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Migration of Platinum Nanoparticles *via* Volatile Platinum Dioxide during Lean High-Temperature Ageing of Diesel Oxidation Catalysts

Characterisation of platinum dioxide migration and mitigation approaches

Shadab Mulla*, Phillip Ross, Glen Spreitzer, Howard Hess, Ceren Aydin
Johnson Matthey, 435 Devon Park Drive,
Suite 600, Wayne, PA 19087, USA

François Moreau, Andrew Chiffey
Johnson Matthey, Orchard Road, Royston,
Hertfordshire, SG8 5HE, UK

***Email:** Shadab.Mulla@jmusa.com

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When platinum-containing diesel oxidation catalysts (DOC) are exposed to high temperatures under lean conditions, the platinum nanoparticles form volatile platinum dioxide on the catalyst surface. The exhaust flow carries the volatile platinum dioxide to the downstream aftertreatment catalyst, such as the selective catalytic reduction (SCR) catalyst, that is responsible for reducing the nitrogen oxides (NOx) emissions and can negatively impact its performance, by promoting the parasitic oxidation of ammonia. Here we investigate the factors such as exposure time, temperature and DOC design characteristics for their impact on the platinum dioxide migration, by characterising the amount of platinum deposited on the SCR catalyst at very low levels (<5 ppm), using inductively coupled plasma optical emission spectroscopy (ICP-OES) fire assay technique. Our results indicate that well-dispersed platinum, not associated with palladium, is most prone to platinum dioxide migration. We also compare several methods to suppress the platinum dioxide migration from the DOC, such as sintering of the platinum nanoparticles, stabilising the platinum nanoparticles *via* interaction with palladium or covering the platinum nanoparticles with a high surface area capture layer to trap the volatile platinum dioxide.

1. Introduction

To meet the emissions standards for diesel-powered engines, it is essential to have separate aftertreatment catalysts for controlling specific tailpipe emissions such as hydrocarbons (HC), carbon monoxide, NOx and particulate matter. An advanced diesel exhaust aftertreatment system consists of channel-flow catalytic converters such as DOC, comprising of various levels of platinum and palladium, SCR catalyst and catalysed soot filter (CSF), each with discrete functions. One example of an aftertreatment system is the SCR forward system (DOC-SCR-CSF), where the engine exhaust gases are pretreated over the DOC, designed to generate nitrogen dioxide for enhanced fast SCR reaction. Having the SCR catalyst placed immediately downstream of the DOC, compared to the CSF forward system (DOC-CSF-SCR), helps in the faster warm up of the SCR catalyst and improves the cold start performance. Besides nitrogen dioxide generation, the DOC also removes HC and other oxidisable emissions and furthermore, aids the high temperature desulfation of the SCR catalyst by generating heat *via* the exothermic HC oxidation reaction.

Due to high temperature events and lean conditions of the diesel exhaust, the platinum nanoparticles in the oxidation catalyst structure can form a film of platinum dioxide on its surface that is volatile (1, 2). On the other hand, palladium forms a thermodynamically stable palladium oxide that has a low vapour pressure (3, 4). Both palladium oxide and palladium are significantly less volatile than platinum dioxide (2, 5–8). Thus, volatile platinum dioxide can migrate to the SCR catalyst, while migration of palladium is found to be almost negligible, even for temperatures up to 850°C (9, 10). Presence of platinum dioxide on the SCR catalyst is not desired as it can promote parasitic oxidation of ammonia, which is typically introduced to the aftertreatment system *via* the injection of a urea solution to reduce NOx. This ammonia oxidation over migrated platinum leads to lower NOx conversion, as it decreases the amount of ammonia available for the SCR reaction, in addition to causing increased NOx and nitrous oxide (N_2O) formation (9, 11–15). A very small amount of platinum (parts per million (ppm) level) can cause severe deactivation to the ammonia-SCR activity. Impact on the SCR catalyst was previously observed for 3–8 ppm platinum detected on a dynamometer-aged iron-SCR catalyst (13) and with 2–6 ppm platinum analysed on a field returned copper-SCR catalyst (12). Depending on the platinum concentration on the SCR catalyst, typically, no major changes in NOx conversion are seen at lower temperatures (up to 250°C). But NOx conversion can start declining at higher temperatures, with larger drop seen as the temperature increases. Peak nitrous oxide changes due to the presence of platinum on the SCR catalyst are typically seen around 250°C for iron-SCR and around 300–350°C for copper-SCR catalysts (9, 12).

In this work, we investigate the transport of volatile platinum dioxide from a DOC to the downstream SCR catalyst, when the DOC is exposed to temperatures exceeding 550°C. The goal of this work was to develop a method to quantify the ppm-level deposition of platinum on the downstream SCR catalyst due to the emission of volatile platinum dioxide species from an industrially relevant DOC design. Conventional X-ray fluorescence method cannot easily detect platinum levels below 20 ppm (weight basis) (13). Using probe reactions on platinum containing SCR catalysts can alternatively offer a non-destructive method for detecting platinum. However, its sensitivity for low platinum concentrations will depend on the probe reaction and the test conditions employed. Moreover, probe reaction technique is not quantitative, nor platinum-specific, as other precious metals can also interfere. Activity of the migrated platinum in the probe reaction will also depend on factors such as dispersion or sintering, oxidation state and poison state (for example, phosphorus or sulfur exposure) of the platinum deposited on the SCR catalyst, thus could yield varied results for the probe reaction for the same amount of platinum (10).

This study employs ICP-OES fire assay technique, capable of quantifying less than 1 ppm levels of platinum. Limit of detection of the ICP-OES was 0.03 ppm. The most appropriate techniques for the determination of such trace levels of platinum include methods such as inductively coupled plasma mass spectrometry and ICP-OES (16). Leistner *et al.* (10) used inductively coupled plasma sector field mass spectrometry (ICP-SFMS) to determine the amount of platinum that migrated from the DOC by analysing the downstream capturing monolith, with a limit of detection of 0.3–0.5 ppm, but observed that the platinum amount in some cases was below the detection limit. Using the ICP-OES method, this study investigates factors such as exposure time, temperature and DOC design characteristics (for example, platinum loading, dispersion and distribution) for their impact on the migration of volatile platinum dioxide and ways to minimise it. Since the vapour pressure of platinum dioxide can be changed by alloying with other elements such as palladium, which have very low vapour pressure in oxygen (5, 17–20), addition of palladium to platinum is explored to form a solid solution and suppress platinum emission. Lastly, we also show that covering the platinum nanoparticles with a protection layer comprising of a high surface area support material can significantly modify the migration of volatile platinum dioxide. The resulting decrease in volatile platinum dioxide migration leads to a lower impact on the SCR catalyst performance.

2. Experimental Details

2.1 Catalysts

The DOC and the SCR catalyst placed downstream to capture the volatile platinum dioxide from the DOC were prepared as monoliths, with a cell density of 400 cells per square inch (cpsi) and

0.004″ wall thickness. The DOC monoliths were either 3″ or 5″ in length, while the SCR monoliths were 6.3″ in length. For the reactor study, cores of 1″ in diameter and 3″ in length were cut from the SCR monolith (from the inlet) and from the 3″ long DOC monolith (to test the full-length DOC cores). For engine study, the full-size SCR monoliths and 5″ long DOC monoliths were used.

An illustration for the DOC designs is shown in **Figure 1**. The reference DOC (DOC-Ref) contains platinum and palladium. It is made of three catalyst doses; D1 = first dose applied from the monolith inlet; D2 = second dose applied from the outlet; D3 = third dose, also applied from the inlet. None of the doses cover the full length of the monolith, such that the resulting fully formulated DOC has a multi-zoned structure from the inlet to the outlet. While D1 and D3 both contain platinum and palladium, the outlet dose D2 is comprised of platinum on a metal oxide support and no palladium (i.e., platinum-only dose).

To suppress the migration of platinum dioxide from the reference DOC, modifications were made to the DOC-Ref design, to create DOC-A and DOC-B. DOC-A added palladium to the outlet D2 dose (platinum only dose), using platinum:palladium ratio of 2:1 (weight ratio). The total platinum group metals (pgms) loading in D2 was nearly doubled, compared to the platinum loading in D2 of DOC-Ref. No changes were made to the inlet D1, D3 doses. DOC-B was created by retaining the same design as the DOC-Ref (D1 to D3) but added a fourth dose, D4 = fourth outlet dose, partially covering the D2 dose. D4 comprised of palladium on a metal oxide support and served as a 'protection layer' to capture the platinum dioxide emission from the DOC-Ref design.

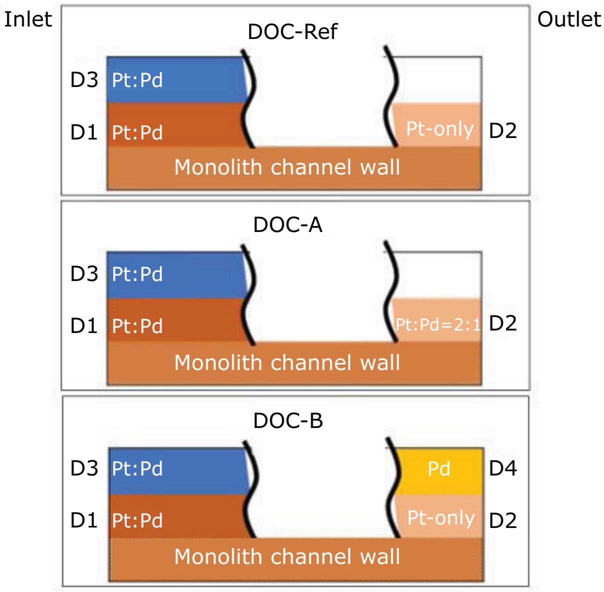


Fig. 1. DOC designs showing the inlet, outlet doses and pgm composition

The SCR catalyst cores used for the reactor ageing are from a iron-zeolite-based catalyst, while a zoned iron-copper-zeolite-based SCR catalyst was used for the engine ageing.

2.2 Platinum Migration Ageing

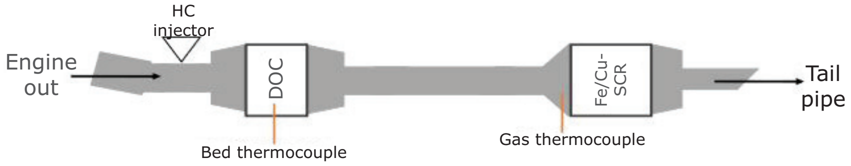
For the laboratory reactor study, fresh DOC core sample of 1″ diameter × 3″ length (full length of the DOC monolith) was placed upstream of a same size fresh iron-SCR catalyst core (taken from the inlet of the SCR monolith), in a tubular furnace. The DOC cores were exposed to gas temperatures of 550°C, 600°C or 650°C (measured at the DOC core inlet) for 24 h in a flow of 10% oxygen, 7% water mixed with nitrogen, at a gas hourly space velocity (GHSV) of 40,000 h^{-1} with respect to the DOC core volume. During this ageing, the gas temperature at the outlet of the downstream SCR catalyst core was maintained at 535°C ± 5°C.

For engine ageing, a full-size fresh DOC block (5″ in length) was arranged upstream of an iron-copper-zeolite zoned SCR catalyst, with the DOC bed temperature at 600°C for 24 h in the engine exhaust flow (DOC GHSV of 100,000 h^{-1}). To achieve the ageing temperature, diesel fuel was injected at the DOC inlet to generate heat within the DOC by the exothermic reaction with the extra fuel. Gas temperature at the SCR catalyst inlet during the engine ageing was about 535°C. In some cases, where a pre-aged DOC-Ref catalyst was used for engine evaluation, the full-size DOC catalyst was first hydrothermally aged in a retort oven at either 650°C or 700°C for 6 h in a flow of 10% water mixed with air. A schematic of the reactor and engine test setup for platinum migration ageing is shown in **Figure 2** and the various platinum migration ageing experiments performed can be found in **Table I**.

2.3 Platinum Measurement on the Selective Catalytic Reduction Catalyst

After platinum migration ageing, the downstream SCR catalyst was analysed to measure the amount of platinum deposited, due to the volatile platinum dioxide migrating from the DOC. For the reactor

(a) Reactor set-up



(b) Engine set-up

Fig. 2. Schematics of the reactor and engine setup used for platinum migration ageing

Table I List of the Platinum Migration Experiments Performed in this Study

Expt. No.	Purpose	Set-up	DOC type, diameter x length	SCR type, size	SCR sample size used for Pt measurement
1	Effect of exposure temperature	Reactor	DOC-Ref, 1″ × 3″	Fe-SCR, 1″ × 3″	1″ × 3″ (full core)
2	Effect of DOC-Ref Doses		DOC-Ref (individual dose), 1″ × 3″		
3	Effect of DOC-B Pd loading in D4		DOC-B, 1″ × 3″		
4	Effect of exposure time	Engine	DOC-Ref, 5″ long	Zoned Fe/Cu-SCR, 6.3″ long	1″ × 1.5″ (inlet)
5	Pt migration along SCR monolith length				1″ × 1.5″ (each 25% length section)
6	Pt migration mitigation		DOC-Ref (fresh or pre-aged) or DOC-A or DOC-B, 5″ long		1″ × 1.5″ (inlet)

study, the entire 1″ diameter × 3″ length iron-SCR core that was aged was used for analysis. For the engine study, 1″ diameter cores taken only from the inlet 1.5″ length (approximately 25%) of the full iron-copper-zeolite zoned SCR catalyst monolith was primarily analysed, to focus on the iron-SCR zone. In one engine study to investigate how platinum deposits along the length of the SCR catalyst monolith, 1″ diameter cores from the four axial monolith section, each 1.5″ in length (or approximately 25% long) were analysed. Sampling details are included in **Table I**.

Platinum analysis of the SCR catalyst was performed by SGS Canada Inc (Lakefield, Ontario) using highly sensitive ICP-OES fire assay technique (21). Briefly, the SCR core is grounded into a powder, mixed with a fluxing agent and lead. The mixture is heated in a furnace where it fuses and separates from the lead 'button', which contains the platinum for analysis. The next step is cupellation, where platinum is extracted from the button. The lead is oxidised and absorbed into the cupel, leaving a platinum bead. The bead is then dissolved in aqua regia for analysis by ICP-OES. Single to triplicate fire assay ICP-OES analysis was performed on the submitted SCR catalyst samples, as well as certain platinum-migration ageing was repeated in their respective reactor and engine evaluations and good reproducibility in the platinum detection was observed (one standard deviation errors are shown in the results). For the ICP-OES analysis, the repeatability and reproducibility are correlated as 0.05 × (average of repeats) + 0.025 ppm, with 0.03 ppm as the limit of detection.

2.4 Selective Catalytic Reduction Performance Testing

Additional test was also conducted to examine the impact on the ammonia-SCR activity due to the deposition of volatile platinum dioxide. After engine ageing for platinum dioxide migration, a full-length core (1″ diameter × 6.3″ length) was taken from the zoned SCR catalyst monolith and tested in a laboratory reactor. Steady state ammonia-SCR activity evaluations were performed. Results are reported at two conditions, as shown in **Table II**, both at the same GHSV of 40,000 h^{-1}. Feed gases were prepared by adjusting the mass flow of the individual gas components, balanced by nitrogen. NOx conversion and nitrous oxide formation over the platinum containing SCR catalysts were compared to a separate fresh SCR catalyst core with no platinum dioxide migration ageing.

3. Results and Discussion

3.1 Platinum Dioxide Migration from the Reference DOC (DOC-Ref)

3.1.1 Effect of Exposure Temperature and Time

Figure 3 shows the effect of DOC exposure temperature from 550°C to 650°C on platinum dioxide migration to the SCR catalyst, as measured on the reactor. The exposure duration was kept the same, at 24 h. As the DOC exposure temperature increased, platinum dioxide migration to the SCR catalyst also increased, from 0.9 ppm (weight basis) at 550°C to 3.5 ppm platinum at 650°C. The fire assay ICP-OES was able to determine platinum at these low levels consistently, as demonstrated by the three repeated ageing at 600°C exposure temperature, as well as distinctly from the baseline platinum level in the SCR (0.1 ppm ± 6 ppb). Similar effect of DOC temperature on platinum dioxide migration to the SCR catalyst was observed by Jen *et al.* (13) from 670°C to 850°C (16 h exposure), based on the changes in the ammonia-SCR activity of the platinum poisoned SCR catalyst and also by Leistner *et al.* (10), from 550°C to 850°C, based on ICP-SFMS. Studies on platinum gauzes, ribbons and disc under oxygen flow have also shown a similar temperature dependency for platinum dioxide vapour pressures or platinum mass loss (2, 6, 22, 23).

Figure 4 shows the effect of DOC exposure time at 600°C on platinum dioxide migration to the SCR catalyst, upon engine ageing. The DOC was exposed to the fixed high temperature for a total duration of 24 h. The fire assay core samples were extracted progressively from the SCR catalyst inlet, after 1 h, 3 h, 6 h and the final 24 h exposure. The core spaces were filled with fresh SCR catalyst cores of the same dimensions before ageing to the next duration. Platinum deposition on the SCR catalyst inlet exceeding the baseline level was seen in the first 1 h of exposure. It progressed

Table II Steady State Selective Catalytic Reduction Test Conditions

SCR inlet temperature, °C	NO, ppm	NO_2, ppm	NH_3, ppm	NH_3:NOx	O_2, %	H_2O, %	CO_2, %
360	370	140	535	1.05	10	7	8
460	620	70	725	1.05	10	7	8

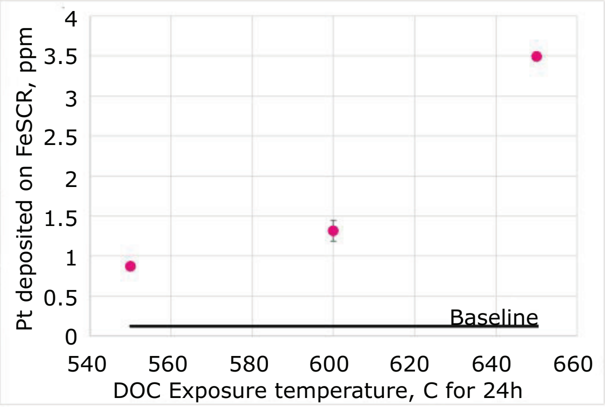


Fig. 3. Amount of platinum deposited on the iron-SCR catalyst during reactor ageing with DOC-Ref exposed to various temperatures for 24h. Baseline platinum level (0.1 ppm) from a fresh iron-SCR catalyst core taken from the same monolith

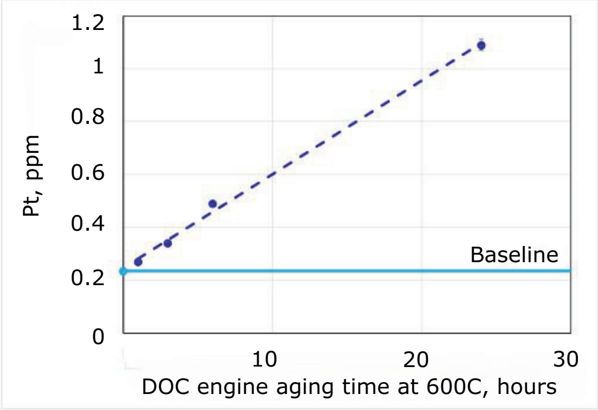


Fig. 4. Amount of platinum deposited on the zoned iron-copper-zeolite SCR catalyst inlet (1.5” length from the 6.3” long monolith) during the engine ageing with the DOC-Ref exposed to 600**°**C for different duration up to 24 h. Baseline platinum level (0.24 ppm) measured from a fresh separate SCR catalyst monolith inlet

linearly with time, i.e., at a constant rate, over the 24 h period. After 24 h, 1.1 ± 0.02 ppm platinum was detected on the SCR catalyst inlet. A similar linear relationship was seen between platinum loss as volatile platinum dioxide and ageing time at 800°C for 7 h by Kunwar *et al.* (24) on a platinum on alumina catalyst by scanning electron microscopy-energy dispersive spectroscopy as well as by Carrillo *et al.* (17) on platinum and platinum-palladium catalysts deposited on model silicon transmission electron microscopy (TEM) wafer grids as determined by electron probe microanalyser. The linear relationship can be postulated by a boundary layer of platinum dioxide that is at equilibrium with the metal, providing a constant vapour pressure of platinum dioxide, regardless of the amount of platinum remaining in the DOC sample (17). Note that the platinum amount migrating from the DOC is very small (approximately 10 ppm of the total amount of platinum in the DOC, in the time period and conditions used in this study), such that the surface area of the platinum nanoparticles on the DOC remains virtually constant, thereby resulting in a constant rate of platinum dioxide migration. Leistner *et al.* (10) also reported a near linear relationship with exposure time at 700°C from 5 h to 40 h for platinum on alumina and platinum-palladium on alumina coated monoliths for platinum volatilisation. While the X-ray diffraction patterns in that study did not show sintering with time, particle size distributions obtained from TEM micrographs showed increased particle sizes at longer duration, more evident for platinum on alumina than platinum-palladium on alumina catalyst. But that loss in platinum dispersion did not appear to have a major effect on the volatilised amounts. However, pre-aged platinum on alumina monoliths (aged 850°C for 15 h) decreased the volatilisation amounts as the sintering increased further. This suggests that exposing the DOC to high temperatures for longer times may decrease the platinum volatilisation due to sintering of the platinum particles. This will be discussed in Section 3.2.

Platinum dioxide migration to the SCR catalyst was also evaluated along its length under the engine ageing conditions (600°C exposure to DOC-Ref for 24 h), as shown in **Figure 5**. While the results reported so far, from the engine ageing, focused on the platinum migration measurement on the SCR catalyst inlet (1.5″ in length), fire assay ICP-OES analysis performed at different length sections of the SCR catalyst indicated significantly lower platinum amounts downstream, comparable to or less than the fresh SCR catalyst's baseline platinum levels. Thus, platinum migration was primarily occurring to the inlet of the zoned iron-copper-zeolite SCR catalyst. Similar axial distribution was seen by Chen *et al.* on field returned SCR catalysts and by Leistner *et al.* in reactor studies, with minor platinum deposition at the outlet of the downstream capture core (10, 12). The iron-zone at the SCR catalyst's inlet helps in suppressing the nitrous oxide formation (25). Thus, the platinum presence in the inlet zone and the resulting higher nitrous oxide formation can negate the iron-SCR function, which is not desired.

3.1.2 Effect of Diesel Oxidation Catalyst Design

Due to the multi-dose design of the DOC-Ref, reactor ageing was performed to understand the impact of its pgm distribution and the contribution of each dose to the overall platinum dioxide volatilisation. Separate DOC monoliths were prepared with only the individual doses applied (i.e., only D1, D2 or D3 applied). The ageing was performed on the reactor by exposing these DOCs to 600°C for 24 h, with the SCR catalyst core placed downstream. All the three doses showed platinum migrating to the SCR catalyst, as reported in **Figure 6**. However, the outlet dose D2 showed the most amount of platinum migration, amounting to nearly 90% of the full DOC-Ref. Interestingly, this platinum-only D2 dose contains a minority of the DOC's total platinum loading, yet is the most prone to platinum dioxide migration. In contrast, the inlet doses D1 and D3, composed of platinum and palladium, respectively showed nearly 60% and 25%

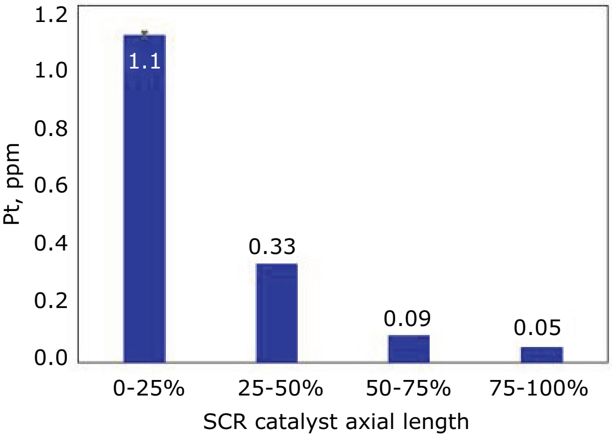


Fig. 5. Amount of platinum deposited along the 6.3″ length of the zoned iron-copper-zeolite SCR catalyst during the engine ageing with the DOC-Ref exposed to 600°C for 24 h

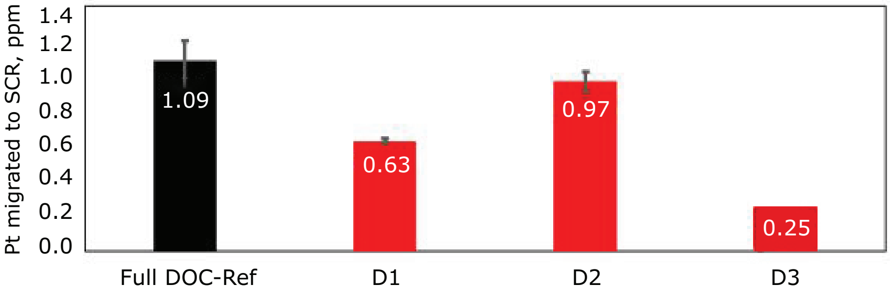


Fig. 6. Amount of platinum deposited on the iron-SCR catalyst during the reactor ageing with DOC monoliths coated only with the individual doses of the DOC-Ref (namely, D1, D2, D3). DOC exposed to 600°C for 24 h. Baseline platinum level of a fresh iron-SCR catalyst core has been removed

of the platinum dioxide migration from the DOC-Ref as a whole. The palladium and platinum co-presence in the inlet doses leads to alloying, which lowers the vapour pressure of platinum dioxide and suppresses the platinum dioxide emission (9, 10, 17, 18, 20). The extent of vapour pressure lowering would depend on the composition of the platinum-palladium alloy in the DOC. Carrillo *et al.* (17) concluded that the role of palladium goes beyond lowering the vapour pressure of platinum dioxide by alloying platinum with palladium. When a platinum-palladium particle is heated in the presence of oxygen, the emission of platinum dioxide forms a metallic core of platinum-palladium and a separate palladium oxide phase (but not as a surface layer or shell of palladium oxide surrounding the platinum-palladium particles). The palladium oxide phase additionally serves to trap the volatile platinum dioxide species.

The platinum dioxide migration amount from each dose combined exceeds that from the whole DOC-Ref. This suggests that the platinum dioxide emission from the inlet doses redeposits at the DOC outlet. The two inlet doses combined (D1, D3), thus, effectively contribute about 10% of the DOC's total amount of platinum dioxide migration and the majority of the platinum dioxide migration is occurring from the outlet D2 dose, which then deposits on the SCR catalyst capture core placed downstream.

3.2 Platinum Dioxide Migration Mitigation from Diesel Oxidation Catalyst-Ref

To decrease the platinum dioxide migration from the DOC-Ref, several mitigation options were evaluated, mostly focusing on the outlet portion of the DOC, based on the findings explained in the previous section. These included hydrothermal ageing (pre-ageing) of the DOC-Ref at high temperatures, such as 650°C or 700°C to induce sintering of the platinum nanoparticles and decrease the platinum dioxide surface area, thereby lowering the volatilisation (10). The pre-ageing can also promote alloying between platinum and palladium, where present (for example in the inlet doses of the DOC-Ref design), thereby stabilising the platinum and leading to a lesser platinum dioxide migration. Other mitigation approaches included modifying the DOC-Ref design at its outlet, such as DOC-A and DOC-B. DOC-A has palladium added to the D2 dose (platinum dose), at a platinum:palladium ratio of 2:1 (weight ratio), to stabilise the platinum, with no changes made to the inlet D1, D3 doses. DOC-B has a fourth dose added (D4, palladium on a metal oxide support) to the DOC-Ref from the outlet, partially covering the D2 dose, to capture the platinum dioxide volatilising from the DOC-Ref.

Figure 7 compares the platinum dioxide migration from the various DOCs to the downstream SCR catalyst upon engine ageing. Compared to the fresh DOC-Ref, the hydrothermally aged (pre-aged) DOC at 650°C and 700°C for 6 h, when exposed to the same platinum dioxide migration ageing on the engine (600°C exposure to the DOC for 24 h), showed respectively 43% and 51% lower platinum dioxide migration. The higher level of mitigation seen for the 700°C pre-ageing compared to the 650°C pre-ageing suggests the higher temperature pre-ageing is more effective, likely due to the increased platinum sintering (10) and alloying between platinum and palladium. It must be noted that, although not measured in this study, the pre-ageing of the DOC can cause a decrease in the DOC catalytic activity, as the catalyst sinters with increasing degree of ageing (26, 27).

A fresh DOC-A, which has palladium added in the outlet D2 dose to alloy with platinum and stabilise it from volatilisation, yielded 44% reduction in platinum dioxide migration, similar to the 650°C pre-aged DOC-Ref. Leistner *et al.* (10) observed platinum volatilisation to decrease as the platinum:palladium ratio was decreased on alumina supported monoliths. At platinum:palladium ratio of approximately

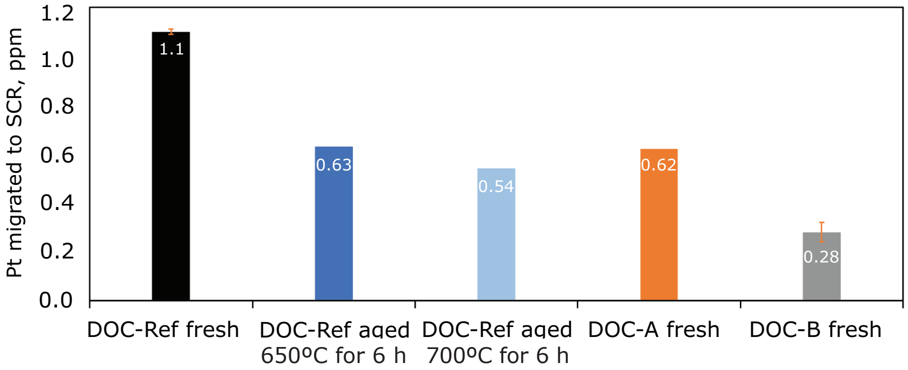


Fig. 7. Amount of platinum deposited on the zoned iron-copper-zeolite SCR catalyst inlet (1.5″ length from the 6.3″ long monolith) during the engine ageing with various DOCs exposed to 600°C for 24 h

3:1 wt/wt (2:1 mol/mol), platinum volatilisation amount was similar to that of a platinum only catalyst, since the alloying at this high platinum:palladium ratio was not sufficient to decrease the volatilisation. As the platinum:palladium ratio was decreased to 1.8:1 wt/wt (1:1 mol/mol) and 0.9:1 wt/wt (0.5:1 mol/mol), the amount of platinum volatilised decreased respectively by 33% and 66% compared to platinum on alumina, for exposure to 700°C for 15 h.

However, the most effective mitigation for platinum dioxide migration was achieved with DOC-B, around 75%. The addition of the D4 dose in DOC-B, containing palladium on metal oxide support partially covering the D2 dose at the outlet, was very effective at capturing the volatile platinum dioxide emission. In addition to the high surface area metal oxide support in D4, the presence of palladium further promoted the capture of the volatile platinum dioxide by providing trapping sites, thereby mitigating the migration of platinum to the SCR, as also reported by others (17, 20, 28, 29). From this data, the ranking of the various mitigation approaches evaluated was determined to be as follows (most to least effective): DOC-B >> hydrothermal ageing of DOC-Ref ≥ DOC-A > DOC-Ref.

For DOC-B, a further improvement in mitigation (i.e., platinum dioxide capture) was achieved as the palladium loading in D4 was increased (figurative results omitted for brevity). Under reactor ageing conditions, where DOC-B showed 55% capture of the platinum dioxide migration from DOC-Ref, doubling of the palladium loading in the D4 dose of DOC-B led to an increase in the platinum capture to 73% (using the same DOC ageing procedure of 600°C for 24 h).

3.3 Influence of the Platinum Dioxide Migration on the Catalytic Performance of Selective Catalytic Reduction Catalyst

Steady state ammonia-SCR activity reactor testing was performed on the zoned iron-copper-zeolite SCR catalysts after the platinum migration ageing on engine. The SCR catalyst aged with the DOC-Ref was compared to that aged with DOC-B, which has the lowest platinum dioxide migration. A 1″ diameter × 6.3″ length (full length) SCR catalyst core was tested in the reactor for ammonia-SCR activity. **Figure 8** shows the impact of the platinum dioxide migration from the two DOC designs on the SCR NOx conversion and nitrous oxide formation. The NOx conversion measured at 460°C showed a 15% drop for the SCR catalyst aged with the DOC-Ref upstream, compared to a fresh reference SCR catalyst. DOC-B, on the other hand, with 75%

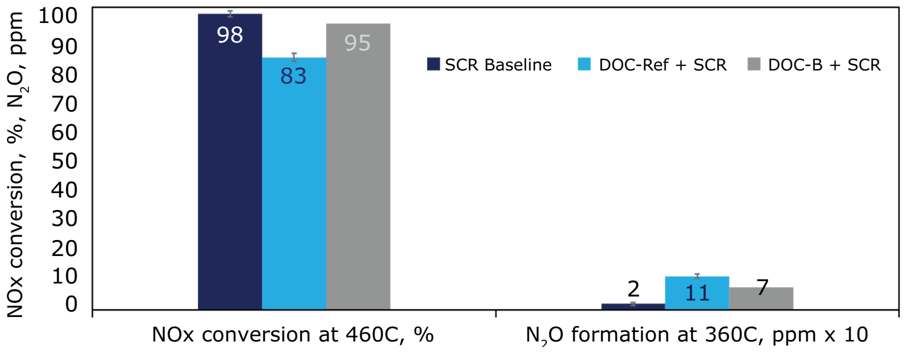


Fig. 8. NOx conversion and N_2O formation of zoned iron-copper-zeolite SCR formulation during the steady state reactor testing after the platinum dioxide migration ageing on the engine with the various DOCs placed upstream

lower platinum migrated to the SCR catalyst during the engine ageing, demonstrated a much smaller NOx conversion loss for the SCR catalyst (3%), relative to the fresh reference SCR catalyst.

The corresponding nitrous oxide formation of the SCR catalyst aged with the two DOC designs correspond well to the NOx conversion ranking. The SCR catalyst aged with the DOC-Ref upstream showed a larger increase in the nitrous oxide generated (about 1 ppm higher than the fresh reference SCR catalyst) than that aged with DOC-B (about 0.5 ppm higher nitrous oxide than the fresh reference SCR catalyst). Thus, the platinum dioxide migration mitigation due to the DOC-B design leads to a lesser impact on the SCR NOx conversion and nitrous oxide formation.

It must be noted that the platinum dioxide amount migrated to the SCR catalyst is not the only factor that impacts the SCR activity. Impact of platinum dioxide migration on the SCR catalyst performance has been shown to be suppressed by high temperature treatment of the SCR catalyst. Exposing the platinum contaminated SCR catalyst to heat treatment at or above 600°C for 2–12 h was found to induce sintering of the platinum deposited on the SCR catalyst (12) as well as platinum oxides formation (14, 15), both of which decrease the platinum nanoparticles' activity for ammonia oxidation, thereby lowering the impact on the SCR performance. The oxidation state or surface structure (10) of the platinum deposited on the SCR catalyst will also be affected by exposures to oxidising and reducing gases in the exhaust reaching the SCR catalyst, such as oxygen, nitrogen dioxide, carbon monoxide, HC, ammonia and can influence its ammonia oxidation activity. Moreover, chemical poisoning by sulfur, phosphorus, will also affect the activity of the platinum towards ammonia oxidation. Due to these factors, even the same amount of platinum deposited on the SCR catalyst can lead to a varied impact on the NOx conversion and nitrous oxide formation, since the poisoning effect of parasitic ammonia oxidation will change with time, depending on the conditions exposed to the poisoned SCR catalyst.

4. Conclusion

An ageing method was developed based on platinum dioxide volatilisation from a DOC under high-temperature lean gas exposure conditions, to intentionally migrate platinum and deposit it on a downstream SCR catalyst and to examine the platinum dioxide migration phenomenon. ICP-OES technique was employed to determine the platinum amount, by preparing and analysing the fire assay lead button from the poisoned SCR catalyst sample. Albeit destructive, the fire assay technique offers a sensitive, consistent, direct and specific way to determine very low levels of platinum present on the SCR catalyst (<5 ppm), with 0.03 ppm as the limit of detection.

Platinum deposition due to the platinum dioxide migration from an upstream DOC was found to largely occur at the SCR catalyst inlet section. It progressed at a constant rate, over the 24 h period evaluated for the 600°C exposure to the DOC and its severity increased at higher DOC exposure temperatures. The platinum dioxide volatilisation method and the fire assay analysis were also employed to investigate the impact of DOC design characteristics as well as the platinum and palladium distribution on the platinum dioxide migration. Our results indicate that the platinum nanoparticles not associated with palladium show the most platinum dioxide migration, while the copresence of platinum and palladium supressed the platinum dioxide emission.

Hydrothermally pre-ageing the DOC to sinter the platinum or stabilising the platinum only regions of the DOC by palladium introduction and alloying, both led to a decrease in platinum dioxide migration. The highest level of mitigation seen in this study was achieved by covering the platinum nanoparticles with a high surface area capture layer consisting of palladium on a metal oxide support, which efficiently trapped the volatile platinum dioxide.

Platinum deposition on the SCR catalyst promoted the undesirable parasitic oxidation of ammonia, leading to a lower NOx conversion (due to NOx remake) and increased nitrous oxide formation. It was shown that the presence of platinum, even at a low level of around 1 ppm at the SCR catalyst inlet, caused a significant ammonia-SCR performance loss, particularly at higher temperatures. Supressing the platinum migration using the mitigation options lowered the impact on the ammonia-SCR performance.

The mitigation approaches discussed here serve as starting points to add more robustness and durability to the DOC design by minimising the platinum dioxide migration to the downstream catalysts. The performance impact on the DOC functions, such as carbon monoxide, HC and nitric oxide oxidation, due to the DOC pre-ageing or design modifications for mitigating the platinum dioxide migration should be investigated. Similarly, better understanding is needed for the influence of chemical poisons and oxidising or reducing gas exposures to the migrated platinum (causing a change in its oxidation state) on its ammonia oxidation activity and the corresponding impact on the ammonia-SCR performance.

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References

1. J. C. Chaston, *Platinum Met. Rev.*, 1975, **19**, (4), 135
2. C. B. Alcock and G.W. Hooper, *Proc. R. Soc. Lond.*, 1960, **254**, (1279), 551
3. G. Bayer and H. G. Wiedemann, *Thermochim. Acta*, 1975, **11**, (1), 79
4. M. Peuckert, *J. Phys. Chem.*, 1985, **89**, (12), 2481
5. E. Raub and W. Plate, *Int. J. Mater. Res.*, 1957, **48**, (8), 444
6. H. Jehn, *J. Less Common Met.*, 1984, **100**, 321
7. H. Shinjoh, H. Muraki, Y. Fujitani, 'Effect of Severe Thermal Aging on Noble Metal Catalysts', in "Catalysis and Automotive Pollution Control II", ed. A. Crucq, Studies in Surface Science and Catalysis Series, Vol. 71, Elsevier BV, Amsterdam, The Netherlands, 1991 pp. 617–628
8. J. W. Arblaster, *Platinum Met. Rev.*, 2007, **51**, (3), 130
9. G. Cavataio, H.-W. Jen, J. W. Girard, D. Dobson, J. R. Warner, C. K. Lambert, *SAE Int. J. Fuels Lubr.*, 2009, **2**, (1), 204
10. K. Leistner, C. Gonzalez Braga, A. Kumar, K. Kamasamudram, L. Olsson, *Appl. Catal. B: Environ.*, 2019, **241**, 338
11. E. Hruby, S. Huang, R. Duddukuri, D. Dou, SAE Technical Paper 2019-01-0740, SAE International, Warrendale, USA, 2019, 12 pp
12. X. Chen, N. Currier, A. Yezerets. K. Kamasamudram, *SAE Int. J. Engines*, 2013, **6**, (2), 856
13. H.-W. Jen, J. W. Girard, G. Cavataio, M. J. Jagner, *SAE Int. J. Fuels Lubr.*, 2008, **1**, (1), 1553
14. T. Yu, M. Xu, Y. Huang, J. Wang, J. Wang, L. Lv, G. Qi, W. Li, M. Shen, *Appl. Catal. B: Environ.*, 2017, **204**, 525
15. H. Zhao, L. Han, Y. Wang, J. Zheng, *Catalysts*, 2021, **11**, (7), 796
16. L. Bencs, K. Ravindra, R. Van Grieken, *Spectrochim. Acta Part B: At. Spectrosc.*, 2003, **58**, (10), 1723
17. C. Carrillo, A. DeLaRiva, H. Xiong, E. J. Peterson, M. N. Spilde, D. Kunwar, R. S. Goeke, M. Wiebenga, S. H. Oh, G. Qi, S. R. Challa and A. K. Datye, *Appl. Catal. B: Environ.*, 2017, **218**, 581
18. J. B. Darby, K. M. Myles, *Metall. Trans.*, 1972, **3**, (3), 653
19. T. R. Johns, R. S. Goeke, V. Ashbacher, P. C. Thüne, J. W. Niemantsverdriet, B. Kiefer, C. H. Kim, M. P. Balogh, A. K. Datye, *J. Catal.*, 2015, **328**, 151
20. S. Porter, A. Ghosh, C. H. Liu, D. Kunwar, C. Thompson, R. Alcala, D. P. Dean, J. T. Miller, A. DeLaRiva, H. Pham, E. Peterson, A. Brearley, J. Watt, E. A. Kyriakidou, A. K. Datye, *ACS Catal.*, 2023, **13**, (8), 5456
21. S. Compernolle, D. Wambeke, I. De Raedt, K. Kimpe, F. Vanhaecke, *J. Anal. At. Spectrom.*, 2011, **26**, (8), 1679
22. G. C. Fryburg, H. M. Petrus, *J. Electrochem. Soc.*, 1961, **108**, (6), 496
23. H. Jehn, *J. Less Common Met.*, 1981, **78**, (2), 33
24. D. Kunwar, C. Carrillo, H. Xiong, E. Peterson, A. DeLaRiva, A. Ghosh, G. Qi, M. Yang, M. Wiebenga, S. Oh, W. Li, A. K. Datye, *Appl. Catal. B: Environ.*, 2020, **266**, 118598
25. O. Kröcher, M. Elsener, *Ind. Eng. Chem. Res.*, 2008, **47**, (22), 8588
26. D. Chan, S. Tischer, J. Heck, C. Diehm, O. Deutschmann, *Appl. Catal. B: Environ.*, 2014, **156**–**157**, 153
27. M. Kaneeda, H. Iizuka, T. Hiratsuka, N. Shinotsuka, M. Arai, *Appl. Catal. B: Environ.*, 2009, **90**, (3–4), 564
28. C. Carrillo, T. R. Johns, H. Xiong, A. DeLaRiva, S. R. Challa, R. S. Goeke, K. Artyushkova, W. Li, C. H. Kim, A. K. Datye, *J. Phys. Chem. Lett.*, 2014, **5**, (12), 2089
29. H. Xiong, E. Peterson, G. Qi, A. K. Datye, *Catal. Today*, 2016, **272**, 80

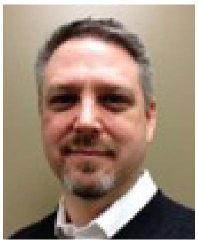
The Authors

Shadab Mulla received his PhD in Chemical Engineering from Purdue University, USA, in 2007. He is currently a Technical Program Manager at Johnson Matthey. He has sixteen years of experience in the field of emission control catalysts. More recently, Mulla has worked on characterisation and testing of aftertreatment catalysts and systems with enhanced activity and durability.

Phil Ross received his BS degree in Mechanical Engineering from Southern Illinois University at Carbondale. Phil joined Johnson Matthey in 2002 as a Resident Engineer, a role he continues in today. Early projects include the launch of NOx adsorber catalyst system on light duty automotive diesel applications later followed by variations of SCR technologies on light duty/MR and heavy duty engine applications.

Howard Hess received his BS degree in Chemical Engineering and MEng degree in Environmental Engineering from Pennsylvania State University. He also received his PhD in Energy and Geo-Environmental Engineering from Pennsylvania State University, focusing on diesel emission control *via* fuel reformulation. Howard has worked at Johnson Matthey for over 30 years and is currently a Testing Centre Manager at Johnson Matthey.

Ceren Aydın received her BS degree in Chemical Engineering from Middle East Technical University in Ankara, Turkey. She pursued MS and PhD degrees in Chemical Engineering from University of California, Davis with focus on heterogeneous catalysis. Ceren joined Johnson Matthey in 2013 and is currently based in Devon, USA. She is a Global Technical Account Director in Johnson Matthey, leading design of emissions control catalysts and systems for OEM applications.



Glen Spreitzer received his BS degree in Chemistry from Oklahoma State University. He also received his PhD in Chemistry focusing on inorganic chemistry from Duquesne University. Glen joined Johnson Matthey in 2010 and is currently a Regional Technical Program Manager in Johnson Matthey leading design of emissions control catalysts and systems for original equipment manufacturer (OEM) applications.

Andrew Chiffey received his PhD in PGM Chemistry at the University of Southampton, UK, in 1995. He has worked in the field of pgm materials at Johnson Matthey for 27 years. Andrew is currently a Global Product Development Manager in Johnson Matthey.

François Moreau received his PhD in heterogeneous catalysis at the University of Poitiers, France, in 2001. Francois joined Johnson Matthey in 2006 and is currently a Global Product Development Manager in Johnson Matthey focusing on pgm technology.