

Development of TWC and PGM Free Catalyst Combination as Gasoline Exhaust Aftertreatment

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ABSTRACT

Reduction of the amount of platinum group metals (PGM: Pt, Pd, Rh) utilized in three-way catalysts (TWC) has been required from a point of resource shortage and cost effectiveness. A conventional TWC system is composed of a close-coupled (CC) catalyst and an underfloor (UF) catalyst, both PGM-based. The CC-TWC promotes HC/CO oxidation and NO_x reduction by CO. The UF-TWC mainly facilitates further NO_x reduction by CO.

In this study, a TWC system comprising a CC catalyst with PGM and an UF catalyst without PGM has been described. The newly developed system, performing reasonably well with a conventional stoichiometric gasoline combustion engine, offers an opportunity to reduce PGM usage. In this system, the UF-non-PGM catalyst is composed of a Ni/CeO₂ bottom layer which functions as a deNO_x catalyst with CO-NO reaction and a zeolite based top layer which works as a deNO_x catalyst with passive NH₃-SCR reaction. The CC catalyst operates as a conventional TWC but also generates a certain amount of NH₃ under rich conditions, and the generated NH₃ is used as the reductant for the SCR reaction on the UF-non-PGM catalyst. The NH₃ generation on the CC-TWC and the specific deNO_x concept in UF-non-PGM catalyst were validated by model gas reactor test, and the performance of the CC-TWC + UF-non-PGM catalyst system was evaluated by chassis test. It was found that such a system showed promising performance in LA4 and US06 evaluations. The NO_x conversions of the UF-non-PGM catalyst were 85% and 40% in LA4 and US06 modes, respectively.

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INTRODUCTION

Recently, the regulations for exhaust gases of gasoline vehicles have become substantially more stringent. The amount of platinum group metals (PGM: Pt, Pd, Rh) that can be used in three-way catalysts (TWC), however, is restricted from a point of resource shortage and cost effectiveness. A PGM-free catalyst has thus drawn considerable attentions and several relevant studies were disclosed.

In the area of base metal oxides (BMO), Hanaki et al. reported that highly dispersed particles of iron and ceria exhibited good exhaust gas purification performance relative to precious metal catalysts, even after aging [1]. Llieva et al. described that a gold catalyst on a ceria support containing 5wt% Fe₂O₃ displayed decent deNO_x activity via CO-NO reaction [2]. Fe-Ni/CeO₂ catalysts [3] and Ni-Cu alloy supported Mg-Al mixed oxide catalysts [4] were observed to give moderate activities for automotive exhaust control. Perovskite type materials were developed for TWC applications by Glisenti et al. who found that LaCo_{0.5}Cu_{0.5}O₃ exhibited an interesting compromise between oxidation and NO reduction activities at low temperatures even with a short contact time [5].

NH₃ selective catalytic reduction (SCR) for gasoline vehicles has also been studied and reported. It has been well known that close-coupled TWC generated a certain amount of NH₃ under rich conditions [6], implying plausible application of passive NH₃-SCR reactions to a gasoline exhaust after-treatment system. Prikhodko et al. reported that TWC+SCR systems had advantage in NO_x control and fuel efficiency for lean burn gasoline engines [7]. Can et al. reported NSR (NO_x storage/reduction) + SCR as a NO_x reduction system for the lean burn exhaust gas abatement [8]. Theis et al. studied TWC+TWC+SCR systems that met emission standards on FTP and US06 tests while allowing lean operation for fuel economy improvement during select driving conditions [9].

Conditions and performance requirements for a common close-coupled (CC) TWC and underfloor (UF) TWC system are compiled in Table 1. It seems quite difficult to apply a non-PGM catalyst in a CC position because of high requirements on durability and catalytic performance. This reflects the fact that PGM-type catalysts have traditionally been used for gasoline exhaust after-treatment. On the other hand, the requirements for a UF catalyst are less demanding.

compared to those for CC-TWC. There exists certain advantages to operate passive NH_3 -SCR on a UF-non-PGM catalyst since NH_3 is available to some extent from CC-TWC and the temperature range of the UF position suits well for such an SCR operation.

Table 1. Conditions and performance requirements for a common CC-TWC + UF-TWC system

	CC-TWC	UF-TWC
HC performance	Required (Cold/Hot)	Required (Hot)
CO performance	Required (Cold/Hot)	Required (Hot)
NO_x performance	Required (Cold/Hot)	Required (Hot)
OSC performance	Required	Not Required
Aging temperature	>950 °C	< 850 °C
P poisoning tolerance	Required	Not Required
Catalyst bed temp. (Hot region)	300 – 600 °C (LA4) 500 – 800 °C (US06)	200–500 °C (LA4) 400- 700 °C (US06)
A/F perturbation	Loose	Tight
Inlet gas NH_3	None	Some from CC-TWC
O_2 concentration	High	Low

In this study, a novel TWC system comprising a CC catalyst (CCC) and a UF catalyst (UFC) was investigated. The CCC is a PGM-based catalyst and, besides functioning as a conventional three-way conversion, generates a certain amount of NH_3 for UFC. The UFC is PGM-free and performs de NO_x via CO-NO reaction and/or NH_3 -SCR reaction.

CONCEPT OF THE NEW CATALYST SYSTEM

The detailed concept of the development system is illustrated in Figure 1. The CCC converts the majority of emissions and generates NH_3 under rich conditions. The UFC is designed to have two layers. The top layer contains Cu-zeolite for passive NH_3 -SCR reaction with the NH_3 supplied by CCC. The bottom layer contains base metal oxides, such as Ni supported on ceria (Ni/CeO₂), which promotes de NO_x via CO-NO reaction. Consequentially, the PGM-free UFC abates NO_x through two different reaction mechanisms.

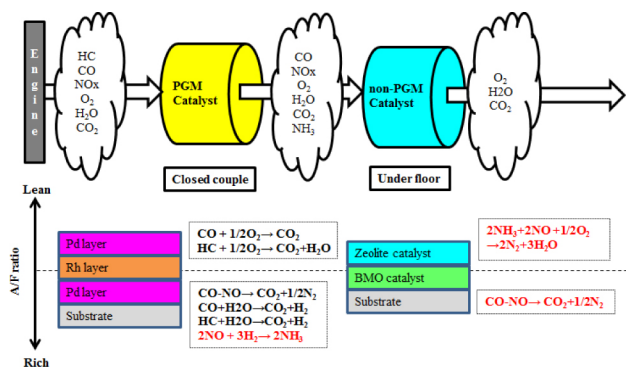


Figure 1. Concept of a new CCC+UFC TWC system

EXPERIMENTAL

Catalyst Preparation - Powders

Powder catalysts were prepared to represent individual layers of CCC and UFC. PGM (Pd or Rh) was deposited onto various supports (Al_2O_3 , ZrO_2 , CeO_2 - ZrO_2 mixed oxide with 45% CeO_2 , and CeO_2) by the conventional incipient wetness impregnation method, using an aqueous solution of PGM nitrate as the precursor. The Pd and Rh loadings were 3.0% and 0.5%, respective, on a weight basis.

For the SCR component in UFC, several metal-exchanged zeolites (Fe-MFI, Fe-Beta, Fe-CHA, and Cu-CHA) [10] were selected. Regarding the base-metal oxide layer in the PGM-free UFC, oxides of Fe, Cu or Ni were deposited onto different supports (ZrO_2 , CeO_2 - ZrO_2 mixed oxides with 30% and 65% CeO_2 , CeO_2) by the conventional incipient wetness impregnation method, using an aqueous nitrate solution of the corresponding BMO as the precursor. The BMO loading was controlled at 5% on a weight basis.

Catalyst Preparation - Coated Catalysts for Model Gas Test

The BMO components for UFC were not only tested at a powder level, but also evaluated on a model gas reactor using washcoated honeycombs. Four monolith catalysts were prepared: i) Ni/CeO₂ type-A, ii) Cu/ZrO₂, iii) Fe/ZrO₂, and iv) Ni/CeO₂ type-B. The first three washcoat materials were obtained by the aforementioned incipient wetness impregnation method. Ni/CeO₂ type-B was prepared by a new method for enhanced dispersion of Ni. Each catalyst contained 5wt% of the corresponding BMO (Fe_2O_3 , CuO or NiO). The slurries of the BMO materials were ball-milled and the pH was adjusted to approximately 4 with acetic acid. The slurries were coated on a honeycomb substrate (600cpsi/4mil, 1 inch diameter by 50mm length) with a washcoat loading of 100g/L.

Catalyst Preparation - Coated Catalysts for Chassis Test

Fully formulated CCC and UFC were prepared for chassis test. CCC was consisted of three layers. The bottom coat (1st coat) was a Pd layer containing Pd/ Al_2O_3 , Pd/OSC and a Ba component. The middle coat (2nd coat) was a Rh layer containing Rh/ Al_2O_3 and Rh/OSC. The top coat (3rd coat) was a Pd layer containing Pd/ Al_2O_3 , Pd/OSC and a Ba component. The layers were sequentially coated on a honeycomb substrate (600cpsi/4mil, Φ 105.7x91mm L, 0.8L). The total PGM loading of CCC was 5.68 g per unit with a Pd/Rh ratio of 14/1. Two types of PGM-free UFC were prepared and the formulations were summarized in Table 2. UFC was coated on a honeycomb substrate (600cpsi/4mil, Φ 118.4 x 91mm L, 1.0L) using slurries of Ni/CeO₂ and Cu-CHA sequentially.

Table 2. Formulations of UFC

	UFC-1	UFC-2
Top layer	Cu-CHA	Cu-CHA
Bottom layer	Ni/CeO ₂ type A	Ni/CeO ₂ type B

Ni/CeO₂ type A was prepared by the conventional incipient wetness impregnation method. Ni/CeO₂ type B was prepared by a new method for enhanced dispersion of Ni.

Model Gas Test Conditions

1. NH₃ Formation of CCC

NH₃ generation performance of CCC was evaluated by a model gas reactor (Microtarck BEL, BELCAT) test using PGM powder samples. The model gas test conditions were summarized in Table 3. Prior to the test, 3.0% Pd and 0.5% Rh samples were aged at 1050°C for 12 hours in air with 10% H₂O.

2. NH₃-SCR Reaction of Top Layer of UFC (Zeolite SCR)

NH₃-SCR reaction activity of the top layer of UFC was evaluated by a model gas reactor (Rigaku TPD type-R) test using various SCR powder samples. The model gas test conditions were summarized Table 4. Prior to the test, the SCR samples were aged at 900 °C for 12 hours in air with 10% H₂O.

3. DeNOx Performance by CO-NO Reaction of Bottom Layer of UFC

Table 3. Model gas test conditions of NH₃ formation

Gas composition	Rich	Stoichio
NO	0.100%	0.100%
CO	0.800%	0.800 %
C ₃ H ₆	0.010%	0.010%
C ₃ H ₈	0.040%	0.040%
H ₂ O	5.000%	5.000 %
O ₂	0 %	0.5 %
N ₂ O	0.050%	0.050%
Balance gas	He	He
Total flow rate	300cc/min	300 cc/min
Lambda	0.839	0.980
A/F perturbation	None	None
Evaluation Temperature	600 °C	600 °C
Sample weight	50 mg	50 mg
Detector	FTIR (IWATA)	FTIR (IWATA)

Table 4. Model gas test conditions of NH₃-SCR reaction and CO-NO reaction with O₂

NO	0.150 %
CO	0.300 %
H ₂ O	1.000 %
NH ₃	0.075 %
O ₂	0.100 %
Balance gas	He
Total flow rate	300 cc/min
Lambda	0.964
Perturbation	None
Evaluation Temperature	200 °C, 300 °C, 400 °C
Sample weight	50 mg
Detector	Mass analyzer (ANELVA)

DeNOx performance of the bottom layer of UFC via NO-CO reaction was evaluated by a model gas reactor (Rigaku TPD type-R) test using BMO powder samples. The model gas test conditions were summarized in Table 5. Prior to the test, the BMO samples were aged at 900 °C for 12 hours in air with 10% H₂O.

Table 5. Model gas test conditions of CO-NO reaction w/o O₂

NO	0.100 %
CO	0.450 %
C ₃ H ₁₂	0.017%
H ₂ O	1.000 %
NH ₃	0.020 %
O ₂	0 %
Evaluation Temperature	400 °C
Balance gas	He
Total flow rate	300 cc/min
Lambda	0.704
Perturbation	None
Sample weight	50 mg
Detector	Mass analyzer (ANELVA)

4. NO Performance under A/F Perturbation of Bottom Layer of UFC

NO performance of the bottom layer of UFC by NO-CO reaction was evaluated by a model gas reactor (HORIBA SIGU4012) test using core-size honeycomb samples. The evaluation was performed in the presence of A/F perturbation. The model gas test conditions were summarized in Table 6. Prior to the test, the samples were aged at 900 °C for 12 hours in air with 10% H₂O.

Table 6. Evaluation conditions of BMO honeycomb catalyst

NO	0.050 %
CO	0.500 %
C ₃ H ₆	0.040%
H ₂ O	10.000%
NH ₃	0 %
O ₂	0.500%
CO ₂	14.000%
H ₂	0.1700%
Evaluation Temperature	400 °C
Balance gas	N ₂
Total flow rate	30 L/min
Lambda	1.000
Perturbation	± 0.041 / 1.0Hz
Sample size	Φ 1inch x 50mmL core (25cc)
Detector	MEXA-7100 (HORIBA)

Chassis Test of CCC+UFC Systems

The CCC+UFC systems were evaluated by chassis test. The aging and test conditions were summarized in Table 7.