain deactivation of the PMs. Consequently, the catalyst applied as a double-layer washcoat has improved thermal stability.

4. Conclusions

In this study of the catalytic activity and thermal stability of an advanced three-way catalyst for low-emission vehicles, the following conclusions were made.

(1) For the fresh catalysts involving double layers of washcoats, Pd-Rh/ γ -Al₂O₃ series are found to be superior to Pd-Pt-Rh/ γ -Al₂O₃ series in terms of catalytic activity.

(2) An optimum composition of PMs impregnated in top and bottom washcoat layers on LOT exists. In this study, the optimum ratio of Pd to Rh was 18/1.

(3) Pd-based catalysts initiate catalytic activity at lower temperatures than do Pt catalysts.

(4) Thermal stability can be improved by using the double-layer washcoat, which reduces the effect of the negative interactions between Rh and Pd during thermal aging.

Acknowledgement

This study is sponsored by the G7 Next Generation Vehicle project and conducted by the author who is a research assistant of the Brain Korea 21 project of the Korean government.

References

- (1) Kitagawa, H., Mibe, T. and Okamatsu, K., L4-Enging Development for a Super Ultra Low Emissions Vehicle, SAE paper No. 2000-01-0887.
- (2) Yamamoto, S., Matsushita, K. and Etoh, S., In-line Hydrocarbon (HC) Adsorber System for Reducing Cold-Start Emissions, SAE paper No. 2000-01-0892.
- (3) Lafyatis, D.S., Will, N.S. and Martin, A.P., Use of High Cell Density Substrates and High Technology Catalysts to Significantly Reduce Vehicle Emissions, SAE paper No. 2000-01-0502.
- (4) Choi, B.C., A Study Cold Start Hydrocarbon Emissions Reaction Technology in Gasoline Engine using the HC Adsorber, The 15th ICE Symposium Int. in Seoul, Paper No. 9935815 (1999).
- (5) Choi, B.C., Lee, N.S. and Son, G.S., A Study on the Reduction of Cold Start Hydrocarbon from Gasoline Engines Using Hydrocarbon Adsorbers, KSME Int. J., Vol. 14, No. 7 (2000), p. 699.
- (6) Son, G.S., Yun, S.W., Kim, D.J., Lee, K.Y. and Choi, B.C., A Study of HC Reduction with Hydrocarbon Adsorber Systems, KSME Int. J., Vol. 14, No. 10 (2000), p. 1168.
- (7) Kikuchi, S., High Cell Density and Thin Wall Substrate for Higher Conversion Ratio Catalyst, SAE Paper No. 1999-01-0268.
- (8) Song, Y.H., Plasma-Assisted Catalytic Technique for Reducing HC Emissions from Cold Start Engines, Seoul 2000 FISITA World Automotive Congress, Paper No. F2000H224.
- (9) Muraki, H., Sobukawa, H., Kimura, M. and Isogai, A., The Effects of Palladium on the Performance of Three-Way Catalyst, SAE Paper No. 9000610 (1990).
- (10) Stenborn, B., Thermal Deactivation of a Three-Way Catalyst: Changes of Structural and Performance Properties, SAE Paper No. 900273 (1990).
- (11) Choi, B.C., Improvement of Excess Air Ratio-Window Range of the Three-Way Catalyst for NGV, SAE Paper No. 2000-01-0848.
- (12) Usmen, R.K. and McCabe, R.W., Techniques for Analyzing Thermal Deactivation of Automotive Catalysts, SAE Paper No. 922336, (1992).
- (13) Yee, A., Morrison, S.J. and Idris, H., A Study of the Reactions of Ethanol on CeO₂ and Pd/CeO₂ by Steady State Reactions, Temperature Programmed Desorption, and In Situ FT-IR, J. of Catalysis 186, (1999), pp. 279-295.
- (14) Linder, D., Lox, E.S., Van Yeren, R., Ostgathe, K. and Kreuzer, T., Reduction of Exhaust Gas Emissions by Using Pd-based Three-Way Catalyst, SAE Paper, No. 960802 (1996).
- (15) Noronha, F.G., Baldanza, M.A.S., CO and NO Adsorption on Alumina-Pd-Mo Catalysts: Effect of the Precursor Salts, J. of Catalysis 188, (1999), pp. 270-280.
- (16) Sewell, G.S. and van Steen, E., Use of TPR/TPO for Characterization of Supported Cobalt Catalysts, Catalysis Letters 37, (1996), pp. 255-260.
- (17) Bouly, C. and Maret, D., TPD-Analysis of Hydrogen Adsorbed at Various Temperatures on Three-Way Exhaust Gas Catalysts, SAE Paper No. 930778 (1993).