A Study of Platinum Group Metals in Three-Way Autocatalysts

Effect of rhodium loading outweighs that of platinum or palladium

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The price differential between platinum and palladium has driven the industry to adopt emissions control catalyst formulations for gasoline engines that contain higher levels of Pd than Pt, and in most cases no Pt. In addition fluctuations in the price of rhodium have led to thrifting of this metal. This study compares the performance of ten different catalyst compositions with varying ratios of Pt, Pd and Rh for a Euro 5 vehicle and under bench test conditions. The results show that a system with low Rh loading can readily be improved by increasing the Rh loading and there is a relatively large effect of doing this by a small amount. Increasing the Pd or Pt loading also improves emissions performance but by a significantly smaller amount than the effect of changing the Rh loading. Conversely it may be possible to decrease the Pt or Pd loading with only a small effect on emissions. Furthermore it was found that Pd outperforms Pt under most conditions, although not significantly. The difference appears greater under more stressful conditions such as high-speed driving or wide perturbation amplitude.

Introduction

Since their introduction in 1974 three-way catalysts (TWCs) have used platinum group metals (pgms) to control emissions of hydrocarbons (HCs), carbon monoxide (CO) and oxides of nitrogen (NOx) in gasoline powered cars (1). A mixture of some or all of Pt, Pd and Rh have always been used, with Rh being especially active for NOx conversion and both Pd and Pt having excellent activity for oxidation reactions of CO and HC species (2). However in the intervening decades a wide range of factors have at various times influenced the usage of these pgms in terms of both type and quantity. These include: fuel quality, especially sulfur content; emissions legislation; vehicle technology including engine calibrations and fuelling systems; exhaust layout, packaging and design; relative prices of the pgms; and catalyst washcoat technology. In recent years Pd/Rh catalysts have been the most common, aided by lower sulfur fuel and improved

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washcoat technology and also attractive due to the >10 year trend of Pd being lower in price than Pt (3). A further recent phenomenon has been the significant efforts focused on thrifting of Rh from TWCs in response to a sharp price spike in 2007 and 2008.

Today the majority of TWCs are Pd/Rh with Pt much less common. It seems reasonable to expect however that there will in future be a similar variety of competing factors which may affect pgm choice just as there has been in the past. For this reason a periodic appraisal of the current status of modern catalysts using the three pgms at a range of typical loadings is of interest. In particular the near 90% fall in the price of Rh since mid-2008 and three-fold increase in the price of Pd since 2009 are reasons why a study may be of interest now.

Catalyst Test Programme

In order to compare the relative activities of TWCs at a range of Pd, Pt and Rh loadings, the following catalysts were prepared. The loadings were chosen without regard to pgm cost, allowing a relevant technical comparison on the basis of pgm mass alone. Details of the compositions are given in **Table I**. Throughout this paper pgm loadings are reported in grams per cubic foot (g ft^{-3}) in the format: T/Pt:Pd:Rh where T is the total pgm loading. All three are included for clarity even though in all cases either the Pt or Pd loading is zero.

All catalysts were made on the same substrate, a 4.16″ × 4.5″ 600/4 ceramic. The catalysts were aged in groups of four at Johnson Matthey in Royston, UK, using a lean spike ageing cycle of 80 hours duration with 950ºC inlet temperature, which is correlated to 160,000 km road ageing. The total pgm loadings were chosen to be towards the lower end of the range of those currently supplied to the market, with a view to being able to compare the relative effects of Pd and Pt at constant Rh, the effect of the absolute loading of each of Pt and Pd and also the effect of Rh loading at constant Pd and Pt. A reference catalyst was included in each set to allow comparison of the ageing runs.

The Pd/Rh catalysts evaluated were a current Johnson Matthey production Euro 5 technology. The Pt/Rh washcoat was modified slightly to better suit Pt but was otherwise unchanged in terms of total washcoat loading, oxygen storage material and total rare earth content to better allow comparison of the

Table I

Platinum Group Metal Loadings on Model Three-Way Catalysts Selected for the Present Study

Set	Catalyst description	Total pgm, g ft^{-3}	Platinum, g ft^{-3}	Palladium, g ft^{-3}	Rhodium, g ft^{-3}
1	Medium Pd + Rh[a]	30	0	25	5
	High Pd + Rh	40	0	35	5
	Low Pd + Rh	20	0	15	5
	High Pt + Rh	40	35	0	5
2	Medium Pd + Rh[a]	30	0	25	5
	High Rh + Pd	32.5	0	25	7.5
	Low Rh + Pd	27	0	25	2
	Low Pt + Rh	20	15	0	5
3	Medium Pd + Rh[a]	30	0	25	5
	Medium Pt + Rh	30	25	0	5
	High Rh + Pt	32.5	25	0	7.5
	Low Rh + Pt	27	25	0	2

[a] *Reference catalyst*

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effect of pgm alone. Furthermore if a hypothetical switch from a Pd/Rh technology to a Pt/Rh one was deemed desirable, taking this approach of changing as little as possible other than the pgm would be the easiest and most likely path and so affords the most relevant comparison.

The catalysts were tested over the Motor Vehicle Emissions Group (MVEG-B) European drive cycle as set out in UN/ECE Regulation number 83 (4) on a 1.2 l vehicle with a (current) Euro 5 calibration and were further tested over light-off and lambda sweep protocols on a 2.0 l Euro 5 bench engine. In the light-off test a stable flow of exhaust gas at 125 kg h^{-1} and λ 0.998 was generated down a bypass exhaust leg, this flow was then diverted by means of a valve to a parallel leg containing a cold catalyst in order to monitor dynamic light-off. A catalyst inlet temperature of 450°C was eventually reached at the end of the test. For the λ sweep test the flow was maintained at the same temperature and flow rate but the engine's air:fuel ratio was adjusted in 15 equal steps from λ 0.99 to λ 1.01 and a perturbation of ±4% λ at 1 Hz was applied. After a stabilisation period of 10 seconds at each condition, gaseous emissions were measured and averaged over a further 5 seconds before moving to the next λ setpoint. These flow conditions are designed to be stressful for the catalyst, representing a similar flow rate to the highest speed part of the European drive cycle but a lower temperature than would ordinarily be seen on a typical close-coupled catalyst at this point of the cycle, with a higher perturbation amplitude.

Vehicle Testing Results

The results of the vehicle tests on the reference catalysts (30/0:25:5) are shown in **Table II**. Each result is the average of at least three tests. These results would be expected to be identical under ideal conditions; however in practice slight differences in ageing severity from run to run combined with test-to-test error has led to some variation in the results observed. In particular the ageing of Set 2 appears to have been slightly milder than the other two and this makes it difficult to compare results across the sets. Nevertheless the data are considered sufficiently close to make useful comparisons between sets, with care. **Table II** also shows the limits specified by Euro 5/6 and it can be seen that in all cases the emissions fall well within those limits.

The results of Set 1 of the test catalysts are shown in **Table III**. This set allows comparison of the effect

Table II

Vehicle Emission Test Results for the Reference Catalysts Compared to Euro 5 and 6 Limits[a]

Set	HC, g km^{-1}	Non-methane HC, g km^{-1}	CO, g km^{-1}	NOx, g km^{-1}
1	0.068	0.052	0.281	0.044
2	0.061	0.047	0.243	0.037
3	0.066	0.051	0.245	0.038
Euro 5/6 limits	0.100	0.068	1.000	0.060

[a] *All Reference catalyst loadings were 30/0:25:5*

Table III

Vehicle Emission Test Results for Catalyst Set 1

Catalyst composition, T/Pt:Pd:Rh	HC, g km^{-1}	Non-methane HC, g km^{-1}	CO, g km^{-1}	NOx, g km^{-1}
30/0:25:5 [a]	0.068	0.052	0.281	0.044
40/0:35:5	0.066	0.051	0.264	0.044
20/0:15:5	0.070	0.054	0.263	0.051
40/35:0:5	0.069	0.055	0.297	0.045

[a] *Reference catalyst*

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of Pd loading at constant Rh and also a comparison of Pt with Pd. In the former case there is a clear but undoubtedly small effect of improved emissions as Pd loading increases. This was, on closer inspection, evident in improved light-off as the Pd loading increased. The emissions of the Pt/Rh catalyst were again clearly, if only slightly, worse for HC and CO. The emissions of all catalysts in this set were actually very similar, suggesting that the most relevant factor is that the Rh loading remains the same in all cases.

Larger differences were seen in Set 2 (**Table IV**). The effect of Rh loading at constant Pd in the first three catalysts was clear, with the NOx emissions of the low Rh catalyst being ~75% higher than those of the high Rh catalyst. This is not unexpected given the well known role of Rh as an excellent catalyst for the removal of NOx. A 27% increase in HC emissions was also seen however, demonstrating that Rh is also important here. Detailed analysis of the second-by-second emissions shows that the NOx benefit could be seen in light-off and also in the extra-urban (high-speed) section of the drive cycle. A consideration of the emissions from this portion of the drive cycle alone showed that the catalyst with 2 g ft^{-3} Rh emitted ~175 mg of NOx, both of the catalysts with 5 g ft^{-3} Rh emitted ~140 mg and the catalyst with 7.5 g ft^{-3} Rh emitted only 90 mg (**Figure 1**).

The HC benefit was mainly seen at light-off, however a small difference was also seen in the high-speed section, again corresponding to the Rh loading for the Pd catalysts. The Pt/Rh catalyst with 5 g ft^{-3} Rh slipped a similar amount of HC in the high-speed section as the Pd/Rh catalyst with 2 g ft^{-3} Rh and more than the Pd/Rh catalyst with 5g ft^{-3} Rh, suggesting a very small inherent deficit in HC conversion for Pt.

Set 3 allows a comparison of Rh loading in a catalyst with constant Pt loading (**Table V**). Once again a large improvement in NOx was seen as Rh increases and

Table IV

Vehicle Emission Test Results for Catalyst Set 2

Catalyst composition, T/Pt:Pd:Rh	HC, g km^{-1}	Non-methane HC, g km^{-1}	CO, g km^{-1}	NOx, g km^{-1}
30/0:25:5 [a]	0.061	0.047	0.243	0.037
32.5/0:25:7.5	0.056	0.042	0.261	0.027
27/0:25:2	0.071	0.056	0.289	0.047
20/15:0:5	0.065	0.050	0.249	0.037

[a] *Reference catalyst*

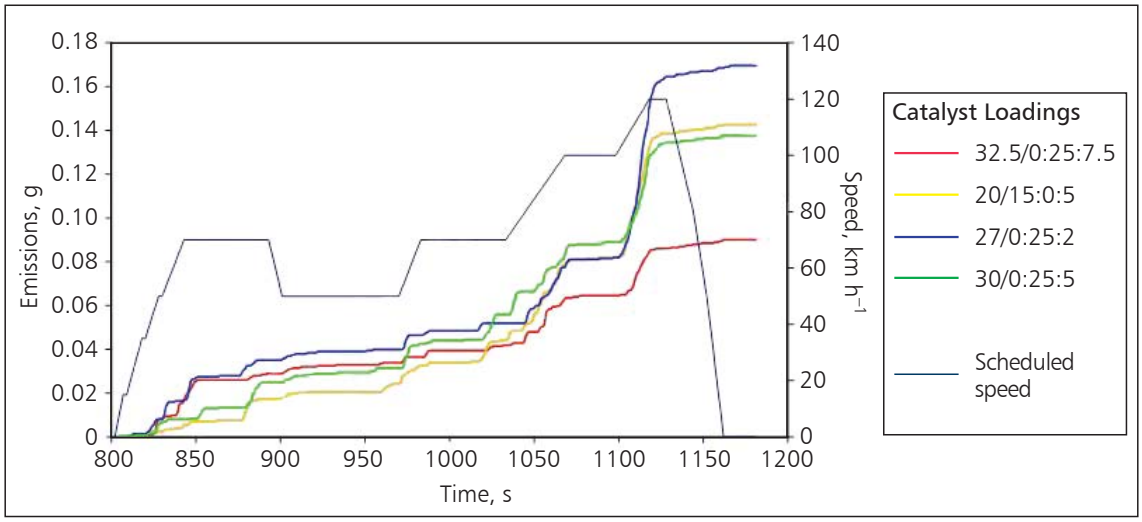

Fig. 1. Normalised EUDC NOx emissions for Set 2 catalysts, showing a clear effect of rhodium loading

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Table V

Vehicle Emission Test Results for Catalyst Set 3

Catalyst composition, T/Pt:Pd:Rh	HC, g km^{-1}	Non-methane HC, g km^{-1}	CO, g km^{-1}	NOx, g km^{-1}
30/0:25:5 [a]	0.066	0.051	0.245	0.038
30/25:0:5	0.065	0.050	0.228	0.035
32.5/25:0:7.5	0.063	0.051	0.242	0.030
27/25:0:2	0.081	0.062	0.304	0.051

[a] *Reference catalyst*

HC also improved, although the benefit on increasing from 5 g ft^{-3} to 7.5 g ft^{-3} was less marked than that seen on going from 2 g ft^{-3} to 5 g ft^{-3}. The emissions from the 27/25:0:2 Pt/Rh catalyst were relatively poor and in fact the weakest of all in this study. The effect of Rh on HC light-off and on NOx light-off and high-speed performance was seen again, with NOx slip in the high-speed section again varying clearly with Rh loading and with similar performance from both the Pt and Pd-containing 30 g ft^{-3} catalysts. The second-by-second HC emissions are shown in **Figure 2**.

Engine Bench Testing Results

Analysis of the second-by-second data shows that the majority of differences occur at the beginning of the test on the pre-lightoff period where there are some variations in engine-out emissions. For this reason analysis was done on emissions post-lightoff or in the Extra-Urban Driving Cycle (EUDC) (4) section of the drive cycle where these cold start effects are not seen.

Here light-off results are reported by reference to the temperature at which 50% conversion efficiency is reached, known as T_{50}, and so a lower figure reflects a more active catalyst. The CO/NOx crossover is a standard measure of catalyst efficiency and is derived from analysis of the separate CO and NOx efficiency curves as a function of λ. A higher reported efficiency naturally reflects a more active catalyst. Typically the crossover occurs just rich of λ 1.00, the stoichiometric air:fuel ratio.

The clear and expected trend of better light-off with more Pd can be seen in the engine bench test results for Set 1 (**Table VI**) and this is also reflected in higher conversion efficiencies. The Pt/Rh catalyst was slightly inferior in light-off and noticeably worse in conversion efficiency under these stressful test conditions.

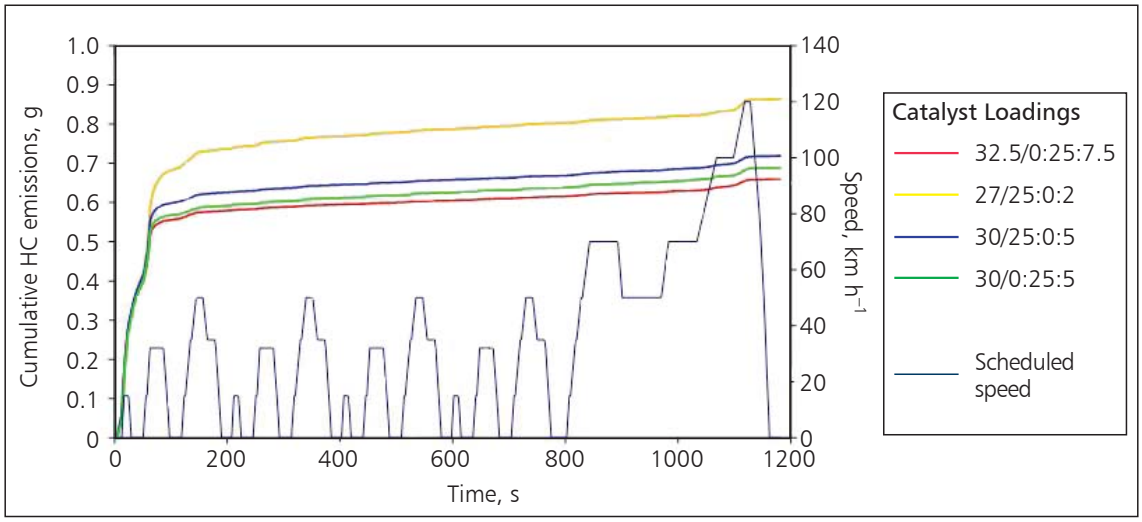

Fig. 2. Second-by-second total hydrocarbon emissions for Set 3 catalysts

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Table VI

Engine Bench Test Results for Catalyst Set 1

Catalyst composition, T/Pt:Pd:Rh	HC T_{50}, °C	NOx T_{50}, °C	Efficiency at CO/NOx crossover, %
30/0:25:5 [a]	370	374	96.6
40/0:35:5	365	371	97.4
20/0:15:5	377	375	94.7
40/35:0:5	379	376	95.6

[a] *Reference catalyst*

The results for Set 2 are shown in **Table VII**. In this case the reference catalyst gave the best HC emissions and the conversion efficiencies were higher overall than for the other two sets, indicative of the milder ageing experienced by this set. Nevertheless the effect of Rh on light-off was once again seen here and the trend in hot efficiencies was the same as that observed for the vehicle tests. The CO/NOx crossover plot is shown in **Figure 3**.

The engine bench results for Set 3 (**Table VIII**), which were all Pt catalysts except for the reference catalyst, show the same broad trends as the vehicle tests. Again the 5 g ft^{-3} Rh and 7.5 g ft^{-3} Rh catalysts were closer in performance than the 2 g ft^{-3} Rh and 5 g ft^{-3} Rh catalysts, suggesting that 2 g ft^{-3} is too low a Rh loading for the Pt/Rh catalyst used in this study and that increasing the loading above 2 g ft^{-3} Rh is highly effective at improving the catalyst performance. There

Table VII

Engine Bench Test Results for Catalyst Set 2

Catalyst composition, T/Pt:Pd:Rh	HC T_{50}, °C	NOx T_{50}, °C	Efficiency at CO/NOx crossover, %
30/0:25:5 [a]	370	375	98.4
32.5/0:25:7.5	354	356	99.0
27/0:25:2	376	379	97.4
20/15:0:5	375	375	97.8

[a] *Reference catalyst*

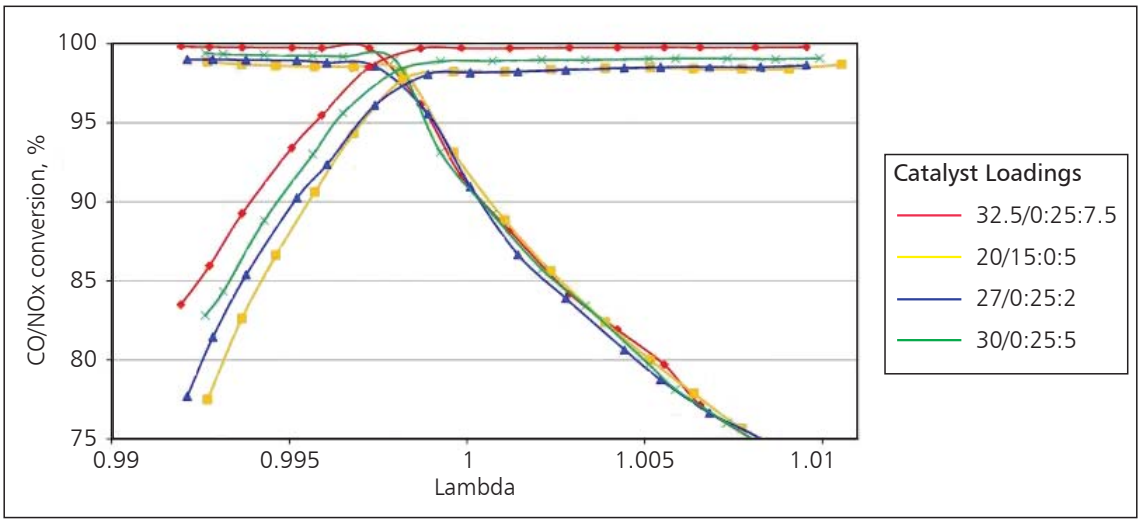

Fig. 3. CO/NOx crossover for Set 2 catalysts

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Table VIII

Engine Bench Test Results for Catalyst Set 3

Catalyst composition, T/Pt:Pd:Rh	HC T_{50}, °C	NOx T_{50}, °C	Efficiency at CO/NOx crossover, %
30/0:25:5 [a]	360	357	98.9
30/25:0:5	380	381	97.4
32.5/25:0:7.5	362	360	99.4
27/25:0:2	383	386	91.7

[a] *Reference catalyst*

is further evidence from the hot conversion efficiency that a Pt/Rh catalyst does not perform as well as a Pd/Rh catalyst under these conditions.

The Effects of Different PGM Loadings

The milder ageing experienced by Set 2 compared to the other two sets makes it difficult to compare the effect of Pt loading when the Rh loading was kept constant at 5 g ft^{-3}, because the tests were carried out across different sets. This may explain why the expected trend towards lower emissions with higher Pt loading cannot clearly be seen. Further tests would be required to confirm this.

Direct comparisons of Pd and Pt are possible both within and between sets. In the vehicle emissions tests the difference was small or even non-existent. However on the engine bench the clear trend was that, when comparing equally loaded Pd/Rh *vs.* Pt/Rh catalysts, the Pd/Rh catalysts performed better by a noticeable margin. The λ sweep test in particular was intended to be stressful for the catalyst, allowing small differences to be exaggerated.

When Pd and Pt are compared, it should be borne in mind that the Pd/Rh catalysts tested were a commercially produced technology which has been optimised for Pd/Rh during development. For the reasons outlined earlier Pt/Rh washcoat development has received less attention and as such the Pt/Rh catalysts tested here should not be considered as fully optimised but as possible readily implemented alternatives to current technology.

Across all sets the effect of a change in the Rh loading was undoubtedly, mass for mass, significantly greater than that of a change in either the Pt or Pd loading. The reduction in emissions which could be achieved by adding a given mass of Rh was greater than that which could be achieved by adding the same mass of either Pd or Pt. Conversely the removal of an equivalent amount would have the largest detrimental effect. Rh has a clear beneficial effect on light-off for all pollutants both on the specific vehicle chosen for this study and on the engine bench. Rh also helped NOx emissions in the high-speed section of the vehicle test and conversion efficiency on the engine bench.

Finally, it must be noted that each of the ten different pgm compositions tested here for a Euro 5 vehicle has been proven to result in emissions below the Euro 5 (and Euro 6) limits (**Table II**). This implied flexibility immediately raises the question of which of these is 'best', or indeed if another system could be designed based on this information which might fit that description. Typically of course this decision will be made on a balance of technical and commercial factors and this study has only begun address the technical aspects of a possible system design.

Conclusions

This study has found, as expected, that increasing either the Pt or Pd loading results in lower emissions and better catalyst performance. The highest and lowest Pd and Pt loadings considered were more than a factor of two different and yet the effect on performance was in the main rather small over the majority of the legislative European drive cycle. The lower amounts of Pd and Pt used were sufficient, at least in this application, and it may be possible to lower them further. There is a small but noticeable deficit in performance when comparing Pt with Pd technology.

A slightly wider relative spread of Rh loadings was investigated and here the effect on emissions and performance was significantly larger. In mass terms the changes investigated were much smaller than for Pt or Pd, yet the effect of increasing Rh loading from the lowest levels considered was much greater. This was primarily seen in NOx emissions but a clear effect on HC emissions was also observed. Rh has been shown therefore to be of significant benefit to both light-off and catalyst performance. Rh thrifting in

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recent years has been in some cases significant and on occasion has been done in conjunction with an increase in overall pgm (most often Pd) loading; this study raises the question of whether in some cases a partial reversal of both of these changes is worthy of serious consideration.

It is not possible in one study to fully evaluate all the many possible combinations of pgms and in terms of legislated vehicle emissions this study is of course confined to one application only. The conclusions therefore are necessarily limited, but the following general statements can be made:

(a) A system with low Rh loading can readily be improved by increasing this Rh loading and there is a relatively large effect of doing this by a small amount.

(b) Increasing Pd or Pt loading improves emissions performance by a significantly smaller amount than the effect of Rh loading. Conversely decreasing Pt or Pd may have only a small effect on emissions.

(c) Pd outperforms Pt by a small margin under most conditions, although the difference appears greater under more stressful conditions such as high-speed driving or wide perturbation amplitude.

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