

The Effect of Pt:Pd Ratio on Heavy-Duty Diesel Oxidation Catalyst Performance: An Experimental and Modeling Study

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ABSTRACT

A combined experimental and modeling study was carried out to investigate the effects of Pt:Pd ratio on the performance of diesel oxidation catalysts (DOC) for heavy-duty applications¹ (PGM<50 g/ft³).

In the first part of this work, transient light-off and steady-state experiments were performed over a series of hydrothermally aged DOCs with different Pt:Pd ratios and PGM loadings. It was found that *n*-decane and NO oxidation activities increased monotonically as the Pt:Pd ratio was increased while the oxidation of unsaturated hydrocarbons (HC) (C₃H₆ and C₇H₈) first increased with an increase in Pt:Pd ratio and then plateaued at higher Pt content. In contrast, the CO oxidation exhibited opposite trend, with the catalyst containing low Pt (high Pd) level being more active. The presence of HC lowered the outlet NO₂/NOx ratio by reducing the NO₂ generated *via* NO oxidation back to NO. The negative effect of HCs on NO₂/NOx ratio increased in the order: C₃H₆<C₇H₈<C₁₀H₂₂. The effect of oxidative and reductive pre-treatments on “inverse hysteresis” phenomena observed during NO oxidation was also studied for selected degreened catalysts. The results show a strong dependence of the NO oxidation on the catalysts' oxidation state for different Pt-Pd DOCs.

In the second part, a comprehensive kinetic model was developed to capture the effect of Pt:Pd ratio and PGM loading on key DOC reactions. The model was then validated against engine data. A case study was also carried out to demonstrate the capabilities of the model in designing an appropriate DOC for a given application.

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INTRODUCTION

The diesel oxidation catalyst (DOC) is a key component of a diesel aftertreatment system. Historically, DOCs were primarily used to remove (oxidize) unburnt HC and CO from the exhaust gas [2]. However, an important function of a modern DOC is also to convert some of the NO to NO₂ to obtain desired NO₂/NOx ratio that would be beneficial for the downstream NOx reduction catalysts such as selective catalytic reduction (SCR) and lean NOx traps (LNT) [3, 4].

The NO₂ formed may also be used for oxidizing soot captured on diesel particulate filters (DPF) [3, 4].

While Pt-only DOCs exhibit excellent oxidation activity specifically towards longer chain HC and NO oxidation, they offer poor thermal durability [4, 5, 6]. High temperature operations are often required for DPF regeneration and as a result Pt-based DOC may not be the ideal choice [4, 5, 6]. On the other hand, Pd-only DOC gives low NO oxidation activity and deactivates at a faster rate upon exposure to

sulfur [5]. In order to circumvent the problems associated with the monometallic DOCs, bimetallic Pt-Pd DOCs have been proposed [1, 4, 5, 6]. Not only is the cost of the catalyst lowered by the use of such bimetallic formulations in DOCs, but also the thermal stability is improved and overall higher activity of CO/HC oxidation is achieved [5]. Few studies have been published in the literature that investigate the effects of Pt:Pd ratio on the performance of the DOC catalyst [5, 6]. Kim et al. [5] carried out a systematic study on the effect of Pt:Pd ratio on the DOC activity and stability using a series of mildly and severely aged model catalysts with varying Pt:Pd ratio at the fixed PGM loading of 50 g/ft³. They found that NO oxidation activity increased monotonically as the Pt content is increased while the propylene oxidation exhibited a maximum at an intermediate Pt:Pd. They also investigated the impact of CO on propylene oxidation and found that the negative effect of CO is more pronounced for samples with higher Pt content. This was attributed to the increased inhibition by CO on Pt-rich catalysts. They also carried out experiments with heavy hydrocarbons (a mixture of *m*-xylene and *n*-dodecane) to simulate the unburned hydrocarbons in the exhaust. They found that oxidation of heavy hydrocarbon depended directly on the Pt content. Their results clearly suggest that light and heavy hydrocarbon

1. Work on light-duty DOC is presented in SAE paper #15PFL-0137 [1]

oxidation has a different dependence on the Pt:Pd ratio. Glover et al. [6] carried out a similar study on a series of lightly loaded (40 g/ft^3) Pt:Pd DOC samples. Their investigation mainly focused on elucidating the effect of Pt:Pd ratio on CO and propylene light-off characteristics and nitrogen containing species formation (NH_3 , N_2O , N_2 and NO_2). The light-off trends observed were consistent with those reported by Kim et al. [5]. They also observed that the addition of Pd lowered the N_2O formation [6].

NO oxidation to NO_2 is a key reaction occurring in DOCs. It is well established that the NO oxidation activity is strongly dependent on the oxidation state of the precious metal [7, 8, 9]. Hauptmann et al. [7] reported NO oxidation “inverse hysteresis” over a fully reduced Pt/ Al_2O_3 catalyst where they observed higher NO oxidation activity during the transient ramp-up of the inlet temperature than during the ramp-down. They attributed the observed behavior to a reversible oxidation of surface Pt by NO_2 during the ramp-up and subsequent reduction by NO during the ramp-down. They successfully modeled the behavior by including additional reactions involving the oxidation and reduction of Pt sites by NO_2 and NO, respectively. A more detailed study on the platinum oxide formation and reduction during NO oxidation was pursued by Hauff et al. [8]. They showed that the oxidation of platinum is largely because of the high concentration of O_2 as opposed to NO_2 claimed by Hauptmann et al. [7]. They performed experiments with and without NO_2 (<150 ppm) and found that small concentration of NO_2 had an insignificant impact on platinum oxidation in the presence of excess oxygen (O_2 concentration = 12%). Based on their experimental study, they developed a simplified macrokinetic model that is able to predict the data reasonably well [9]. Watling et al. [3] also modified the NO oxidation kinetics to account for the “oxide effect”. The advanced NO oxidation model gave much improved predictions. Unlike the studies by Hauptmann et al. [7] and Hauff et al. [8, 9] an opposite hysteresis behavior was observed by Watling et al. [3]. The authors speculated the differences could be because of the catalyst formulation and oxidation state. The catalyst sample used in the work by Watling et al. [3] has been taken from a part that had been previously tested on a vehicle.

In addition to the catalyst's oxidation state, the presence of CO and HC in the exhaust also impacts the outlet NO_2/NO_x ratio as some of the NO_2 formed during NO oxidation is readily converted back to NO by CO and HC [5, 10]. Abedi et al. [11] investigated the impact of axial distribution of Pt in a zoned DOC catalyst and compared the performance of zoned catalyst against the uniformly distributed catalyst with same PGM loading. They showed that higher NO, CO and C_3H_6 conversion can be attained by using high loading of Pt in the front zone. Because of higher activity at the inlet zone, most of the CO and C_3H_6 are reacted close to inlet creating not only the exotherm beneficial for the downstream catalyst but also minimizing the inhibition effects of CO and C_3H_6 on NO conversion to NO_2 . Therefore, by carefully zoning the catalyst with different PGM loading and activity, one can achieve desired performance in terms of CO/HC conversion and NO_2/NO_x ratio.

The main objective of this study is to carry out a combined modeling and experimental study to investigate and advance the current understanding on the effect of Pt:Pd ratio on the performance of DOC

catalysts. The catalysts used in this study are targeted towards heavy duty application (lightly loaded catalysts). A study on high PGM loading catalysts for light duty applications is presented in a separate manuscript [1].

In the first part of the study, transient light-off tests were conducted over various Pt-Pd DOCs with different fraction of individual metals to compare the CO and HC (propylene, toluene and *n*-decane) light-off characteristics. Likewise, steady-state experiments were conducted to assess the impact of Pt:Pd ratio on NO oxidation activity in the presence and absence of CO and HC. Finally, transient ramp-up and ramp-down experiments were performed to investigate the effect of catalyst pretreatment (oxidative and reductive) on different Pt-Pd DOCs.

In the second part of the study, a comprehensive model capable of predicting the main characteristics of the Pt-Pd DOC performance as a function of Pt:Pd ratio and PGM loading was developed. The model calibrated using the reactor data was validated against engine data. The model was then utilized to perform a case study wherein the performance of catalysts with different Pt:Pd ratio is compared. The modeling results provide useful insights on designing a suitable catalyst for a given application.

EXPERIMENTAL

Catalyst Samples

The reactor testing was carried out using samples of HDD Pt-Pd DOCs having different Pt:Pd ratios and total PGM loading of 11 and 45 g/ft^3 . The effect of Pt:Pd ratio was found to be very similar on both the catalyst sets (PGM = 11 g/ft^3 and 45 g/ft^3). Hence, for the sake of brevity, only the results obtained for the 11 g/ft^3 samples are reported here. The actual ratios (ratio by weight and % mol of Pt content) of the samples are provided in Table 1. Bench reactor and engine data for model development and validation were collected over samples that were hydrothermally aged at 600°C for 100 h. Experiments were also carried out over degreened samples (600°C for 2 h) to compare the steady-state NO oxidation performance against the aged samples. These samples were also used to study the NO oxidation “inverse hysteresis” effect. Unless otherwise stated, the results presented in this manuscript are for the aged samples. The catalyst dimension used for reactor experiments was $1'' \times 3''$ (Diameter $\times$ Length) with cell density/wall thickness of 400/4 (cordierite substrate). A zoned HDD DOC catalyst (PGM $\approx 30\text{ g/ft}^3$) was used for engine testing.

Table 1. Samples used in this study. The Pt and Pd content is expressed as Pt:Pd ratio by weight and as molar percentage of Pt.

Pt:Pd Ratio by Weight	Pt Content / mol%
1:3	15
1:1	35
3:1	62
10:1	85

Reactor Testing

Laboratory reactor data were collected using a stainless steel reactor. Most data were collected at a space velocity of $60\,000\text{ h}^{-1}$. All tests were run with 5% CO_2 and 7% H_2O in the gas feed, since these gases are always present in vehicle exhaust. C_3H_6 , C_7H_8 , $n\text{-C}_{10}\text{H}_{22}$ and H_2O , were introduced using thermostated saturators. Heated lines were used to deliver gas from the reactor exit to the analyzers. O_2 was analyzed using a magneto pneumatic analyzer, THC using a flame ionization detector; other components were analyzed using an FTIR bench.

Transient and steady-state experiments were carried out in the bench reactor. Transient light-off tests were performed to characterize the CO and HC oxidation activity. During these experiments, the inlet temperature was ramped from 120°C to 450°C with the ramp rate of $10^\circ\text{C}/\text{min}$. Steady-state experiments were conducted to measure the NO oxidation activities in the presence and absence of CO and/or hydrocarbons. In these experiments, the temperature was first raised to 500°C and ramped down to desired temperature to record the steady-state conversion. The reactor was held at each temperature for approximately 30 min to ensure (pseudo) steady-state conversion was reached. In addition to steady-state NO oxidation experiments, dedicated transient ramp-up and ramp-down experiments were also carried out over degreened samples (600°C for 2 h with 10% H_2O) to investigate the “inverse” hysteresis phenomena observed during NO oxidation. Prior to these experiments, oxidative (O_2) and reductive (CO) pre-treatments were carried out to understand the effects of pre-conditioning on the catalyst performance. The pre-treatments were carried out at 500°C for 1 h.

Engine Testing

Steady-state engine testing was done in a test cell using standard procedures and equipment. Ultra low sulfur diesel fuel was used during all tests. The test cell was equipped with a 600 hp Eddy current dynamometer and an interim T4 >130kW engine. Exhaust emissions were measured using a Horiba MEXA 7100D Series bench and a MKS 2030-HS Series FTIR. In addition, a heated flame ionization detector was utilized to measure total HC. These analyzers could sample either at the engine out or DOC out positions. The test cell was equipped with a commercial airless in-exhaust hydrocarbon injection (HCI) system. The injection module was installed at a 45° angle on a section of straight pipe downstream of the turbocharger. Approximately six feet of exhaust pipe with one 90 degree bend was extended between the fuel injector and the DOC inlet. The DOC and exhaust pipe were insulated using ceramic fiber blanket to reduce heat loss and to minimize test variability. The DOCs were evaluated for NO oxidation on an 8-point steady-state test to achieve inlet temperatures from $225\text{--}300^\circ\text{C}$ and gas hourly space velocities (GHSV) from $40,000$ to $65,000\text{ h}^{-1}$ (based on 7.5L DOC). In addition, a 6-point steady-state test for HC injection was carried out to generate an exotherm through the DOC at six different inlet temperatures and GHSV. HC slip was measured at DOC outlet.

MODELING

A one-dimensional model of the catalytic monolith was used in this study. A detailed description of the model is provided in the paper by Ahmadinejad et al. [12]. The governing equation includes species and energy balances in the fluid and solid phase. The transverse gradients in the fluid phase are accounted by the external heat and mass transfer terms. The physical properties of the catalyst such as channel dimensions, thermal conductivity, heat capacity, etc. were obtained from substrate manufacturer's datasheets with allowance made for the washcoat.

The DOC kinetic model is based on the work of Watling et al. [3]. The original model was developed using an extensive set of experimental data (~ 75 data sets) and includes all the important reactions occurring over a DOC, viz., CO/NO/HC/ H_2 oxidation, NO_2 reduction by CO and HC, steam reforming and HC SCR. For more details on the model, we refer readers to reference [3]. For completeness, the reaction scheme is provided in Table 2.

The original kinetic parameters were modified to predict the data collected over the aged samples used in this study. As stated earlier, we only present the results for samples with PGM loading of $11\text{ g}/\text{ft}^3$. However, the model was developed using the data collected over both the sample sets (PGM loading= $11\text{ g}/\text{ft}^3$ and $45\text{ g}/\text{ft}^3$). Simple correlations were then developed to account for the change in activity for different reactions when the Pt:Pd ratio is varied. For most of the reactions, it was found that a simple change in the pre-exponential factors and inhibition parameters was enough to obtain a good fit of the data. One may expect that the activation energies of the reactions would also change when the Pt:Pd ratio is changed. However, in this study, we have not varied the activation energies simply to minimize the number of parameters to be tuned. As we will show later, except for certain reaction system, the assumption that the apparent activation energy remains largely unaffected with the change in Pt:Pd ratio gives good model predictions.

Table 2. Reactions included in the DOC model

1.	CO oxidation: $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$
2.	Oxidation of HC or oxygenate: $\text{C}_x\text{H}_y\text{O}_z + (x+y/4-z/2)\text{O}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O}$
3.	Steam reforming: $\text{C}_x\text{H}_y + (x-\text{N}_{\text{WGS}})\text{H}_2\text{O} + \text{N}_{\text{WGS}}\text{CO}_2 \rightarrow (x+\text{N}_{\text{WGS}})\text{CO} + (x+y/2-\text{N}_{\text{WGS}})\text{H}_2$
4.	HC SCR: $(1-\text{S}_{\text{N}_2\text{O}}/2)\text{C}_3\text{H}_6 + 9\text{NO} \rightarrow 3(1-\text{S}_{\text{N}_2\text{O}}/2)\text{CO}_2 + 3(1-\text{S}_{\text{N}_2\text{O}}/2)\text{H}_2\text{O} + 4\frac{1}{2}\text{S}_{\text{N}_2\text{O}}\text{N}_2\text{O} + 4\frac{1}{2}(1-\text{S}_{\text{N}_2\text{O}})\text{N}_2$
5.	H_2 oxidation: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$
6.	NO oxidation: $\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2$
7.	NO_2 reduction by CO: $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$
8.	NO_2 reduction by HC: $\text{C}_x\text{H}_y + (2x+y/2)\text{NO}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O} + (2x+y/2)\text{NO}$

RESULTS AND DISCUSSION

Reactor Data and Kinetic Model Development

HC Oxidation

The actual engine exhaust contains complex mixture of different hydrocarbons. For simplicity, it is acceptable to group these hydrocarbons into three different types: alkenes, alkanes and aromatics. In this study, we have used propylene, *n*-decane and toluene to represent alkene, alkane and aromatic HCs, respectively. The dependence of HC oxidation kinetics on Pt:Pd ratio is discussed below.

Alkene (Propylene) Oxidation

The light-off curves for propylene oxidation over the 11 g/ft³ samples are shown in Figure 1. The light-off temperature (T_{50}), defined as the temperature corresponding to 50% conversion, first decreases with the increase in Pt:Pd ratio and then plateaus at higher Pt content (3:1/11 and 10:1/11 catalysts). The observed behavior is consistent with the results reported by other investigators [1, 5]. Kim et al. [5] observed that the addition of small fraction of Pd (~12% wt Pd, 7:1) significantly improved the oxidation activity of propylene. However, further increase in Pd up to 70% wt only resulted in minor improvement in performance. They also reported that all bimetallic catalysts were better than monometallic Pt or Pd only catalysts, i.e., the activity first increased with the addition of Pd and then decreased with further increase beyond 80% wt Pd. Similar results were also observed in the study of Etheridge et al., [1] where they observed maximum activity for the 10:1 catalyst and the activity lowered with increasing or decreasing the Pt fraction.

The comparison of model predictions against the data is also shown in Figure 1 (symbols=data, lines=model). It was found that a minor tuning in the pre-exponential factor of the propylene oxidation reaction was enough to accurately predict the light-off characteristics of all the four samples as shown in Figure 1. Based on the tuned pre-exponential factors, a simple correlation as a function of Pt:Pd ratio was developed.

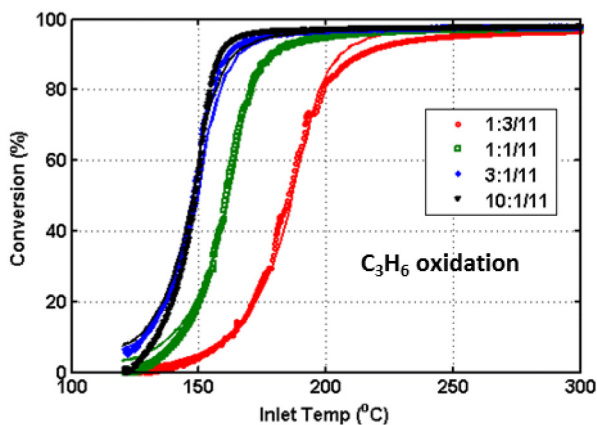


Figure 1. C_3H_6 oxidation: Comparison of measured (symbols) and simulated (lines) C_3H_6 conversion as a function of inlet temperature. Feed: 1000 ppm C_3H_6 (as C1), 12% O_2 , 7% H_2O , 5% CO_2 and balance N_2 . GHSV=60 k/h.

Alkane (*n*-Decane) oxidation

The light-off characteristics of *n*-decane oxidation over the DOC samples are shown in Figure 2. The plot shows that the oxidation activity of *n*-decane increases monotonically with an increase in Pt:Pd ratio. Again, this trend is in line with that reported in the literature [1, 5, 6]. Unlike propylene, the oxidation activity of decane oxidation is directly related to the Pt content. This shows that for modeling Pt:Pd ratios for hydrocarbon oxidation, at least two different correlations have to be used to represent the HC oxidation characteristics.

Figure 2 also compares the data against the model predictions. Similar to the propylene oxidation kinetics, only pre-exponential factors had to be tuned to get a good model fit. This clearly suggests that the apparent activation energy for *n*-decane oxidation reaction was largely unaffected when the Pt:Pd ratio is varied.

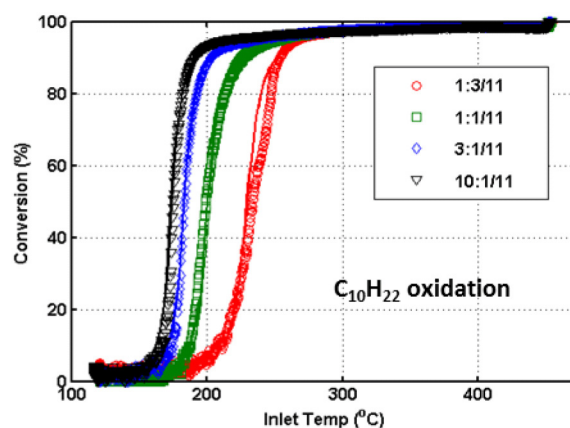


Figure 2. $n-C_{10}H_{22}$ oxidation: Comparison of measured (symbols) and simulated (lines) $C_{10}H_{22}$ conversion as a function of inlet temperature. Feed: 10000 ppm $n-C_{10}H_{22}$ (as C1), 12% O_2 , 7% H_2O , 5% CO_2 and balance N_2 . GHSV=60 k/h.

Aromatic (Toluene) Oxidation

The light-off curves for toluene oxidation over the 11 g/ft³ DOC samples with different Pt:Pd ratio are shown in Figure 3. Similar to propylene oxidation, the oxidation activity of toluene first increases with an increase in Pt fraction and remains almost same with further increase in Pt:Pd ratio. The model predictions for these data sets are also shown in Figure 3. As was done for the decane and propylene oxidation kinetics, only the pre-exponential factor was adjusted. Unlike previous cases (propylene and decane oxidation), there seems to be a change in activation energy especially for the 1:1/11 catalyst whose light-off characteristic (slope of the curve) is distinctly different from the other catalysts. Since we have not tuned the activation energy, the predictions for 1:1/11 catalyst is not as good. As mentioned earlier, we try to minimize the number of tunable parameters and therefore did not attempt to change any of the activation energies as a function of Pt:Pd ratio. Further investigation is needed to explain this behavior.