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Enhancing the low temperature oxidation performance over a Pt and a Pt-Pd diesel oxidation catalyst

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ABSTRACT

The influence of hydrogen over platinum and combined platinum-palladium diesel oxidation catalysts were investigated on the oxidation kinetics of CO, HC and NO. Although H₂ has been reported to have a positive effect on CO and HC oxidation as well as NO₂ formation over platinum catalysts, there is still uncertainty whether this is due to the temperature rise caused by H₂ oxidation or the result of a change in the reaction kinetics of CO, HC and NO oxidation by the production of intermediate species. The results have showed smaller H₂ concentrations are more effective in improving the catalyst light-off temperature as well as promoting NO oxidation over both platinum and platinum-palladium catalysts. It is suggested that these benefits are a result of not only the exothermic reactions which in turn increase the local catalyst temperature but also H₂ increasing the rate of reactions and the species accessibility to the catalyst active sites thus further CO, HC and NO oxidation can occur at lower catalyst temperatures.

Keywords: Hydrogen, Diesel Oxidation Catalyst, Platinum, Palladium, exhaust emissions

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1. Introduction

Diesel oxidation catalysts (DOC) are used to control CO, gas phase HC and the organic fraction of diesel particulates to form harmless exhaust products. Additional reactions such as the oxidation of NO to NO₂ also occurs with the key interest attributed in facilitating passive diesel particulate filter (DPF) regenerations [1]-[2] as well as in enhancing the performance of some selective catalytic reductions (SCR) catalysts [3]-[4].

Platinum has traditionally been the catalyst of choice for diesel oxidation catalysts. However, with increased availability in low sulphur fuels, palladium has been incorporated for commercial catalysed DPFs as well as DOCs to obtain comparable performance to platinum-based coatings at a lower cost [5].

Earlier studies have demonstrated there to be some synergetic effects in terms of light-off and thermal stability during the interaction of platinum with palladium [6]-[8]. Results from earlier studies have shown platinum is able to prevent palladium oxidation after it has undergone hydrothermal aging within the exhaust (Morlang et al.). Besides, Morlang et al. [6] and Kaneeda et al. [7] reported that the addition of Pd to Pt catalysts prevents the sintering of Pt species. Kim et al. found a non-linear relation between Pt:Pd proportion on HC and CO light-off and stability after aging under simulated engine exhaust conditions. It was concluded that the optimal catalyst proportion (defined as a weight ratio) in terms of light-off and stability after aging ranged from 1:2 to 2:1 (Pt:Pd).

However, there are some issues concerning to the low temperature performance of diesel oxidation catalyst, especially at cold start, where most of the CO and THC are produced. Currently, this has vital importance as it is expected that diesel exhaust temperatures will be lower as a result of downsizing, fuel economy, etc. Therefore, efforts should be made to improve the catalyst performance in this new low temperature operation range of diesel engines. Different approaches could be taken in terms of improving the physical properties of the catalysts, different loadings (both composition and quantity), the study of promoters such as hydrogen or more interestingly the combination of them.

Concerning the use of promoters added upstream the catalyst, it has been already reported that hydrogen (H_2) has a positive effect in CO, in hydrocarbons oxidation and in NO_2 formation over different diesel oxidation catalysts [9]. Some researchers [10] attributed the beneficial effect of hydrogen on CO oxidation to the exotherm from hydrogen combustion increasing the local catalyst temperature. However, the results of Salomons et al. [11] suggested that the exotherm from hydrogen cannot account for the reduction in CO light-off temperature over the DOC. This study showed that CO oxidation started earlier than hydrogen oxidation within this specific catalyst. Results from other investigations [12]-[13] suggested that hydrogen could increase the rate of CO desorption from the active sites of the catalyst increasing the active surface sites within the catalyst to oxidise other species. A more recent study showed that the presence of hydrogen increased the formation of some hydrogen-containing oxidising species (e.g. OH radical) which increased the rate of CO oxidation [14]. Although there have been numerous reports in literature of this ‘Hydrogen effect’, no general conclusion has been agreed to whether this is due to the temperature rise caused by H_2 oxidation or if it is really influencing the reaction kinetics.

This study aims to show the potential synergetic effects of the interaction between different catalyst loading (Pt and Pd forming a bimetallic catalyst) and the addition of different hydrogen concentrations under real exhaust engine conditions.

2. Experimental

A single cylinder experimental diesel engine has been used to generate the exhaust emission pollutants (see Figure 1 for the experimental setup). The main engine specifications are given in Table 1. An electric dynamometer with motor and a load cell was used to load the engine. Other standard engine test rig instrumentation used to monitor intake air, exhaust gas recirculation, temperatures (oil, air, inlet manifold and exhaust) and pressures were included in the test rig. A MultiGas 2030, FTIR spectrometry based analyser was also used for the measurement of gaseous emissions such as CO, HC, NO_2 and N_2O .

Two mini DOCs, one loaded with platinum and the other with platinum-palladium at a 1:1 weight ratio provided by Johnson Matthey Plc., were positioned inside a mini-reactor specifically designed to study the effects of catalyst performance under actual diesel exhaust gas (see Table 2 for exhaust gas emissions). The monolith has a cell density of 400cps and 3mil wall thickness. The loading of the catalyst was chosen to be within the optimal platinum:palladium weight proportions previously mentioned [8]. The total catalyst loading in terms of mass is maintained constant for both catalysts (120 g/ft^3) with alumina washcoat (2.6 g/in^3 loading) with a surface area of approximately $100 \text{ m}^2/\text{g}$ coated on a cordierite honeycomb monolith of 1" x 3.6" dimensions. The catalyst had been hydrothermally aged at 780°C during 10h. The reactor was placed in a tubular furnace with the temperature successively increased from 80°C to 400°C in intervals of 10°C with a heating temperature ramp of $2^\circ\text{C}/\text{min}$ under a gas hourly space velocity of 35000 h^{-1} . The catalysts were thermally conditioned in a furnace at 500°C during 4 hours before the light-off tests to limit any possible physisorption or chemisorption effects.

Exhaust gas from a steady state engine operation (i.e. engine speed of 1500 rpm and engine load of 3 bar IMEP reflecting approximately 40% of full load) was used for this study. The engine was operated with ultra low sulphur diesel fuel (ULSD) which basic properties are given in Table 3. The ULSD was provided by Shell Global Solutions UK. The exhaust gas composition corresponding to this engine condition is shown in Table 2. Pure H_2 from a gas cylinder was introduced upstream of the DOC at various hydrogen concentrations which include 500, 1000, 2500 and 8000 ppm. Additionally, H_2 concentrations were measured both upstream and downstream the catalyst by sampling the gas-stream through a Hewlett-Packard (HP) gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

It has to be noted that the exhaust gas volumetric flow rate over the DOC was controlled using calibrated flow meters to ensure consistency between the gas hourly space velocities (GHSV) for all the tests. GHSV is defined as the volumetric flow rate of the reactant feed (i.e. exhaust gas) divided by the external volume of the monolith catalyst which was maintained at 35000 h^{-1} .

3. Results and discussion

In general, as the temperature increases so does the oxidation rate of CO and HC, while at higher temperatures the catalyst performance stabilises forming a plateau at a high conversion efficiency level for both catalysts (Figure 2 and 3). The apparent higher conversion for hydrocarbons at low temperature might be due to the presence of zeolites within the washcoat which trap the hydrocarbons at low temperature or the possibility of hydrocarbon condensation either within the catalyst itself and/or in the exhaust stream. Another reason could be that the HC may oxidise in the presence of NO₂, which will be discussed later in the NO_x section.

The conversion rate of CO is higher than that of HC, due to the higher reactivity of CO with respect to some hydrocarbon species. It has been previously reported that CO has a higher reactivity over the DOC compared to other exhaust components [15]-[16] which is also influenced by the platinum coating. The catalyst light-off temperature for CO and HC oxidation is around 10°C lower for the platinum catalyst (Figure 2a and Figure 3a) compared to the platinum-palladium catalyst (Figure 2b and Figure 3d). In the case of CO, the results show that once the light-off temperature is reached CO was finally fully oxidised to CO₂ for both catalysts. Nevertheless in the case of total hydrocarbons emissions (HC) the maximum conversion efficiency did not reach 100%, being higher for the platinum catalyst with respect to the platinum-palladium.

This incomplete conversion in unburnt total hydrocarbons suggests the presence of some hydrocarbons species which are more difficult to be oxidised. This is more noticeable in the case of the platinum-palladium compared to the platinum catalyst. Figure 4a shows the engine output exhaust hydrocarbon distribution (upstream the diesel oxidation catalysts). It can be seen that the exhaust hydrocarbon distribution is mainly composed of medium-heavy hydrocarbons denoted as 'medium-heavy HC' (these are composed of alkanes, alkenes, aromatics, etc.). The proportion of some light hydrocarbons both saturated (methane, ethane, propane) and unsaturated (ethylene, propylene, acetylene, etc.) is very small. In Figure 4 it is also shown the hydrocarbon distribution downstream the platinum diesel oxidation catalyst at three different

temperatures (170°C, 250°C and 400°C). The first temperature represents the onset of hydrocarbon oxidation, 250°C is chosen as the temperature when hydrocarbon oxidation starts to be stable and 400 is the maximum studied temperature. A similar hydrocarbon distribution than upstream the DOC but with lower total hydrocarbon concentration is obtained at 170°C confirming the light-off temperature of hydrocarbon oxidation. However, when the temperature is increased to 250°C the hydrocarbon distribution is changed. The contribution of 'medium-heavy HC' hydrocarbon to total hydrocarbons has been reduced from around 89 to 46.5%, while some light alkane hydrocarbons such as methane and ethane are now present representing approximately 35% and 18.6% of total hydrocarbons, respectively. However, alkene hydrocarbons have been completely oxidised over the catalyst.

These trends confirm the differences in reactivity of the different hydrocarbon species. Saturated hydrocarbons are more difficult to be oxidised than the unsaturated hydrocarbons, as reported in literature [17]. Concerning saturated hydrocarbons, short chain hydrocarbons such as methane are more difficult to oxidise than ethane as the proportion of methane increases considerably at 250°C with respect to 170°C. The hydrocarbon species distribution at 400°C shows a reduction of ethane and methane, while the 'medium-heavy HC' increases. Therefore, it is suggested that the incomplete conversion of hydrocarbons is due to the presence of some long chain saturated hydrocarbons, where oxidation is limited by mass transfer to the active sites of the catalyst and/or aromatics components in those denoted as 'medium-heavy HC' as well as the presence of methane and ethane in the engine exhaust composition.

Platinum catalysts are known to be more effective in oxidising hydrocarbons compared to palladium catalysts, enabling lower temperature oxidation at a greater reaction rate (as being shown on the Figure 5) with no alkenes and formaldehyde and a higher reduction of medium-heavy hydrocarbons at 250°C. It can also be seen that Platinum allows an enhanced conversion of the more stable hydrocarbons (alkanes) at 400°C compared to the platinum-palladium oxidation catalyst.

The addition of H₂ significantly promoted CO low temperature oxidation (see Figure 3). In fact, approximately 1000 ppm hydrogen addition reduced the light-off temperature of both

catalysts by up to 30°C. An estimation of the catalyst outlet temperature assuming adiabatic conditions and complete hydrogen oxidation has been made. In addition, the temperatures downstream of the catalyst for the different hydrogen additions have been recorded (see Table 4). It can be observed that the improvement in the light-off temperature (30°C) is higher than the estimated and measured increase in the catalyst temperature (4 and 3°C, respectively). As the hydrogen concentration was increased in the range of 1000 – 2500 ppm the catalysts light-off temperature was further improved. However, when the hydrogen concentration was further increased from 2500 ppm to 8000 ppm no additional improvements were observed in the start of oxidation, even though a high exotherm effect has been recorded downstream the catalyst (+ 60°C). This comparison shows that CO earlier light-off cannot be linked with hydrogen exothermic effect only as it remains limited at low temperatures. The results are in accordance to those obtained by Salomons et al. [11]. They suggested that CO oxidation starts earlier than hydrogen oxidation, but hydrogen adsorbed species could in the meantime increase CO desorption rate and reduce CO active sites coverage which delays its start of oxidation. This would eventually increase the availability of active sites for the adsorption of oxygen and other exhaust species and promote CO light-off at lower temperatures [11]. Nevertheless, steeper light off curves can be noticed for greater hydrogen concentrations. Therefore, it is assumed that while hydrogen exothermic effect is not the main promoter for CO and HC oxidation at low temperatures, the increase in hydrogen and CO combustion exothermic effect as the temperature rises enables a promotion in CO oxidation reaction rates which translates into steeper light-off curves.

In the presence of hydrogen, the light-off and oxidation rate of hydrocarbons was substantially improved reaching almost 100% conversion. As hydrogen concentration was increased to 2500 ppm the low temperature hydrocarbon oxidation window was improved. However, any further increase in hydrogen concentration (e.g. 8000 ppm) did not show any further improvements in hydrocarbon oxidation, similarly to CO light-off. Figure 5 shows that hydrogen promotes both the oxidation of saturated and unsaturated hydrocarbons. This effect is more noticeable in the platinum-palladium catalyst which, without hydrogen, showed a lower

oxidation capability towards saturated species compared to platinum only. As a result, the oxidation of the different hydrocarbon species in the case of the platinum-palladium catalyst with hydrogen addition is similar to the oxidation of those species in the platinum catalyst, producing a significant benefit compared to the platinum-palladium catalyst without hydrogen addition.

The results suggest that the hydrogen improvement in the hydrocarbon light-off temperature and rate of oxidation is due to the combination of different factors rather than exclusively the hydrogen exothermic effect. This seems to be a plausible explanation as with the addition of hydrogen a higher total hydrocarbon conversion is reached than in the case without hydrogen at any temperature. It is especially noticeable when the catalyst is fully warmed (400°C) as the addition of hydrogen still improves the HC maximum conversion efficiency which cannot be accounted for the heat release from hydrogen oxidation. Therefore, based on these experimental results it is proposed that the effect of hydrogen on the hydrocarbon oxidation is due to the combination of the following factors: (a) presence of hydrogen containing active species adsorbed in the catalyst active sites, (b) higher availability of active sites for HC and oxygen, as CO has been oxidised at lower temperature, (c) exothermic effect of CO and (d) exothermic effect of hydrogen.

In terms of NO to NO₂ oxidation, a limit is reached for this reaction over the platinum catalyst at temperatures higher than 300°C (Figure 6a), where NO₂ concentration is probably equilibrium limited as it has been previously suggested in [18]. Once the equilibrium is reached, NO₂ concentration starts to decrease as temperature increases. Higher NO₂ concentration downstream the DOC was obtained for the platinum catalyst compared to the Pt:Pd catalyst (Figure 6b) for up to 300-350°C, where the thermodynamic limit is reached. It has to be noted that at low temperature, the NO₂ concentration downstream of the diesel oxidation catalyst in both cases is lower than upstream the DOC (engine output, see Table 2). It is suggested to be a result of the reaction of NO₂ with CO and hydrocarbons. This reaction will result in a reduction of the NO₂ concentration within the catalyst, while the NO concentration should increase, resulting in a negligible NO_x conversion in the catalyst (Figure 7a and b). As temperature was

increased the concentration of CO and HC was reduced (once the light-off is reached) and the NO₂ concentration was increased. This suggests the relevant role of the presence of CO and HC to determine the NO₂ concentration after the catalyst which has also been previously extensively studied [19]-[23].

It is important to optimise NO₂ production at a specific temperature range, where NO₂ is effective in oxidising particulate matter. It has been previously reported that the rate of soot oxidation by NO₂ is higher than in the case of oxygen from approximately 150°C to 400°C [24]-[25]. For both catalysts H₂ presence increases the NO₂ concentration, this being more noticeable at lower temperatures. Thus greater NO₂ can be obtained under lower exhaust gas temperatures which could result in a beneficial effect in DPF passive regeneration at low temperature. Hydrogen does not show a linear effect on NO₂ production over the catalysts, particularly the highest H₂ concentration (8000ppm) did not further increase NO₂ after the catalyst. The results suggest that the interactions of various species and mechanisms overall determines the NO₂ concentration downstream the catalyst. One possibility is the enhancement of NO to NO₂ oxidation due to the thermal effect of hydrogen oxidation. According to our interpretation this will shift the curve of NO₂ concentration (downstream the catalyst) to lower temperatures. In these experiments an increase in the NO₂ concentration was also seen at different temperatures. This increase in the NO₂ concentration at low-medium temperatures (after the CO and HC light-off) could be partially related to the oxidation of CO and hydrocarbons. As the concentration of these carbonaceous species is reduced, NO₂ can not be used in the active sites of the catalyst to oxidise them. In addition, and in agreement to the HC and CO oxidation studies, it can be also hypothesised that hydrogen addition could produce some hydrogen-containing oxidising species (e.g. OH, HO₂) which could promote not only HC oxidation but also NO to NO₂ oxidation.

Overall, suggesting that the benefit of H₂ additions for NO₂ production is a result of not only the exothermic reactions increasing the catalyst local temperature but also the oxidation of HC and production of hydrogen containing oxidising species could have a relevant effect. This is dependent on H₂ concentration, with smaller concentrations around 1000ppm being more advantageous.

Nitrous oxide (N_2O) which is not commonly included in NO_x emissions should also be investigated as it is known to be a harmful greenhouse gas promoter and responsible for ozone destruction. It has been previously reported that N_2O can be produced under low exhaust gas temperatures over platinum catalysts [26]. The results obtained here confirmed the higher selectivity of platinum catalysts compared to platinum-palladium to N_2O formation, reducing more extensively NO_x to N_2O . The effect of H_2 on the N_2O formation can be observed in Figure 8a and b. The addition of hydrogen enhanced N_2O formation at low temperature, especially when more than 1000ppm of hydrogen is added in the platinum catalyst. It is suggested that at these low temperatures, below the light-off temperature of the HC, N_2O is formed by H_2 -SCR reactions rather than through the typical HC-SCR reaction. As it is proposed in [26], the addition of hydrogen enhances the reduction of the platinum active sites previously oxidised by NO chemisorption allowing more NO to adsorb, dissociate and form N_2O .

4. Conclusions

This work has shown that H_2 is effective in promoting CO and HC oxidation as well as improving the catalyst light-off temperature for both types of catalysts (Pt/Pd and Pt only). As a result, it is suggested the addition of small hydrogen concentrations to the platinum-palladium catalyst, resulting in similar light-off temperature, and CO and HC oxidation within the catalyst compared to the platinum diesel oxidation catalyst without hydrogen. It is suggested that the beneficial effects of hydrogen on the CO and HC oxidation are a result of the combination of a reduction in competitive adsorption (CO desorption rate and oxidation), the presence of hydrogen-containing species and thermal effects (exothermic effect of hydrogen and CO oxidation).

It is believed that the increase in NO_2 downstream of the catalyst at lower temperatures is a result of not only the exothermic reactions, but also a more indirect effect from hydrogen promoting other species removal. As H_2 enhances the rate of CO and HC oxidation, this eases NO accessibility to the active sites, while reducing the rate of depletion of NO_2 through its

reduction by HC. This higher production of NO₂ and higher oxidation rate of CO and HC at lower temperature is ideal for low temperature passive DPF regeneration. For practical applications, the hydrogen injected to promote the DOC activity could be produced on board rather than being store in a reservoir in the car. It would therefore be possible to use exhaust gas reforming and/or electrolysis applications to produce the required amount of hydrogen.

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Tables

Table 1. Engine specifications

Engine Specification	
Number of Cylinders	1
Bore/Stroke	98.4mm/101.6mm
Connecting Rod Length	165mm
Displacement Volume	733cm ³
Compression Ratio	15.5:1
Rated Power (kW)	8.6@2500rpm
Peak Torque (Nm)	39.2@1800rpm
Injection System	Three holes pump-line-nozzle
Injection Timing (°bTDC)	22
Engine Piston	Bowl-in-piston

Table 2. Engine output emissions concentration

Emission	Concentration
CO (ppm)	141
HC (ppm)	450
NO (ppm)	445
NO ₂ (ppm)	55
NO _x (ppm)	500
N ₂ O (ppm)	0
CO ₂ (%)	3.2
H ₂ O (%)	3.7

Table 3. Ultra low sulphur diesel fuel properties

Fuel Analysis		Method
Cetane number	53.9	ASTM D613
Density at 15°C (kg m ⁻³)	827.1	ASTM D4052
Viscosity at 40°C (m ² s ⁻¹)	2.467 E-06	ASTM D445
50% distillation (°C)	264	ASTM D86
90% distillation (°C)	329	ASTM D86
LCV (MJ kg ⁻¹)	42.6	
Sulphur (mg kg ⁻¹)	46	ASTM D2622

Table 4. Catalyst temperature increase under hydrogen addition

Hydrogen concentration (ppm)	Temperature increase estimated under adiabatic conditions	Temperature increase measured along the catalyst
500 ppm	4°C	3°C
1000 ppm	8°C	7°C
2500 ppm	20°C	17°C
8000 ppm	65°C	60°C

Figure Captions

Figure 1: Experimental setup

Figure 2: Hydrogen effect on CO conversion over (a) platinum catalyst and (b) platinum-palladium catalyst.

Figure 3: Hydrogen effect on HC conversion over (a) platinum catalyst and (b) platinum-palladium catalyst.

Figure 4: Hydrocarbon distribution (a) upstream the platinum catalyst, (b) downstream the platinum catalyst at 170°C, (c) downstream the platinum catalyst at 250°C and (d) downstream the platinum catalyst at 400°C.

Figure 5: Hydrocarbon species (a) upstream the catalysts, (b) downstream the catalysts at 170°C, (c) downstream the catalysts at 250°C and (d) downstream the catalysts at 400°C.

Figure 6: Hydrogen effect on NO₂ production over (a) platinum catalyst and (b) platinum-palladium catalyst.

Figure 7: Hydrogen effect on NO_x (NO+NO₂) conversion over (a) platinum catalyst and (b) platinum-palladium catalyst.

Figure 8: Hydrogen effect on (a) N₂O production over the platinum catalyst and (b) N₂O production over the platinum-palladium catalyst.