

SAE 2012 World Congress

Vehicular emissions control highlights of the annual Society of Automotive Engineers (SAE) international congress

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The annual SAE Congress is the vehicle industry's largest conference and covers all aspects of automotive engineering. The 2012 congress took place in Detroit, USA, from 24th–26th April 2012. There were upwards of a dozen sessions focused on vehicle emissions technology, with most of these on diesel emissions. More than 70 papers were presented on this topic. In addition, there were two sessions on gasoline engine emissions control with eight papers presented. Attendance was up relative to the previous year, with most sessions having perhaps 100 attendees, but some had more than 200.

This review focuses on key developments from the conference related to platinum group metals (pgms) for both diesel and gasoline engine emissions control. Papers can be purchased and downloaded from the SAE website (1). As in previous years, the diesel sessions were opened with a review paper of key developments in both diesel and gasoline emissions control from 2011 (2).

Lean NOx Traps

The lean NOx trap (LNT) is currently the leading deNOx concept for smaller lean-burn (diesel and direct injection gasoline) passenger cars and is of interest in applications with limited space or in which urea usage is difficult. The deNOx efficiency is nominally 70–80%, much lower than that of the next generation selective catalytic reduction (SCR) system at >95% and the pgm usage is high (~8–12 g for a 2 l engine). As a result, efforts are focused on improving efficiency while reducing pgm loadings. Only two papers on LNTs were reported this year, much reduced from previous years.

Katsuo Suga *et al.* (Nissan Motor Co Ltd, Japan) used a selective pgm deposition process to enhance platinum dispersion (3). The concept is to use a surfactant to preferentially apply the Pt to the ceria rather than to the alumina in the washcoat. Upon ageing, the grain growth of Pt is greatly constrained by the small size of the CeO₂ grains, **Figure 1**. Usage of pgm is cut by 50% without compromise in NOx emissions. The researchers have also identified that

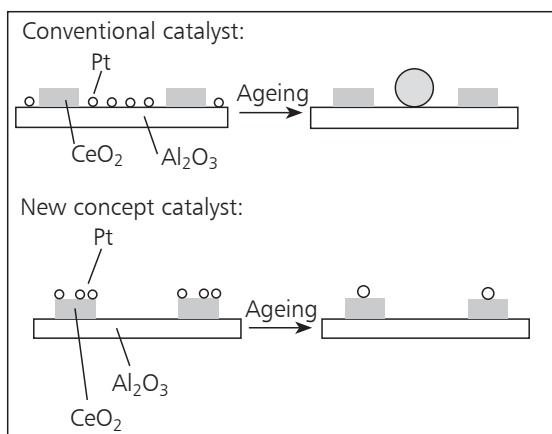


Fig. 1. Platinum is preferentially deposited on small ceria grains to minimise grain growth upon ageing of a new concept NO_x trap catalyst (3)

the NO_x desorption rate is considerably slower than either adsorption or catalyst reactions at low temperatures. The NO_x desorption rate appears to be increased by enhancing contact with CeO₂ and baria, the NO_x trapping material. Work is continuing to verify the effect.

Diesel Particulate Filters

Although diesel particulate filters (DPFs) have been in commercial production for original equipment manufacturer (OEM) application for more than 10 years, there is still much optimisation activity in the field. Papers were offered on DPF regeneration and several papers were presented on next generation DPF substrates.

Contrary to light-duty diesel applications, wherein system architecture and operating conditions necessitate burning of the collected soot using mostly thermal means at temperatures of about 600°C, in heavy-duty applications most (or all) of the soot is burned passively using nitrogen dioxide (NO₂) generated in a pgm-based diesel oxidation catalyst (DOC) and in the catalysed filter. Kenneth Lee Shiel *et al.* (Michigan Technological University, USA) quantified this effect for ultra-low sulfur diesel (ULSD) fuel and biodiesel blends (5). They loaded the filters to about 2 g l⁻¹ soot in a controlled fashion and then introduced exhaust gas with the desired composition and temperature to measure oxidation of the soot with the NO₂. They found that soot generated by burning biodiesel oxidised slightly more slowly than that from ULSD fuel, contradicting other studies

which have shown enhanced reactivity for biodiesel soot in thermal regeneration. The Arrhenius plot did not take into account the possibility of lowered DOC activity, which can occur with biodiesel usage due to more severe ash poisoning and thermal degradation. Interestingly, the investigators quantified the internal generation of NO₂ in the catalysed filter, wherein NO₂ first passes through and reacts with the soot; the resulting nitric oxide (NO) is oxidised back to NO₂ in the underlying catalyst and recycled back for another round of soot oxidation. Recycling rates were quite low at temperatures less than 300°C, but were very high (each NO molecule recycled three to four times) at 450°C.

Carl Justin Kamp *et al.* (Massachusetts Institute of Technology, USA) (6) looked at the recycling of the NO molecule, among other phenomena, in catalysed filters in an entirely different way – they used a novel ‘focused beam ion milling’ technique to vaporise away layers of material, ending up with a clean cross-section of the substrate, washcoat, catalyst, ash and soot. **Figure 2** shows one such image. There are voids between the soot and the catalyst that are likely formed by the back diffusion of NO₂ generated by the catalyst. Other images show metal oxide ash (from wear and burning lubricant oil) coating the catalyst, but mostly not interfering with this recycling phenomenon. Curiously, images were shown of ash agglomerates measuring 20 μm in diameter that mostly consisted of relatively large voids.

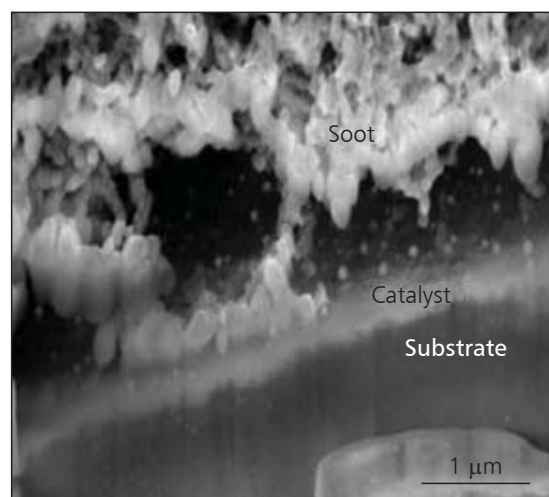


Fig. 2. Cross-section of the soot-catalyst layer in a platinum-catalysed diesel particulate filter made possible by a new ion milling technique (6)

Particulate oxidation catalysts (POCs) are a cross between a DPF and a DOC wherein the soot is trapped by turbulence mechanisms, forcing particles to make contact with the Pt-catalysed filter. POCs are a leading approach to particulate emissions control in developing countries because they do not require active regeneration. However, these countries might not have low-sulfur fuel. Piotr Bielaczyc (BOSMAL Automotive R&D Institute Ltd, Poland) *et al.* (7) looked at the effects of fuel sulfur on the performance of these devices. Although the dry soot coming from the engine was the same in all tests, the total particulate matter (PM) coming from the engine increased with increasing levels of sulfate. Between 20 h and 40 h of operation the filtration efficiency using a high sulfur fuel (365 ppm) dropped by about 10% across the particle size range, while that of a clean (sulfur-free) fuel changed very little. The loss of efficiency seen in the high-sulfur fuel is likely due to the reduced availability of NO₂ for cleaning and maintaining the filter efficiency, since NO₂ generation in the DOC is hampered by the presence of sulfur.

An important emerging trend is to coat DPFs with an SCR catalyst as a way of consolidating parts and getting the SCR closer to the turbocharger for faster heating. Friedemann Schrade *et al.* (IAV GmbH, Germany) (8) showed that when soot is on the Cu-zeolite coated filter, the change in NO₂ levels across the soot layer caused by soot oxidation can impact SCR performance. If the NO₂ level going into the filter is higher than ideal for the 'fast' SCR reaction, the soot

can improve performance. Conversely, if the NO₂ level is at or below the optimum 50% (of total NO_x) level, the soot can impair the SCR performance.

Diesel Oxidation Catalysts

DOCs are generally catalysed with platinum and/or palladium. They play two primary roles in commercial emissions control systems: (a) to oxidise hydrocarbons (HCs) and carbon monoxide, either to reduce emissions coming from the engine or to create exothermic heat used to regenerate a DPF; and (b) to oxidise NO to NO₂, which is required to continuously oxidise soot on a DPF and/or to enhance the SCR deNO_x reactions, particularly at low temperatures.

Ageing of DOCs is a critical phenomenon to understand. It can impact HC emissions, DPF regeneration and SCR performance. Junhui Li *et al.* (Cummins Inc, USA) (9) retrieved several field-aged DOCs from in-use vehicles, sectioned them and studied the ageing characteristics of the segments. As shown in Figure 3, irreversible ageing caused different types of deterioration. Catalyst samples cut from the rear of the DOC had a higher NO light-off temperature than those taken from the front. The opposite was true for HC (propene) oxidation, wherein the rear parts had a lower light-off temperature. The front catalysts were aged primarily by ash contamination, while the back catalysts were generally thermally aged. The overall light-off characteristics of the catalyst deteriorated due to both effects as the mileage increased. The authors also reported reversible deterioration caused by HC

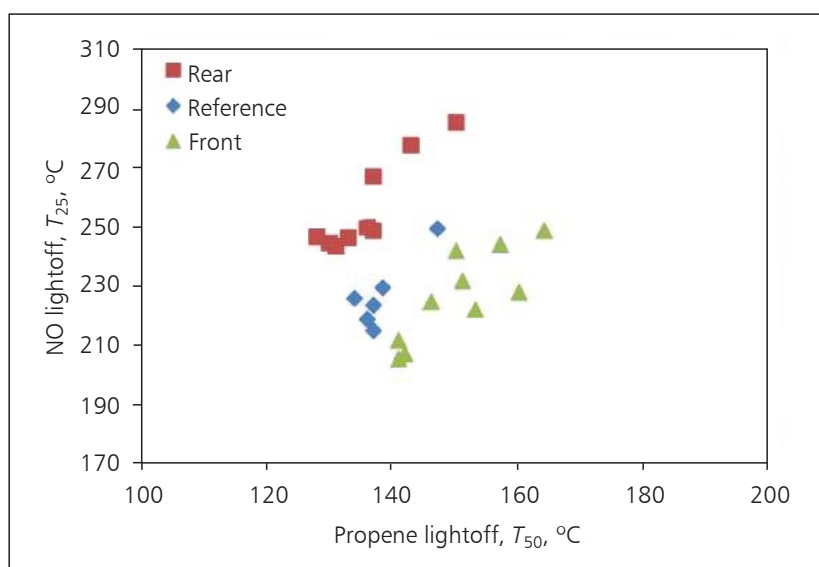


Fig. 3. NO and hydrocarbon (propene) light-off properties for samples taken from the front and rear of field-aged platinum-based diesel oxidation catalysts. The reference catalyst was laboratory aged (9)

and sulfur poisoning, which could be removed with a thermal treatment.

A new type of DOC was reported by Federico Millo and Davide Fezza (Politecnico de Torino, Italy). They added a low-temperature NO_x adsorber material (probably an alkaline earth oxide) to the DOC (10). The material stores NO_x (presumably as a nitrate) at low temperatures and then releases the NO_x at higher temperatures when the downstream SCR catalyst is operative. The adsorber aged substantially, but could still provide significantly better NO_x removal than an SCR-only configuration. This 'passive NO_x adsorber' (PNA) concept is being developed by Cary Henry *et al.* (Cummins Inc, USA) and Howard Hess *et al.* (Johnson Matthey Inc, USA) with quite impressive results (11).

Gasoline Emissions Control

Catalytic gasoline emissions control has been commercialised for more than 35 years and the three-way catalyst (TWC) for more than 30 years. Yet, it is still evolving and showing significant improvements. Since the mid-1990s, when the TWC was perhaps in its third generation, emissions have dropped by more than 95% and pgm loading is down by upwards of 70% of what it was then. The progress is still continuing.

For example, Yoshiaki Matsuzono *et al.* (Honda R&D Co, Japan) and Takashi Yamada *et al.* (Johnson Matthey Japan Inc) described a new layered catalyst for improving the performance of both close-coupled and underbody catalysts (13). The improvements cut pgm usage by 75% while meeting the new California Low Emission Vehicle III, Super Ultralow Emission

Vehicle – 30 mg mile⁻¹ non-methane HC+NO_x (LEV III SULEV30) standard. The close-coupled catalyst is layered with higher activity Pd and a lower activity oxygen storage capacity (OSC) on the top, to better withstand phosphorous poisoning and to achieve better HC conversion. The catalyst demonstrates that Pd-only catalysts can have application for the lowest emissions applications. The underbody catalyst utilises a zirconia-based OSC, allowing 50% less Rh to be used *versus* the current version of the catalyst.

System design and calibration are significant contributors to lowering emissions from gasoline vehicles. Douglas Ball and David Moser (Umicore Autocat Inc, USA) (14) benchmarked five of the cleanest gasoline engine vehicles on the market with a variety of hardware calibration strategies, including port-fueled and direct injection, with and without secondary air, and with different injection timings, engine speeds and air:fuel ratios. The light-off strategies used various combinations of high idle speed, aggressive ignition retard, secondary air and split injections. All designs achieved catalyst light-off during idle before the first hill in the test cycle. Secondary air was not necessarily needed, but helped the catalyst heat to 950°C in the first idle. Only 500°C was reached in the same time without secondary air. Turbocharged direct injection engines use split injection, secondary air and late injection to aid cold start. The investigators ran emissions tests to help estimate what volume of catalyst will be needed to meet the new California regulations. **Figure 4** shows the case for a highly calibrated, port-fuel injected, naturally aspirated 2.0 l engine without secondary air.

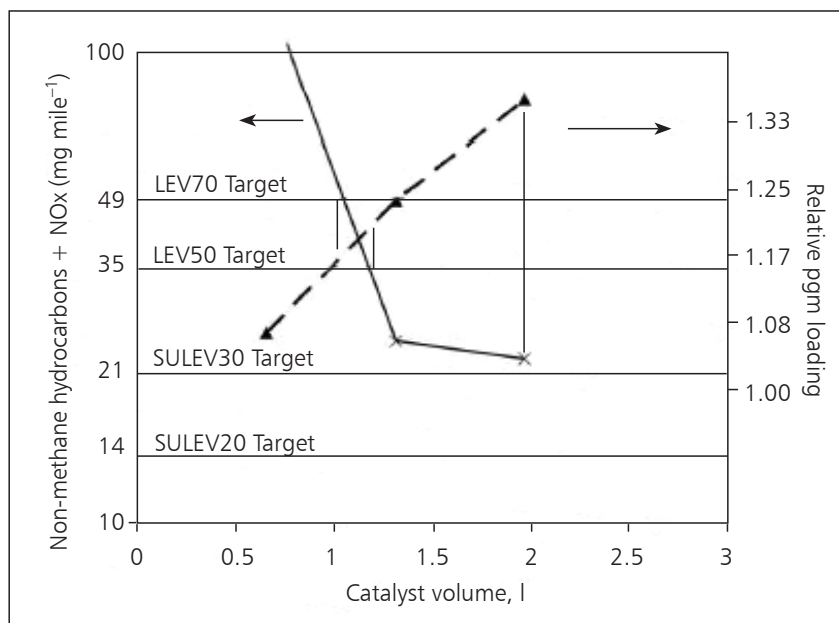


Fig. 4. Estimated required amount of pgm catalyst to achieve various emissions levels on a 2.0 l port-injection fuelled engine without secondary air (14)

Approximately 2 l of catalyst will be needed to achieve the SULEV 30 target, compared with about 2.5 l of catalyst to achieve the same result on a 2.4 l engine with secondary air.

In an entirely different approach to evaluating pgm loadings and emissions, Michael Zammit (Chrysler Group LLC, USA) *et al.* (15) changed the distance from the engine of a close-coupled TWC and measured the emissions. They made estimates of the increased pgm loadings to offset the increased distance while keeping the emissions the same: an additional 37–50 mg Pd per cm of distance from the engine.

To meet the new gasoline particle number regulations of the light-duty Euro 6 regulation in 2017, there is much interest in gasoline particulate filters (GPFs). Early testing was done with uncatalysed filters, but current evaluations use a TWC coating on the filter. Joerg Michael Richter *et al.* (Umicore Autocat Luxembourg) (16) evaluated two different coated configurations with identical total pgm loadings. In one configuration the pgm was distributed evenly between the close-coupled TWC and the GPF; in another configuration, the close-coupled catalyst was optimised by zone-coating the Pd so that 80% of it is on the front half. The investigators found that the NO_x emissions dropped by 20% in the first coated GPF configuration compared to the baseline configuration without a GPF. With an optimised zone coating on the close-coupled catalyst, 6% less pgm was used compared to the baseline, NO_x emissions remained at the low level, but CO emissions were reduced by 30% compared to the other GPF configuration. The researchers reported that the TWC on the GPF aided filter regeneration. No fuel penalty was observed when the GPF was applied.

Conclusion

Work is continuing on utilising Pt and other precious metals more effectively to meet tightening tailpipe emission regulations and reduce costs. Examples highlighted in this Congress review include the more efficient use of Pt in LNTs by distributing it preferentially on the CeO₂ portion of the washcoat. In other work, Pt was applied to a DPF resulting in the enhancement of soot burn by NO₂ by three or four times at 450°C due to the recycling of the NO_x molecule in the vicinity of the soot layer. Soot oxidation by NO₂ was found to be adversely impacted by sulfur in fuel and this could impair the performance of POCs. The functionality

of Pt in field-aged DOCs was impaired by ash in the front portions, adversely impacting HC oxidation, and by thermal ageing in the back, affecting NO oxidation. The pgm loading of TWCs could be cut by 75% by layering the catalyst, placing higher activity Pd and a lower activity oxygen storage catalyst in the top layer. Also, more is being learned on whole system design, such as the effects of catalyst placement, turbocharging, secondary air and fuel injection strategies, and the impacts that these factors have on catalyst loadings. Finally, this Congress featured catalysed GPFs for the first time, showing better system performance if some pgm was moved from the close-coupled catalyst to the GPF.

References

- 1 SAE International: <http://www.sae.org/> (Accessed on 29th January 2013)
- 2 T. V. Johnson, 'Vehicular Emissions in Review', *SAE Int. J. Engines*, 2012, **5**, (2), 216
- 3 K. Suga, T. Naito, Y. Hanaki, M. Nakamura, K. Shiratori, Y. Hiramoto and Y. Tanaka, 'High-Efficiency NO_x Trap Catalyst with Highly Dispersed Precious Metal for Low Precious Metal Loading', SAE Paper 2012-01-1246
- 4 Y. Tsukamoto, H. Nishioka, D. Imai, Y. Sobue, N. Takagi, T. Tanaka and T. Hamaguchi, 'Development of New Concept Catalyst for Low CO₂ Emission Diesel Engine Using NO_x Adsorption at Low Temperatures', SAE Paper 2012-01-0370
- 5 K. L. Shiel, J. Naber, J. Johnson and C. Hutton, 'Catalyzed Particulate Filter Passive Oxidation Study with ULSD and Biodiesel Blended Fuel', SAE Paper 2012-01-0837
- 6 C. J. Kamp, A. Sappok and V. Wong, 'Soot and Ash Deposition Characteristics at the Catalyst-Substrate Interface and Intra-Layer Interactions in Aged Diesel Particulate Filters Illustrated Using Focused Ion Beam (FIB) Milling', SAE Paper 2012-01-0836
- 7 P. Bielaczyc, J. Keskinen, J. Dzida, R. Sala, T. Ronkko, T. Kinnunen, P. Matilainen, P. Karjalainen and M. J. Happonen, 'Performance of Particle Oxidation Catalyst and Particle Formation Studies with Sulphur Containing Fuels', SAE Paper 2012-01-0366
- 8 F. Schrade, M. Brammer, J. Schaeffner, K. Langeheinecke and L. Kraemer, 'Physico-Chemical Modeling of an Integrated SCR on DPF (SCR/DPF) System', SAE Paper 2012-01-1083
- 9 J. Li, T. Szailer, A. Watts, N. Currier and A. Yezerets, 'Investigation of the Impact of Real-World Aging on Diesel Oxidation Catalysts', SAE Paper 2012-01-1094
- 10 F. Mollo and D. Vezza, 'Characterization of a New Advanced Diesel Oxidation Catalyst with Low Temperature NO_x Storage Capability for LD Diesel', SAE Paper 2012-01-0373

- 11 C. Henry, A. Gupta, N. Currier, M. Ruth, H. Hess, M. Naseri, L. Cumararatunge and H.-Y. Chen, 'Advanced Technology Light Duty Diesel Aftertreatment System', US Department of Energy 2012 Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Dearborn, Michigan, USA, 16th–19th October, 2012
- 12 K. Ishizaki, N. Mitsuda, N. Ohya, H. Ohno, T. Naka, A. Abe, H. Takagi and A. Sugimoto, 'A Study of PGM-Free Oxidation Catalyst γMnO_3 for Diesel Exhaust Aftertreatment', SAE Paper 2012-01-0365
- 13 Y. Matsuzono, K. Kuroki, T. Nishi, N. Suzuki, T. Yamada, T. Hirota and G. Zhang, 'Development of Advanced and Low PGM TWC System for LEV2 PZ EV and LEV3 SULEV30', SAE Paper 2012-01-1242
- 14 D. Ball and D. Moser, 'Cold Start Calibration of Current PZEV Vehicles and the Impact of LEV-III Emission Regulations', SAE Paper 2012-01-1245
- 15 M. Zammit, J. Wuttke, P. Ravindran and S. Aaltonen, 'The Effects of Catalytic Converter Location and Palladium Loading on Tailpipe Emissions', SAE Paper 2012-01-1247
- 16 J. M. Richter, R. Klingmann, S. Spiess and K.-F. Wong, 'Application of Catalyzed Gasoline Particulate Filters to GDI Vehicles', SAE Paper 2012-01-1244

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