Investigation of performances of commercial diesel oxidation catalysts for CO, C₃H₆, and NO oxidation

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Abstract: Four commercial monolithic diesel oxidation catalysts (DOCs) with two different platinum group metal (PGM) loadings and Pt:Pd ratios of 1:0, 2:1, 3:1 (w/w) were investigated systematically for CO, C₃H₆, and NO oxidation, CO-C₃H₆ co-oxidation, and CO-C₃H₆-NO oxidation reactions via transient activity measurements in a simulated diesel engine exhaust environment. As PGM loading increased, light-off curves shifted to lower temperatures for individual and co-oxidation reactions of CO and C₃H₆. CO and C₃H₆ were observed to inhibit the oxidation of themselves and each other. Addition of Pd to Pt was found to enhance CO and C₃H₆ oxidation performance of the catalysts while the presence and amount of Pd was found to increase the extent of self-inhibition of NO oxidation. NO inhibited CO and C₃H₆ oxidation reactions while NO oxidation performance was enhanced in the presence of CO and C₃H₆ probably due to the occurrence of reduced Pt and Pd sites during CO and C₃H₆ oxidations. The optimum Pt:Pd ratio for individual and co-oxidations of CO, C₃H₆, and NO was found to be Pt:Pd = 3:1 (w/w) in the range of experimental conditions investigated in this study.

Key words: aftertreatment systems, diesel oxidation catalyst, bimetallic catalyst, platinum, palladium, commercial monolith

1. Introduction

Aftertreatment systems (ATSs) are used to abate exhaust emissions of diesel vehicles. In many of the currently employed configurations, diesel oxidation catalyst (DOC) is the first unit in the ATS of a heavy-duty diesel vehicle. The primary function of DOC is the oxidation of NO, CO, and unburnt hydrocarbons to NOₓ, CO₂, and H₂O. Moreover, the heat generated by highly exothermic oxidation of injected diesel in DOC is utilized for active regeneration of the diesel particulate filter (DPF) which is generally placed after the DOC. NOₓ resulting from oxidation of NO in DOC is also used as an oxidant for passive regeneration of the DPF. Additionally, the ratio of NOₓ to NO influences the rate of NOₓ reduction in selective catalytic reduction (SCR) unit, which is usually placed after the DPF [1]. Although hydrocarbon oxidation by O₂ is highly favored in lean exhaust conditions of diesel engines, NOₓ reduction by hydrocarbons and CO also takes place in the DOC, which is known as hydrocarbon-SCR (HC-SCR) and CO-SCR, where hydrocarbons and CO are oxidized by NOₓ and NO; yielding NOₓ, N₂O, N₂, H₂O and CO₂ [2].

DOCs used in ATSs are usually wash coated on cordierite monoliths with square channels [1]. Platinum group metals (PGMs) are generally used as the active metal in DOCs and Pt is the widely used PGM. Since PGM cost is the major contributor to the ATS cost, numerous studies have been made to decrease the amount of PGM in DOCs [3–12]. The addition of Pd was shown to increase thermal stability and sintering resistance of the catalyst [1,6,7]. There have been many efforts to find the optimum Pt:Pd ratio for maximizing oxidation performance of DOCs while maintaining high durability. Shakya et al. reported the performances of four bimetallic Pt/Pd/Al₂O₃ DOCs with 11 g/ft³ PGM loading for the oxidation of CO, NO, and various hydrocarbons [8]. CO oxidation activity of the catalyst increased with decreasing Pt:Pd ratio, while unsaturated hydrocarbon oxidation activity of the catalyst firstly increased and then reached a plateau with increasing Pt:Pd ratio. NO oxidation performance monotonically increased with increasing Pt:Pd ratio. Kim et al. reported similar results for the catalytic activity of NO oxidation [9]. In their experiments, catalysts with 50 g/ft³ PGM loading were used. Pt-only catalyst and bimetallic Pt/Pd/Al₂O₃ with Pt:Pd ratio of 7:1 (w/w) performed very similarly for NO oxidation. Hazlett et al. showed that Pt was more prone to poisoning by CO and partial oxidation products of C₃H₆ compared to
Another important factor which affects DOC performance for a particular component is promotion and inhibition effect associated with the composition of the exhaust mixture [14]. These effects also depend on the PGM loading and Pt:Pd ratio of the catalysts. Khosravi et al. studied oxidation of CH$_4$ and NO along with C$_3$H$_6$-SCR of NO via transient measurements using two commercial monolithic DOCs with a total PGM loading of 95 g/ft$^3$ [15]. One of the monoliths was Pt-based, and the other contained a bimetallic catalyst with Pt:Pd ratio of 4:1 (w/w). Conversion of NO to NO$_2$ started after conversion of CH$_4$ had reached 100%. They also observed that NO inhibited C$_3$H$_6$-SCR reactions while CH$_4$ promoted them. Similar results were reported for C$_3$H$_6$-SCR reactions by Watling et al. for a commercial monolithic DOC with 120 g/ft$^3$ PGM loading and Pt:Pd ratio of 2:1 (w/w) [16]. Kim et al. also showed the sensitivity of NO oxidation to the presence of hydrocarbons [9]. They demonstrated the inhibitory effects of several hydrocarbons on NO oxidation over monolithic DOCs with various Pt:Pd ratios. Shakya et al. observed that the NO/NO$_2$ ratio at the outlet decreased in the presence of various hydrocarbons due to HC-SCR reactions over bimetallic DOCs with total PGM loading of 11 g/ft$^3$ and Pt:Pd ratios of 1:3, 1:1, 3:1, and 10:1 [8]. Similarly, presence of CO decreased NO/NO$_2$ ratio at the outlet due to CO-SCR reactions. Hauff et al. investigated CO and NO oxidations and their influence on the oxidation of each other over a commercial monolithic Pt-based DOC with 130 g/ft$^3$ PGM loading [17]. CO oxidation was inhibited by the presence of NO, and NO oxidation started after 100% CO conversion was reached when a Pt-based DOC was used. Maximum NO conversion in the presence of CO was higher than that in NO-only oxidation reactions. The promotion of NO oxidation was explained by the prevention of Pt oxide formation at temperatures providing high CO coverage.

This paper investigates the performances of four monolithic commercial DOCs for the aftertreatment of heavy-duty diesel engines for CO, C$_3$H$_6$, and NO oxidation, CO-C$_3$H$_6$ co-oxidation, and CO-C$_3$H$_6$-NO oxidation with various feed concentrations and gas hourly space velocities (GHSVs) via transient activity measurements in synthetic engine exhaust environment (10% O$_2$, 7% CO$_2$, 5% H$_2$O, and N$_2$ as the balance gas). Effect of Pt:Pd ratio and total PGM loading on oxidation performance were investigated. Light-off temperatures were compared for C$_3$H$_6$ and CO oxidation reactions while maximum conversion and T$_{50}$ temperature at 20% conversion, were compared for NO oxidation reaction to assess catalyst performances. Self-inhibition of the feed gases on oxidation reactions as well as their inhibition/promotion effects on the oxidation of one another in the presence of Pt and Pd were also investigated.

2. Materials and methods

2.1. Materials

Pt/Al$_2$O$_3$ and PtPd/Al$_2$O$_3$ washcoated honeycomb commercial DOCs (300 cps) for the aftertreatment of heavy-duty diesel engines were used in this study. Pt:Pd ratios of the DOCs are given Table 1. DOCs were named after their Pt:Pd ratio (w/w). The monometallic Pt DOC was named as PtPd1:0. Bimetallic DOCs with Pt:Pd ratio of 3:1 (w/w) and 2:1 (w/w) were named as PtPd3:1 and PtPd2:1, respectively. Bimetallic DOC with approximately 15% lower total PGM loading and Pt:Pd ratio of 2:1 (w/w) was named as PtPd2:1L. Carbon dioxide, nitrogen, and oxygen (99.998%) were purchased from Air Liquide. Water was deionized before usage (18 mΩ). CO (10%, balance N$_2$) gas was purchased from Messer. C$_3$H$_6$ (49%, balance He) and NO (2%, balance N$_2$) gases were purchased from Elite Gaz.

2.2. Activity measurements

Experimental setup is given in Figure 1. DOC monolithic cylinders with 1.7 cm diameter and 2.5 cm length were drilled out of commercial DOCs which were 13 cm long and had a diameter of 30 cm. The DOC monolithic cylinders were wrapped with insulation to avoid bypass and placed in a stainless-steel tube. Two thermocouples (Omega Inc., CT, USA) were placed at the entrance and at the center of the monoliths. The tube was placed in an electrical furnace (Split Tube Furnace XST-2-0-12-1V2-E28, Thermcraft, NC, USA). Water was delivered by an evaporator-liquid mass flow controller (MFC) system (Controlled evaporator mixer (CEM) system W-202A-220-K, Bronkhors, Nijverheidsstraat, NL t). All other gas flows were controlled via calibrated thermal MFCs (5850E, Brooks Instruments, PA, USA). All lines to and from the reactor furnace were heated above 100 °C to avoid water condensation. The concentration of the gases leaving the reactor were measured by an FTIR continuous gas analyzer (MultiGas 2030, MKS Instruments Inc., MA, USA). DOCs were pretreated at 550 °C with 10% O$_2$, 5% H$_2$O, and N$_2$ as the balance gas for 5 h. After each run, the catalysts were treated with 10% O$_2$ and 90% N$_2$ at 450 °C for 20 min to clean the surface of the catalyst of any residues. In all experiments, a base feed gas stream composed of 10% O$_2$, 5% H$_2$O, 7% CO$_2$, and N$_2$ as the balance gas was used to mimic exhaust gas composition. All experiments were conducted at GHSVs of 75,000 h$^{-1}$ or 100,000 h$^{-1}$. Feed concentrations for CO, C$_3$H$_6$, and NO ranged between 250–500 ppm, 300–400 ppm, and 140–1000 ppm, respectively. Feed concentrations and GHSVs of individual...
experiments are summarized in Table 2-5 respectively for PtPd 2:1, PtPd 1:0, PtPd 3:1, and PtPd 2:1L catalysts. Light-off measurements were conducted with a temperature ramp of 10 °C/min. The temperature ramp was started after the effluent concentrations of all gases from the reactor were steady. During our experiments, possible byproducts of C$_3$H$_6$ partial oxidation such as CO, ethylene, formaldehyde, and acetaldehyde were also monitored and no traces of these byproducts were present in the effluent gas stream.

3. Results and discussion

3.1. CO oxidation

Light-off curves of CO oxidation for all DOCs are given in Figure 2. Light-off temperatures for CO oxidation are summarized in Tables 2–5. CO oxidation experiments were conducted with two feed CO concentrations for PtPd 2:1. Light-off temperature increased from 146 °C to 173 °C with increasing feed CO concentration from 250 ppm to 500 ppm, indicating self-inhibition of CO within the concentration range investigated [1,18,19].

Performances of PtPd 2:1 and PtPd 2:1L for CO oxidation were compared using the light-off data obtained with a feed CO concentration of 500 ppm and at 75,000 h$^{-1}$ GHSV. It was shown that a 15% decrease in total PGM loading resulted in a 14 °C increase in CO light-off temperature. CO oxidation performances of PtPd 1:0 and PtPd 3:1 were compared using the light-off data obtained with a feed CO concentration of 500 ppm and at 100,000 h$^{-1}$ GHSV. A 10 °C lower light-off temperature was achieved by PtPd 3:1. This indicated that addition of Pd as a secondary metal with constant total PGM amount decreased the CO light-off temperature. This was probably due to lower rate of self-inhibition of CO in the presence of Pd [10,20].

Table 1. Pt:Pd ratios of the commercial DOCs.

| Catalyst name | Pt:Pd (w/w) |
|---------------|-------------|
| PtPd 2:1      | 2:1         |
| PtPd 1:0      | 1:0         |
| PtPd 3:1      | 3:1         |
| PtPd 2:1L     | 2:1         |

Figure 1. Experimental setup used in activity measurements.
3.2. C<sub>3</sub>H<sub>6</sub> oxidation

Light-off curves for C<sub>3</sub>H<sub>6</sub> oxidation for all DOCs are given in Figure 3 and C<sub>3</sub>H<sub>6</sub> light-off temperatures are summarized in Tables 2–5. All experiments were conducted with feed C<sub>3</sub>H<sub>6</sub> concentration ranging between 300–400 ppm and at GHSV's 75,000 h<sup>−1</sup> and 100,000 h<sup>−1</sup>.

The lowest C<sub>3</sub>H<sub>6</sub> light-off temperature was obtained by PtPd 3:1. C<sub>3</sub>H<sub>6</sub> oxidation performances of PtPd 2:1 and PtPd 3:1 were compared to investigate the effect of Pd amount of the bimetallic catalysts. PtPd 3:1 resulted in more than 50°C lower C<sub>3</sub>H<sub>6</sub> light-off temperatures both at 75,000 h<sup>−1</sup> and 100,000 h<sup>−1</sup>, compared to PtPd 2:1. The PtPd 1:0 catalyst resulted in a similar light-off temperature with the PtPd 2:1, but the light-off curve was steeper than that of PtPd 2:1. These results

Table 2. T<sub>50</sub> values for CO and C<sub>3</sub>H<sub>6</sub> in CO, C<sub>3</sub>H<sub>6</sub>, CO-C<sub>3</sub>H<sub>6</sub> and CO-C<sub>3</sub>H<sub>6</sub>-NO oxidation reactions and T<sub>20</sub> values for NO in NO and CO-C<sub>3</sub>H<sub>6</sub>-NO oxidation reactions for PtPd2:1 catalyst.

| Feed Concentration | GHSV (h<sup>−1</sup>) | T<sub>50</sub> and T<sub>20</sub> Values |
|--------------------|----------------------|-------------------|
| CO (ppm) C<sub>3</sub>H<sub>6</sub> (ppm) NO (ppm) | 75,000 100,000 | CO T<sub>50</sub> (°C) C<sub>3</sub>H<sub>6</sub> T<sub>50</sub> (°C) NO T<sub>20</sub> (°C) |
| 250 - - | 146 - - |
| 500 - - | 173 - - |
| - 300 - | - 200 - |
| - 300 - | 100,000 - 215 - |
| - 500 - | 75,000 - 342 |
| - 1000 - | 75,000 - 400 |
| 250 350 - | 75,000 171 194 |
| 500 350 - | 75,000 227 228 |
| 500 350 500 | 75,000 244 265 339 |

Table 3. T<sub>50</sub> values for CO and C<sub>3</sub>H<sub>6</sub> in CO, C<sub>3</sub>H<sub>6</sub>, CO-C<sub>3</sub>H<sub>6</sub> and CO-C<sub>3</sub>H<sub>6</sub>-NO oxidation reactions and T<sub>20</sub> values for NO in NO and CO-C<sub>3</sub>H<sub>6</sub>-NO oxidation reactions for PtPd 1:0 catalyst.

| Feed Concentration | GHSV (h<sup>−1</sup>) | T<sub>50</sub> and T<sub>20</sub> Values |
|--------------------|----------------------|-------------------|
| CO (ppm) C<sub>3</sub>H<sub>6</sub> (ppm) NO (ppm) | 100,000 75,000 | CO T<sub>50</sub> (°C) C<sub>3</sub>H<sub>6</sub> T<sub>50</sub> (°C) NO T<sub>20</sub> (°C) |
| 500 - - | 192 - - |
| - 350 - | 214 - - |
| - - 500 | 100,000 - 293 |
| - - 1000 | 100,000 - 300 |
| 500 350 - | 100,000 216 216 |
| 500 350 140 | 100,000 255 259 272 |

Table 4. T<sub>50</sub> values for CO and C<sub>3</sub>H<sub>6</sub> in CO, C<sub>3</sub>H<sub>6</sub>, CO-C<sub>3</sub>H<sub>6</sub> and CO-C<sub>3</sub>H<sub>6</sub>-NO oxidation reactions and T<sub>20</sub> values for NO in NO and CO-C<sub>3</sub>H<sub>6</sub>-NO oxidation reactions for PtPd 3:1 catalyst.

| Feed Concentration | GHSV (h<sup>−1</sup>) | T<sub>50</sub> and T<sub>20</sub> Values |
|--------------------|----------------------|-------------------|
| CO (ppm) C<sub>3</sub>H<sub>6</sub> (ppm) NO (ppm) | 100,000 75,000 | CO T<sub>50</sub> (°C) C<sub>3</sub>H<sub>6</sub> T<sub>50</sub> (°C) NO T<sub>20</sub> (°C) |
| 500 - - | 182 - - |
| - 350 - | 134 - - |
| - 350 - | 159 - - |
| - 180 - | 100,000 - 290 |
| 500 350 - | 100,000 168 173 |
| 500 350 180 | 100,000 220 244 257 |
NO oxidation are given in Table 5. CO and C₃H₆ in CO, C₃H₆, CO-C₃H₆, and CO-C₃H₆-NO oxidation reactions and T₀ values for NO in NO and CO-C₃H₆-NO oxidation reactions for PtPd 2:1L catalyst.

| Feed concentration | GHSV (h⁻¹) | T₀ values | CO T₀ (°C) | C₃H₆ T₀ (°C) | NO T₀ (°C) |
|--------------------|------------|-----------|------------|--------------|------------|
| CO (ppm) | C₃H₆ (ppm) | NO (ppm) | 75,000 | 100,000 | 100,000 |
| 500 | - | 350 | - | 75,000 | - | - | 187 | - | - |
| 500 | - | - | 100,000 | 210 | - | - | - | - |
| - | 350 | - | 75,000 | - | 174 | - | - | - |
| - | 400 | - | 100,000 | - | 209 | - | - | - |
| - | - | 500 | 75,000 | - | - | 277 | - | - |
| - | - | 1000 | 75,000 | - | - | 287 | - | - |
| - | - | 500 | 100,000 | - | - | 290 | - | - |
| - | - | 1000 | 100,000 | - | - | 325 | - | - |
| 500 | 350 | - | 100,000 | 265 | 265 | - |
| 500 | 350 | 500 | 100,000 | 255 | 278 | >400 |

indicate an optimum of Pt:Pd ratio of 3:1 for maximum C₃H₆ conversion at a particular temperature. Similarly, Dadi et al. compared monometallic Pt, Pd, and bimetallic PtPd DOCs with different Pt:Pd ratios and found that the lowest light-off temperature was obtained by bimetallic DOC with a Pt:Pd molar ratio of 2.3:1 [20].

3.3. NO oxidation

NO oxidation performances of DOCs are given in Figure 4. T₀ values are summarized in Tables 2–5. In general, T₀ values increased with increasing NO feed concentration, which points to the self-inhibition of NO. The self-inhibition was the strongest in PtPd 2:1, which had the highest Pd loading among all catalysts, while it was least pronounced in monometallic PtPd 1:0: PtPd 2:1L performed very similarly with PtPd 1:0 when NO feed was 500 ppm and GHSV was 100,000 h⁻¹. When the feed NO concentration was increased to 1000 ppm, a 35 °C increase was observed in T₀ of PtPd 2:1L compared to the 7 °C increase in T₀ of PtPd 1:0. These results suggest that the presence and the amount of Pd has a significant contribution to the self-inhibitory effect of NO on its oxidation. Comparison of the performances of PtPd 2:1 and PtPd 1:0 for NO oxidation showed that although the experiments with PtPt 1:0 were conducted at higher GHSV, T₀ values were lower than that obtained when PtPd 2:1 was used. As a result, it may be deduced that addition of Pd while keeping total PGM amount constant did not enhance NO oxidation performance of DOC for NO-only oxidation experiments in line with literature [8,9].

3.4. CO-C₃H₆ co-oxidation

Light-off curves for CO-C₃H₆ co-oxidation are given in Figure 5. Light-off temperatures for CO and C₃H₆ are listed in Tables 2–5. CO started to oxidize before C₃H₆ in all experiments. This was attributed to stronger adsorption of CO on the active sites compared to C₃H₆ [13,21]. Experiments conducted with different CO feed concentrations (250 and 500 ppm) and constant C₃H₆ feed concentration (350 ppm) indicated that the presence of CO inhibits C₃H₆ oxidation and the extent of the inhibition increases with increasing CO concentration within the feed concentration range. Comparison of these results with CO-only oxidation experiments indicate that C₃H₆ also inhibits CO oxidation reaction. These could be interpreted as competitive oxidation of CO and C₃H₆ on the catalyst surface. Inhibition of CO oxidation by the presence of C₃H₆ was shown to result from the competition of CO with intermediate species of C₃H₆ oxidation for adsorption sites on the surface of Pt/Al₂O₃ catalyst [22]. DRIFTS conducted by Hazlett and Epling showed that adsorbed ethylene, adsorbed formaldehyde, and adsorbed acetates were formed as surface intermediates during C₃H₆ oxidation, which inhibited both CO and C₃H₆ oxidation reactions [21]. Although CO oxidation starts at lower temperatures compared to C₃H₆ oxidation, light-off temperatures for CO and C₃H₆ were very similar in all experiments conducted with a feed gas mixture containing 500 ppm CO and 350 ppm C₃H₆. The lowest light-off temperature for both CO and C₃H₆ during co-oxidation were obtained in PtPd3:1, while the highest light-off temperatures were obtained in PtPd 2:1L. These results underline the relation between total metal loading and light-off temperature for CO and C₃H₆ oxidation. In this regard, Hauff et al. showed that total amount of metal loading has a direct effect on light-off temperature of C₃H₆ and CO during both individual and co-oxidation experiments conducted using monolithic.

3.5. CO-C₃H₆-NO oxidation

Performances of DOCs for CO-C₃H₆-NO oxidation are given in Figure 6. T₀ for CO and C₃H₆ and T₀ for NO are given in Tables 2–5. Addition of NO to feed mixture inhibited both CO and C₃H₆ oxidations, as observed by the increase in light-
off temperatures of both CO and C\textsubscript{3}H\textsubscript{6}. This points to the inhibition of CO and C\textsubscript{3}H\textsubscript{6} oxidation reactions by the presence of NO. The lowest light-off temperatures for CO and C\textsubscript{3}H\textsubscript{6} oxidation during CO-C\textsubscript{3}H\textsubscript{6}-NO oxidation were obtained by PtPd3:1.

At high temperatures, although N\textsubscript{2}O yield is zero, amount of NO converted is higher than NO\textsubscript{2} yield. The difference between NO conversion and NO\textsubscript{2} yield was attributed to the formation of N\textsubscript{2} through C\textsubscript{3}H\textsubscript{6}-SCR and CO-SCR at high temperatures [15,23,24].

Overall C\textsubscript{3}H\textsubscript{6}-SCR reactions taking place on DOCs are given Reactions (1–3) as proposed by Khosravi et al. [15].

\[
\begin{align*}
\text{C}_3\text{H}_6 + 2\text{NO} + 3.5\text{O}_2 &\rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3\text{CO}_2 \\
\text{C}_3\text{H}_6 + 2\text{NO} + 4\text{O}_2 &\rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O} + 3\text{CO}_2 \\
\text{C}_3\text{H}_6 + \text{NO}_2 + 4\text{O}_2 &\rightarrow \text{NO} + 3\text{H}_2\text{O} + 3\text{CO}_2
\end{align*}
\]

CO-SCR reactions were mostly pronounced in studies concerning three-way catalysts for aftertreatment of gasoline engine exhaust, however they also take place in DOCs. CO-SCR reactions over noble metal catalysts are given in Reactions (4–6) [25].

\[
\begin{align*}
2\text{CO} + 2\text{NO} &\rightarrow \text{N}_2 + 2\text{CO}_2 \\
\text{CO} + 2\text{NO} &\rightarrow \text{N}_2 + \text{O}_2 + \text{CO}_2 \\
\text{CO} + \text{N}_2 &\rightarrow \text{N}_2 + \text{CO}_2
\end{align*}
\]

When the extent of NO conversion was compared for NO-only and CO-C\textsubscript{3}H\textsubscript{6}-NO oxidation experiments, it was observed that the maximum NO conversion in the presence of CO and C\textsubscript{3}H\textsubscript{6} were lower than those in NO-only oxidation reactions except for PtPd2:1; where presence of CO and C\textsubscript{3}H\textsubscript{6} did not significantly affect NO oxidation profile. However,
NO oxidation was considerably hindered by CO and C\textsubscript{3}H\textsubscript{6} over PtPd 2:1L catalyst. At temperatures lower than 330 °C, NO oxidation was enhanced by the presence of CO and C\textsubscript{3}H\textsubscript{6} for PtPd 1:0 and PtPd 3:1, which was indicated by lower T\textsubscript{20} values compared to NO-only oxidation. The decrease in T\textsubscript{20} values can be explained by the conversion of Pt and Pd oxides via C\textsubscript{3}H\textsubscript{6} and CO at lower temperatures, resulting in reduced Pt and Pd sites, which are more active for NO oxidation [26,27]. The occurrence of C\textsubscript{3}H\textsubscript{6}-SCR and CO-SCR reactions also assisted to the increase of NO conversion at temperatures lower than 300 °C. N\textsubscript{2}O yield increased with temperature up to 300 °C, and then diminished at higher temperatures. Formation of N\textsubscript{2}O was attributed to C\textsubscript{3}H\textsubscript{6}-SCR and CO-SCR reactions. Higher N\textsubscript{2}O yields were observed by PtPd 1:0 and PtPd 3:1, where NO feed concentrations were lower than that in PtPd 2:1 and PtPd 2:1L. Since NO inhibits C\textsubscript{3}H\textsubscript{6}-SCR [15,28], lower feed NO concentration resulted in higher N\textsubscript{2}O yield and lower NO\textsubscript{2}/NO\textsubscript{x} ratio.

4. Conclusions
Performances of four commercial DOCs with various total PGM loadings and Pt:Pd ratios were investigated for CO, C\textsubscript{3}H\textsubscript{6} and NO oxidation, CO-C\textsubscript{3}H\textsubscript{6} co-oxidation, and CO-C\textsubscript{3}H\textsubscript{6}-NO oxidation reactions. Oxidation performances of the DOCs were evaluated by the comparison of light-off temperatures for CO and C\textsubscript{3}H\textsubscript{6} and maximum conversion and T\textsubscript{20} values for NO with different gas feed concentrations and GHSV\textsubscript{s} via transient measurements in synthetic engine exhaust environment (10% O\textsubscript{2}, 7% CO\textsubscript{2}, 5% H\textsubscript{2}O and N\textsubscript{2} as the balance gas). Effect of PGM loading and Pt:Pd ratio on oxidation performances of these DOCs were investigated and the main conclusions are summarized below:

· It was found that as PGM loading increased, light-off temperature of CO and C\textsubscript{3}H\textsubscript{6} decreased during individual and co-oxidation reactions.
Figure 4. NO oxidation performances of the DOCs. a) PtPd 2:1; b) PtPd 1:0; c) PtPd 3:1; d) PtPd 2:1L. Other gases and their compositions in the feed mixture were 10% O₂, 5% H₂O, 7% CO₂, and N₂ as the balance gas.

Figure 5. CO-C₆H₁₀ co-oxidation performances of the DOCs. a) PtPd 2:1; b) PtPd 1:0; c) PtPd 3:1; d) PtPd 2:1L. Other gases and their compositions in the feed mixture were 10% O₂, 5% H₂O, 7% CO₂, and N₂ as the balance gas.
Addition of Pd as a secondary metal decreased CO light-off temperature. The optimum Pt:Pd ratio for maximum CO and C\textsubscript{3}H\textsubscript{6} performance was found to be Pt:Pd = 3:1 (w/w) for the range of experimental conditions. Presence and amount of Pd was found to increase the extent of self-inhibition of NO oxidation. The lowest T\textsubscript{20} for NO were obtained by PtPd 1:0 and PtPd 2:1; while PtPd 2:1 was more prone to self-inhibition of NO oxidation compared to PtPd 1:0.

CO and C\textsubscript{3}H\textsubscript{6} were found to inhibit the oxidation of one another. The extent of C\textsubscript{3}H\textsubscript{6} oxidation inhibition by CO increased with increasing CO feed concentration in the range was investigated. NO inhibited both CO and C\textsubscript{3}H\textsubscript{6} oxidation reactions during CO-C\textsubscript{3}H\textsubscript{6}-NO oxidation experiments.

At temperatures up to 300 °C, NO oxidation over PtPd 1:0 and PtPd 3:1 were enhanced due to C\textsubscript{3}H\textsubscript{6}-SCR and CO-SCR reactions and the occurrence of reduced Pt and Pd sites due to C\textsubscript{3}H\textsubscript{6} and CO oxidation.

In general, addition of Pd enhanced catalytic performance for CO and C\textsubscript{3}H\textsubscript{6} oxidation. The optimum Pt:Pd ratio for CO, C\textsubscript{3}H\textsubscript{6} and NO oxidations was found to be 3:1 (w/w) for the range of experimental conditions investigated in this study.

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