

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

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ABSTRACT

This paper presents a two-part study on the effect of Pt:Pd ratio (at a constant total Pt+Pd loading of 120 g ft^{-3}) on the catalytic performance of a Diesel Oxidation Catalyst (DOC) intended for light-duty applications, covering ratios across the full range from 100% Pd to 100% Pt. (Work on a heavy-duty DOC is presented in SAE 2015-01-1052).

The first part of this paper presents a reactor study on the effect of Pt:Pd ratio on the catalytic activity of key reactions occurring individually over the DOC, including the oxidation of CO , C_3H_6 , $n\text{-C}_{10}\text{H}_{22}$, CH_4 and NO . For some reactions, activity increases continuously with Pt content (oxidation of $n\text{-C}_{10}\text{H}_{22}$ and NO); in contrast the activity for CH_4 oxidation increases with decreasing Pt content (increasing Pd content), while CO and C_3H_6 oxidation exhibit more complicated dependencies.

The second part presents the development of a one-dimensional model capable of predicting the effect of Pt:Pd ratio on DOC performance. The model was based on a previous DOC model with selected parameters being varied to account for the change in Pt:Pd ratio. The variation in each kinetic parameter with ratio was described by a function to facilitate interpolation to any Pt:Pd ratio. For pragmatic reasons (the complexity of Pt-Pd catalysts), the model was developed directly from NEDC test data with kinetic parameters being optimised to achieve best fit to measured data for each ratio. The model gave a good prediction of post-catalyst CO , THC and NO_2 emissions over the NEDC across the full range of Pt:Pd ratios.

CITATION: Etheridge, J., Watling, T., Izzard, A., and Paterson, M., "The Effect of Pt:Pd Ratio on Light-Duty Diesel Oxidation Catalyst Performance: An Experimental and Modelling Study," *SAE Int. J. Engines* 8(3):2015, doi:10.4271/2015-01-1053.

1. INTRODUCTION

The use of Platinum Group Metal (PGM) based oxidation catalysts to remove unburnt hydrocarbons (HCs) from the exhaust of vehicles was first suggested by Frenkel in 1909 [1,2]. Since then considerable progress has been made in the development of catalytic aftertreatment. The modern Diesel Oxidation Catalyst (DOC) serves not only to remove CO and unburnt HCs from the exhaust of diesel engines, but also to generate exotherms for active regeneration and for producing NO_2 used by downstream components [3,4,5,6,7]. NO_2 produced by the DOC may be used for oxidising soot trapped on a Diesel Particulate Filter (DPF) [6,8,9,10] or may influence the activity of a downstream NH_3 Selective Catalytic Reduction (SCR) catalyst [6,11] or Lean NO_x Trap (LNT) [6,12]. An extensive review of the research on DOCs has been written by Russell and Epling [6].

The original DOCs were Pt based [5,7], but modern DOCs are predominantly bimetallic Pt-Pd based catalysts [6,7]. Pt-Pd DOCs

have the advantage over Pt-only DOCs of reduced cost [6,7,13] and improved resistance to thermal aging (sintering) [5,6,13,14,15,16,17,18]. Figure 1 shows how the PGM cost of a DOC falls as the proportion of Pt replaced by Pd is increased. While Pd is more susceptible to sulphur poisoning than Pt [6,20,21,22,23], the introduction of Ultra-Low Sulphur Diesel (ULSD) means that this is no longer a significant problem [3,5,7,13]. Pt-Pd DOCs work well in systems with a DPF using active regeneration; the elevated temperature encountered during DPF regeneration facilitates removal of accumulated sulphur from the DOC and makes the improved resistance to sintering of Pt-Pd DOCs advantageous / necessary [5,7,13]. For some reactions occurring over DOCs bimetallic Pt-Pd catalysts are reported to be more active than either Pt or Pd [17,18,24,25], but for other reactions pure Pt or pure Pd may be the most active catalyst [17,24,25]. It is thus important to understand the effect of Pt:Pd ratio on DOC performance.

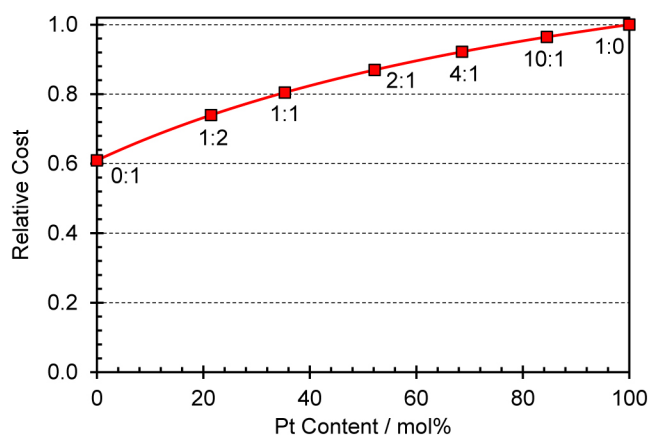


Figure 1. The relative cost of the PGM in a Pt-Pd DOC (at constant total PGM loading) as a function of the composition. Calculated from the metal prices on 12th September 2014 (Pt: \$1370 /troy oz, Pd: \$835 /troy oz [19]). The compositions of the samples used in this study are also marked (points), together with their Pt:Pd ratio by mass.

This paper presents a two-part study on the effect of Pt:Pd ratio on the performance of a DOC intended for Light-Duty Diesel (LDD) applications. The first part (section 3) presents a reactor study on the effect of Pt:Pd ratio on the catalytic activity of key reactions occurring in isolation over the DOC, *e.g.* oxidation of CO, HCs and NO. The second part (section 4) presents the development of a one-dimensional computer model capable of predicting the effect of Pt:Pd ratio on DOC performance. This represents an extension of an earlier model developed for a single Pt:Pd ratio (2:1) [26]. For pragmatic reasons (the complexity of Pt-Pd catalysts), this model is developed directly from vehicle / engine data measured over the New European Drive Cycle (NEDC). This study covers the full range of ratios from 100% Pd to 100% Pt at a total PGM loading of 120 g ft⁻³.

While this paper presents a study on an LDD DOC, further work done on a DOC intended for heavy-duty diesel applications is presented in a separate paper [27]; it covers four Pt:Pd ratios (1:3, 1:1, 3:1, 10:1) at a total PGM loading of 11 g ft⁻³.

Other reactor studies on Pt:Pd DOCs include those by Glover et al. [24], who used commercial DOC samples with five Pt:Pd ratios (0:1, 1:3, 1:1, 3:1, 1:0) at a total PGM loading of 40 g ft⁻³; Kim et al. [17], who used commercial DOC samples with six ratios (0:1, 1:5, 1:2, 2:1, 7:1, 1:0) at a total PGM loading of 50 g ft⁻³; Skoglundh et al. [25], who used multiple samples of Pt-Pd/Al₂O₃ from 0:1 to 1:0 at total PGM loadings¹ of 5, 10 and 20 μmol g⁻¹; and Haneda et al. [18], who used five samples (0:1, 1:3, 1:1, 3:1, 1:0) of 1 wt% Pt-Pd/Al₂O₃. Unlike those studies, this study is for a much higher PGM loading (120 g ft⁻³), typical of an LDD application. This study also arguably covers a wider range of reactions than the previous studies. There are also other studies looking at the impact of Pt:Pd ratio on DOC performance over engine or vehicle tests [13,14,28,29]. However, unlike this study, none of them covers the full range of ratios from all Pt to all Pd.

A note on nomenclature: The composition of Pt-Pd DOCs is typically referred to by the ratio of Pt:Pd by mass. In this work we will also use the Pt content, defined as the molar percentage of the total PGM which is Pt, *i.e.*

$$\text{Pt Content} = \frac{\text{moles Pt}}{\text{moles Pt} + \text{moles Pd}} \times 100\% \quad (1)$$

This has the advantage of being a more obvious and continuous scale for comparing compositions. Furthermore, as it is based on the number of atoms rather than mass, it better reflects the relative numbers of potentially active sites.

2. EXPERIMENTAL

2.1. Samples

Reactor testing and engine / vehicle testing was carried out using samples of a commercial LDD Pt-Pd DOC with a total PGM loading of 120 g ft⁻³. The catalyst consists of a single layer of washcoat with uniform PGM and washcoat loading and contains zeolite as a HC storage component. The same washcoat was used for all samples. These samples (seven in total) had different Pt:Pd ratios ranging from 100% Pd to 100% Pt. The actual ratios used are given in Table 1. This table expresses the composition both as Pt:Pd ratio by mass and as molar percentage of Pt. In terms of molar Pt content (Eq. 1), these samples are reasonably evenly spread between 100% Pd and 100% Pt (Fig. 1). These catalysts were hydrothermally aged for 10 h at 780°C. This ageing is correlated to the thermal exposure typically experienced inside the catalyst over 160 000 km of use on an LDD application where elevated temperatures are periodically encountered during DPF regeneration. The catalysts were coated on 4.66 (diameter) × 3.60 in (118.4×91.4 mm), 400/4.3 (620 000 cells/m², 0.11 mm wall thickness), cordierite substrates. These catalysts were smaller than would normally be fitted on the engines used to collect NEDC data to ensure near constant CO and HC slip throughout the NEDC; modelling this data is a better test for the model than data for a larger part that would show zero slip through much of the test.

Table 1. Samples used in this study. The Pt and Pd content is expressed as Pt:Pd ratio by mass and as molar percentage of Pt (Eq. 1). All samples had a total PGM loading of 120 g ft⁻³.

Pt:Pd Ratio by Mass	Pt Content / mol%
0:1	0
1:2	21
1:1	35
2:1	52
4:1	69
10:1	85
1:0	100

1. Estimated to be equivalent to 16, 33 and 66 g ft⁻³ for 1:0 Pt:Pd and 9, 18 and 36 g ft⁻³ for 0:1 Pt:Pd, assuming a 400 cpsi substrate was used and PGM loadings were quoted per unit mass of washcoat.

2.2. Reactor Testing

Laboratory reactor data was collected using a stainless steel reactor. To minimise the influence of heat and mass transfer on the measured conversions, tests were performed using a packed bed obtained by grinding and sieving cores taken from a monolith sample to give tiny catalyst pellets of well-defined size (250 - 355 μm). The monolith samples were vehicle tested before taking samples for reactor testing, so that the catalyst used for reactor testing was in the same state as a catalyst on a vehicle. A fresh catalyst sample was used for each test (0.8 g). The flows of reactant gases and diluent (N_2) were controlled by mass flow controllers. The total gas flow was 2.0 L min^{-1} . All tests were run with 4.5% CO_2 and 4.5% H_2O in the gas feed, since these gases are always present in vehicle exhaust. The flow of liquid H_2O into the reactor was controlled by a peristaltic pump. Liquid HCs could be introduced into the gas feed using a thermostated saturator. The reactor was heated in an oven. Experiments were run with a temperature ramp of 5°C min^{-1} . Gas from the reactor exit was led to analysers by heated lines. Separate analyser units were used to measure the concentration of CO (infra-red), CO_2 (infra-red), NO and NO_x (chemiluminescence), total hydrocarbon (THC, flame ionisation) and O_2 (electrochemical cell). The reactor inlet concentration was measured by moving the gas sampling point from the reactor exit to the inlet using a valve.

When comparing the measured light-off curves, it is useful to have an idea of the uncertainty in the data. From comparison of repeated experiments, the error in the position of the light-off curves is estimated to be $\pm 5^\circ\text{C}$.

2.3. Vehicle / Engine Testing

Vehicle / engine data from two different LDD engines was used in this study. Two sets of data were used in order to provide a better test for the model developed. This data will henceforth be denoted as coming from “engine A” or “engine B”.

Data for engine A was obtained on a chassis dynamometer using a 1.5 L, EU4 passenger car, while data for engine B was obtained on an engine bench dynamometer using a 2.4 L, LDD engine with an EU5 calibration. Both engines had a common rail fuel system and EGR. European ULSD was used.

NEDC [30] tests were run according to standard procedures. In each case, a number of repeat tests were done to ensure the data were representative. During the NEDC there was no rich operation, as would be encountered during an LNT regeneration, or unusually high HC levels for exotherm generation. Emissions were measured simultaneously before and after the DOC. With both engines NO_x and NO emissions at the DOC inlet were measured using separate chemiluminescence analysers; NO_2 was determined by difference. Outlet NO and NO_2 were determined in the same way with engine B. A different method was used for engine A: here total outlet NO_x was measured by another chemiluminescence analyser, while NO and NO_2 were determined by an FTIR bench. The outlet NO and NO_2 concentration values were then calculated from the total tailpipe NO_x (measured by chemiluminescence) and the $\text{NO}/(\text{NO} + \text{NO}_2)$ and $\text{NO}_2/(\text{NO} + \text{NO}_2)$ ratios obtained from the FTIR. Other gas analysis was performed using standard analysers and methods.

The temperature of the exhaust gas before and after the catalyst was measured using 1.5 mm diameter thermocouples placed 25 mm in front or behind of the catalyst with the tips in line with the centre of the catalyst.

When comparing the engine / vehicle data with model predictions, it is useful to have an idea of the uncertainty in the data. From analysis of the variability in repeat tests, the absolute error in the measured percentage conversion over the whole NEDC is estimated to be $\pm 6\%$ for CO and $\pm 3\%$ for THC and NO_2 .

2.4. Simulations

Computer simulations of engine / vehicle tests were carried out using a one-dimensional model for a monolith reactor, which has been described in more detail elsewhere [31,32]. The model treats the gas and solid (monolith) phases separately with heat and mass transfer between the gas and solid being described by correlations. The physical properties of the catalyst (channel dimensions, thermal conductivity, heat capacity, etc.) were based on values given in the substrate manufacturer's datasheet with allowance made for the washcoat. An account of the history of development of one-dimensional models for simulation of automotive emissions control catalysts has been written by Depcik and Assanis [33].

Table 2. Reactions included in the DOC model.

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:	
$\text{C}_x\text{H}_y + (x-\text{N}_{\text{WGS}})\text{H}_2\text{O} + \text{N}_{\text{WGS}}\text{CO}_2 \rightarrow (x+\text{N}_{\text{WGS}})\text{CO} + \dots$ $+ (x+y/2-\text{N}_{\text{WGS}})\text{H}_2$	(4)
HC SCR:	
$(1-\text{S}_{\text{N}_2\text{O}/2})\text{C}_3\text{H}_6 + 9\text{NO} \rightarrow 3(1-\text{S}_{\text{N}_2\text{O}/2})\text{CO}_2 + \dots$ $+ 3(1-\text{S}_{\text{N}_2\text{O}/2})\text{H}_2\text{O} + 4\frac{1}{2}\text{S}_{\text{N}_2\text{O}}\text{N}_2\text{O} + 4\frac{1}{2}(1-\text{S}_{\text{N}_2\text{O}})\text{N}_2$	(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:	
$\text{C}_x\text{H}_y + (2x+y/2)\text{NO}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O} + (2x+y/2)\text{NO}$	(9)
Extra reaction to explain NO_x conversion during vehicle test:	
$\text{NO}_2 \rightarrow \frac{1}{2}\text{N}_2 + \text{O}_2$	(10)



Reaction kinetics were based on our previously published Pt-Pd DOC model [26]. The reaction scheme used here is the same as in that work (Table 2). This reaction scheme is mostly self-explanatory and has previously been discussed in detail [26]. The one reaction that will be commented on here, however, is Eq. 10. This reaction was not observed in reactor tests, but was required in the final model to explain the approx. 5% NO_x conversion observed over vehicle tests [26]. (The HC SCR kinetics developed from reactor data (Eq. 5) predicted negligible NO_x conversion over the NEDC [26] suggesting that the NO_x conversion observed over vehicle tests is due to a different (unknown) mechanism.) The rate of each reaction was described by Langmuir Hinshelwood type rate equations [34,35].

3. Reactor Study

3.1. HC Oxidation

3.1.1. *n*-C₁₀H₂₂ Oxidation

Light-off curves for *n*-C₁₀H₂₂ oxidation over all seven DOC samples are shown in Fig. 2. Activity for *n*-C₁₀H₂₂ oxidation generally decreases in the order:

$$1:0 > 10:1 > 4:1 > 2:1 > 1:1 > 1:2 \gg 0:1$$

i.e. in order of decreasing Pt content

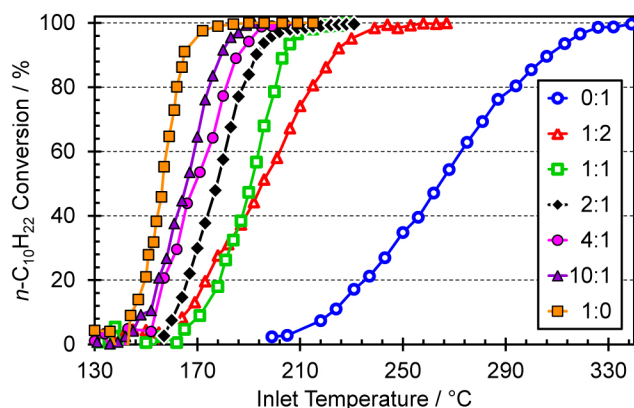


Figure 2. Effect of Pt:Pd ratio on *n*-C₁₀H₂₂ light-off under lean conditions. Feed: 105 ppm *n*-C₁₀H₂₂, 4.5% CO₂, 4.5% H₂O, 16% O₂.

The sole exception to this general trend is the 1:2 Pt:Pd sample, which is more active than the 1:1 below 30% conversion. The light-off curve for the 1:2 sample is shallower than that of the other Pt containing samples indicating that this sample has a lower apparent activation energy for C₁₀H₂₂ oxidation (and potentially even a different reaction mechanism) due to its low Pt content / high Pd content.

The 100% Pd sample (0:1) is significantly less active for C₁₀H₂₂ oxidation than the other (Pt containing) samples; there is a 70°C shift in the temperature for 50% conversion between the 0:1 and the next most active sample (1:2), while the temperatures for 50% conversion for the Pt containing samples are all within a 41°C temperature window. A possible explanation for the different behaviour of the 100% Pd catalyst is that this catalyst is in an oxidic form while the others are in a predominantly metallic form. Generally, under lean

conditions the Pd in a Pd catalyst is all in the form of PdO (except at elevated temperatures) while a Pt catalyst is in a metallic form [16,20,22,36,37]. Clearly this difference in the state of the active surface will result in different catalytic behaviour. With Pt-Pd catalysts, Pd is present as a mixture of PdO and metallic Pd (possibly alloyed to Pt); the metallic nature of the catalyst increases with Pt content and, if PdO is detected, it is often reported to be in a highly dispersed form [15,16,18,36,37,38]. Thus, the different behaviour of the all Pd catalyst (low activity, in this case) compared to the other samples could be because of its oxidic nature. Similarly, the shallower light-off of the 1:2 sample compared to the 1:1 may also be because it is more (but not completely) oxidic in nature.

The decrease in activity for *n*-C₁₀H₂₂ oxidation with decreasing Pt content is consistent with the literature. Pd is known to be less active than Pt for oxidation of alkanes (excluding CH₄ and possibly C₂H₆ and C₃H₈) [20,39,40,41]. Shakya et al. [27] also report *n*-C₁₀H₂₂ oxidation activity to increase with Pt content. Similarly, Kim et al. [17] report the activity for oxidation of higher HCs (albeit a mixture of *n*-C₁₂H₂₆ and *m*-xylene, rather than *n*-C₁₀H₂₂) to increase with Pt content. On the other hand, Hanada et al. [18] report maximum activity for oxidation of a mixture of *n*-C₁₀H₂₂ and 1-methylnaphthalene with 3:1 Pt:Pd. This shows that reported activity trends may be sensitive to the exact catalyst used, catalyst aging, total PGM loading, gas composition used for reactor testing, etc.

When comparing the activity of these catalysts, it is worth remembering that while all have the same total PGM loading by mass, the amount of PGM on an atomic basis increases as the Pt content is decreased as the molecular mass of Pd (106.42 g mol⁻¹) is less than that of Pt (195.08 g mol⁻¹).

3.1.2. CH₄ Oxidation

CH₄ oxidation (Fig. 3) exhibits the opposite trend to *n*-C₁₀H₂₂ oxidation with activity increasing with decreasing Pt content (increasing Pd content). Activity for CH₄ oxidation decreases in the order:

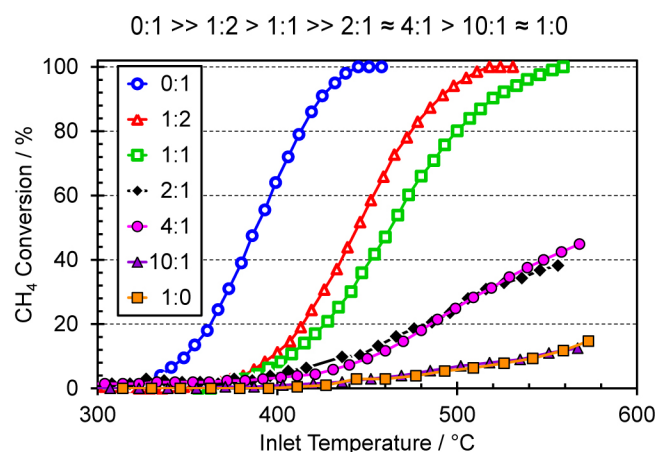


Figure 3. Effect of Pt:Pd ratio on CH₄ light-off under lean conditions. Feed: 200 ppm CH₄, 4.5% CO₂, 4.5% H₂O, 16% O₂.

2. Reports vary as to whether Pt or Pd is more active for C₃H₈ oxidation. Pt [39,40] and Pd [41] are reported to be more active for C₃H₈ oxidation. Presumably which catalyst is more active depends on the exact catalyst and reaction conditions.

The 100% Pd sample (0:1) is significantly more active for CH₄ oxidation than any of the other samples, with 50% conversion being achieved at a temperature about 55°C lower than the next most active sample (1:2).

The observed activity trend is consistent with the literature in that Pd is well known to be more active than Pt for CH₄ oxidation *e.g.* [20,21,22,23,36,38,39,41]. However, reported trends with Pt:Pd ratio are often more complex than the simple trend observed in this work; Pt-Pd catalysts may be more active than monometallic Pd (typically with Pd-rich catalysts) or less active than monometallic Pt (typically with Pt rich catalysts) [36,38]. Comparison of activities can be complicated by the fact that CH₄ oxidation activity over PGM catalysts often varies with time on stream and the rate of this variation depends on the Pt:Pd ratio; activity may increase or decrease with time on stream depending on the Pt:Pd ratio [22,36].

3.1.3. C₃H₆ Oxidation and Steam Reforming

C₃H₆ oxidation (when lean) exhibits yet a different trend (Fig. 4). In this case maximum activity is obtained at an intermediate Pt content (10:1), albeit a high Pt one. Activity for C₃H₆ oxidation under lean conditions generally decreases in order:

$$10:1 > 4:1 \approx 1:0 > 2:1 > 1:1 > 1:2 \gg 0:1$$

Thus, activity falls off monotonically from the most active sample (10:1) with increasing and decreasing Pt content. In actual fact there is not much to differentiate the three most active (and highest Pt content) samples; they all reach 50% conversion within a 9°C window and the conversion curves cross. Thus, below about 70% conversion 4:1 is more active than 1:0, but less active than it at higher conversions. Similarly, the 10:1 becomes less active than the 1:0 above about 95% conversion. This highlights the problem of characterising relative catalyst activity with over simplistic indices (such as temperature required for a particular conversion) or lists of activity order; for an accurate picture one needs to compare the conversion curves in their entirety.

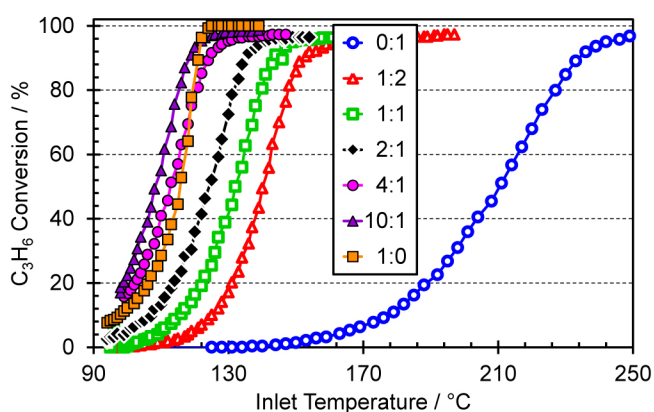


Figure 4. Effect of Pt:Pd ratio on C₃H₆ light-off under lean conditions. Feed: 100 ppm C₃H₆, 4.5% CO₂, 4.5% H₂O, 16% O₂.

The activity order for the remaining ratios (2:1, 1:1, 1:2, 0:1) is more clear cut. For these samples activity decreases with decreasing Pt content. As with *n*-C₁₀H₂₂ oxidation, the 100% Pd sample (0:1) is much less active than the Pt containing samples; the temperature

required for 50% conversion with 0:1 is about 70°C higher than that required with 1:2, while the Pt containing samples all achieve 50% conversion within a 35°C window.

There is no clear consensus in the literature on the effect of Pt:Pd ratio on C₃H₆ oxidation under lean conditions. Kim et al. [17] report maximum activity with 7:1 Pt:Pd, *i.e.* at a high Pt content as in this work, and that Pt is more active than Pd (as here), but unlike here they report monometallic Pt to be less active than all Pt-Pd samples. Shakya et al. [27] also found maximum activity at a high Pt content (10:1 and 3:1 were equally active), but their study did not include a comparison with all Pt or all Pd, so the possibility that all Pt is the most active catalyst cannot be excluded. In contrast, Glover et al. [24] observed no clear trend with Pt:Pd; they observed equal best activity with 1:3 and 3:1 Pt:Pd and (unlike here) they found Pd to be more active than Pt. Skoglundh et al. [25] observed a more complicated trend with monometallic Pt being the most active catalyst (just), activity then fell with decreasing Pt content, before rising again to 2:1 Pt:Pd, which was almost as active as monometallic Pt; activity then decreased again to monometallic Pd, which was the least active catalyst. Skoglundh et al.'s results are at least consistent with this study in that monometallic Pt was found to be more active than monometallic Pd. Note that Skoglundh et al.'s comparison was based on a series of catalysts with a constant amount (number of moles) of PGM rather than a constant mass of PGM.

A possible reason for the lack of consensus on the effect of Pt:Pd ratio on C₃H₆ oxidation is that the activity series changes with the feed composition due to changes in reaction kinetics with Pt:Pd ratio. This is clearly illustrated in work by Khosravi et al. [42], which presents C₃H₆ light-off curves for a series of C₃H₆ concentrations over a Pt and a 4:1 Pt-Pd catalyst. With 230 ppm C₃H₆ both catalysts give 50% conversion at about the same temperature (although the slopes of the light-off curves are different), but for concentrations above about 450 ppm the Pt-Pd catalyst is clearly more active.

The activity order observed here applies only for this aging; with more severe aging, Pt-Pd samples may show a greater advantage over 100% Pt (1:0) as the former are known to be more resistant to aging (sintering) [5,6,13,14,15,16,17,18]. This effect is another potential reason for the variation in the activity series reported in the literature for C₃H₆ oxidation.

Rather intriguingly the activity order for C₃H₆ oxidation under rich conditions (Fig. 5) is completely different to that under lean conditions (Fig. 4), *e.g.* while 100% Pd was least active under lean conditions, it is the most active under rich conditions. Activity under rich conditions is of interest for systems including an LNT which will briefly experience rich conditions during an LNT (deNO_x) regeneration. This figure shows both C₃H₆ oxidation (to approx. 35% conversion) and steam reforming (Eq. 4). Activities for both reactions decrease approximately in the order:

$$0:1 > 1:2 \approx 1:1 > 2:1 > 4:1 \approx 10:1 > 1:0$$

i.e. in order of decreasing Pt content. This activity order is somewhat subjective; while (for both reactions) all Pd (0:1) is clearly the most active sample and all Pt (1:0) is clearly the least active, conversion

curves for the other samples cross each other and are clustered together in a 21°C window (at 20% conversion). The comparison is complicated by the fact that a small variation in the inlet concentrations results in changes in the relative amounts of C_3H_6 consumed by oxidation and steam reforming. Whittington et al. [40] also report Pd to be more active for steam reforming than Pt. Of course for normal (lean) operation of a DOC this trend is unimportant. However, it does raise the possibility that the observed activity series may change with less drastic changes in gas composition, perhaps due to variations in kinetics (concentration dependencies of reaction rates) or changes in the redox state of the catalyst.

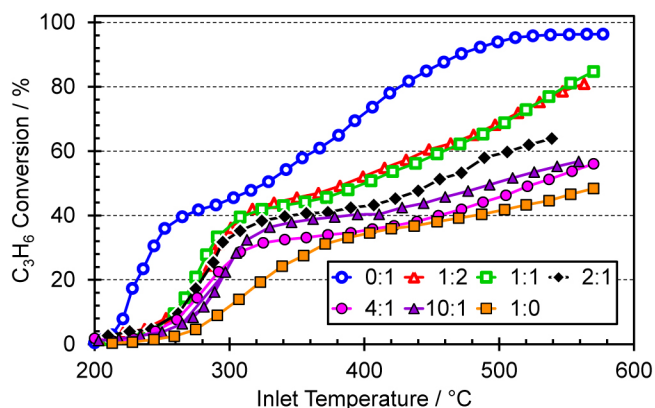


Figure 5. Effect of Pt:Pd ratio on C_3H_6 light-off under rich conditions. Feed: 2000 ppm C_3H_6 , 4.5% CO_2 , 4.5% H_2O , 0.3% O_2 .

3.2. NO Oxidation to NO_2

Activity for NO oxidation (Fig. 6) generally decreases in order:

$$1:0 \approx 10:1 > 4:1 > 2:1 > 1:1 > 1:2 \gg 0:1$$

i.e. activity decreases with decreasing Pt content, with the all Pd sample (0:1) being much less active than the other (Pt containing) samples.

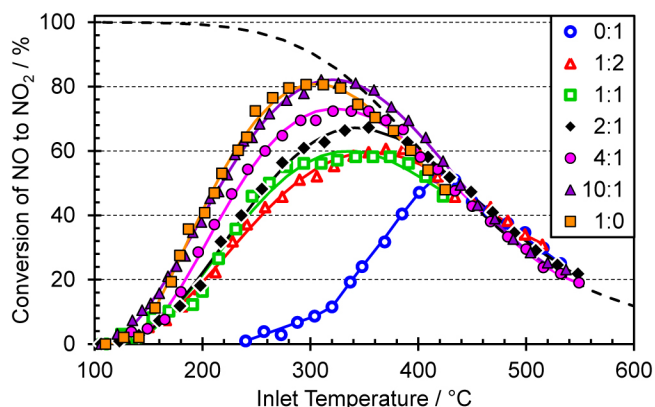


Figure 6. Effect of Pt:Pd ratio on NO oxidation to NO_2 . Feed: 4.5% CO_2 , 4.5% H_2O , 100 ppm NO, 16% O_2 . The lines through the points are intended to guide the eye. The dashed line indicates the conversion at thermodynamic equilibrium.

These results are consistent with the literature: Pt is reported to be more active than Pd for NO oxidation [24,43,44]. Khosravi et al. [42] found monometallic Pt to be much more active than a 4:1 Pt-Pd catalyst for NO oxidation. Glover et al. [24] also observe NO oxidation activity to increase with Pt content for a series of Pt DOC samples from all Pd to all Pt. Shakya et al. [27] observe the same trend (but over a narrower range of Pt:Pd ratios). Rather interestingly, Kim et al. [17] report the same trend for mildly aged samples (2.4 h, 750°C, hydrothermal), but find that 7:1 Pt:Pd is more active than monometallic Pt after severe aging (72 h, 750°C, hydrothermal). This is presumably because the enhanced resistance to sintering due to the Pd [5,6,13,14,15,16,17,18] offsets the lower activity of Pd for NO oxidation. Apart from the 7:1 sample, they found activity for NO oxidation still increased monotonically with Pt content. This example demonstrates how the activity order can be dependent on catalyst aging.

3.3. CO Oxidation

CO conversion curves are shown in Fig. 7. The 100% Pd (0:1) sample exhibits a different trend to the other samples. This sample starts to light off before the other samples, but the light-off curve is shallow (i.e. the apparent activation energy is lower than that of the other samples) so it crosses the curve of the 4:1 sample at about 52% conversion. Thus below 52% conversion, 0:1 is the most active sample, but above this 4:1 is the most active. The reason for the different behaviour of the 0:1 is not known for sure. However, it could be that CO oxidation has a different mechanism / kinetics on this sample, perhaps because it is in an oxidic form (as mentioned in section 3.1.1) or it could be that some (deactivating) change in the state of the catalyst during the experiment (e.g. PdO being reduced to Pd metal by CO) results in a relatively flat light-off curve. This was not investigated further. Note that the high activity of the 0:1 for CO oxidation was not seen in NEDC tests (see section 4); this sample showed the lowest activity for CO oxidation over the NEDC.

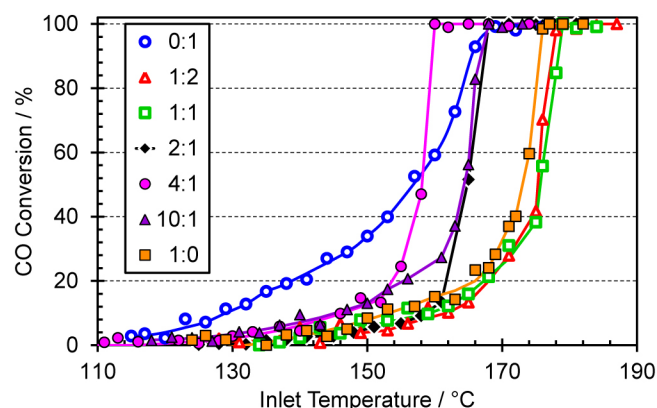


Figure 7. Effect of Pt:Pd ratio on CO light-off under lean conditions. Feed: 2000 ppm CO, 4.5% CO_2 , 4.5% H_2O , 16% O_2 . The lines through the points are intended to guide the eye.

Activity for CO oxidation thus decreases in order:

$$(0:1) > 4:1 > (0:1) > 10:1 \approx 2:1 > 1:0 > 1:1 \approx 1:2$$