Advanced Exhaust Emissions Control

A SELECTIVE REVIEW OF THE DETROIT 2000 SAE WORLD CONGRESS

This selective review covers papers, involving platinum group metal (PGM) catalysts, presented at the Society of Automotive Engineers (SAE) annual Detroit World Congress, held from 6th to 9th March, 2000. The Congress attracts large numbers of attendees (49,249 this year from more than 80 countries), and there were some 1,300 exhibiting companies with a similar number of papers presented at the well-attended technical sessions. Almost all of the published papers referred to here are conveniently collected together in SAE "Single Publications" (1), and reference is given in parenthesis to each cited paper to enable those interested to easily access them.

Towards and Beyond SULEV

The effectiveness of PGMs in three-way catalysts (TWCs) has increased over recent years as more advanced washcoat formulations have been introduced. The distribution of PGMs in the catalyst is important, and ASEC (2000-01-0860) found that by having a palladium-only front catalyst followed by one containing platinum and rhodium was an effective solution in some LEV/ULEV applications because the palladium catalyst ensured optimal hydrocarbon light-off. The design of such low emissions systems has become relatively commonplace. The next major emissions target is the American SULEV (half ULEV levels) which seriously challenges all of the available technologies. Here advanced catalysts are incorporated into systems that push technology to the limits to give the lowest possible emissions for conventional gasoline engines.

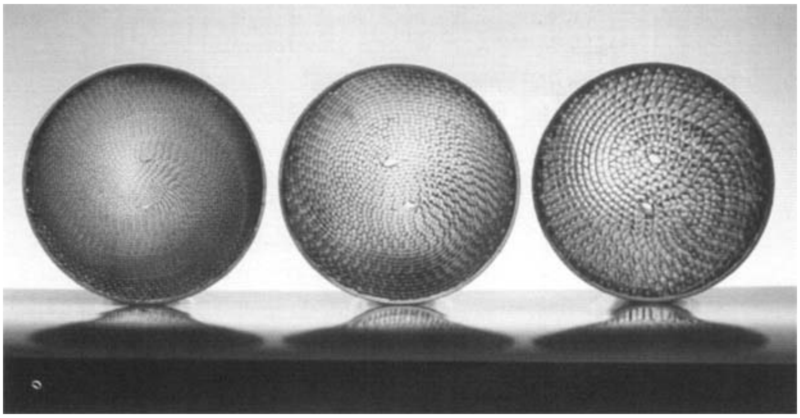
High Cell Density Catalysts

Thin wall high cell density substrates provide high geometric surface area, that can be accompanied by low heat capacity which can shorten the time it takes for catalysts to light-off during the cold start of conventional gasoline engines – the key parameter in achieving very low emissions. This was an important theme at the last congress (2), and the trend continued this year. Denso (2000-01-0496) discussed ultra thin wall 3 or 2 mil (75, 50 μm) cordierite substrate, and highlighted material requirements of the front face, particularly when located close to the exhaust manifold. To increase strength, the walls of the outermost cells were made thicker than the inner ones. This could exacerbate radial maldistribution of gas across the catalyst, and the practical consequences of this have yet to be explored. NGK and Environex (2000-01-0494) developed computer models to predict performance of catalysts based on ultra thin wall high cell density substrates. Their results showed that reducing wall thickness to reduce thermal mass offers the greatest benefit in reducing light-off time. Higher cell density *per se* is however accompanied by extra thermal mass, and a cell density of around 1200 cpsi appeared to give optimum light-off. Johnson Matthey (2000-01-0502) also reported computer simulation of these effects, and gave extensive results for catalysts with cell densities up to 900 cpsi (2 mil walls) on laboratory engines and cars. Significant benefits were observed with palladium/rhodium and palladium-only formulations on high cell density substrates, but appropriate engine calibration is vital. There may be little benefit obtained from using high cell density catalysts if the engine calibration is poor: for example, a European Stage 2 car with a rich start-up strategy showed a nitrogen oxides (NOx) advantage with high cell density catalyst, but hydrocarbon (HC) and carbon monoxide (CO) advantages were swamped.

Another requirement for advanced substrates is that the catalyst formulation must have very good thermal durability, because high cell density catalyst will experience high temperatures caused by more intensive chemical exotherms.

Metallic Substrates

These can be made from very thin metal foil to achieve high cell densities; but disadvantages can include the higher thermal capacity of metals



Although less commonly used than their ceramic (cordierite) counterparts, metal catalyst substrates have been used in automotive applications for many years. Manufacturing techniques have been developed to produce them in very high cell density forms using extremely thin metal foil

compared to porous ceramic materials. For several years Bosal (2000-01-0497) have been working with pre-coated metal foil, and they described how they produce a modular block design catalyst using 50 μm metal foil. These are assembled into V-shapes across the exhaust gas flow. This design offers the advantage of being able to use high cell density units without overly increasing pressure drop as the facial area can be increased in proportion to the cell density, provided the necessary space is available.

In a joint paper AVL and Emitec (2000-01-0500) used computer simulation to probe the behaviour of normal high cell density catalyst designs in a cascade modular arrangement with an electrically heated catalyst. Tests were carried out on an ULEV production vehicle, and with the electrically heated catalyst operating for 25 seconds at 2.5 kW the light-off time shortened from 30 to 22 seconds, but SULEV HC levels were not achieved.

Hydrocarbon Traps

Trapping HCs formed during the cold start in a material such as a zeolite until the TWC has reached light-off temperature is a potential route to very low emissions. The University of Thessaly (2000-01-0655) developed a computer model for a system with a HC-trap in front of a main catalyst. With this configuration, desorption from the HC-trap, before the catalyst reaches operating temperature, is a major problem that is difficult to circumvent. Ford (2000-01-0654) modelled a catalysed HC-trap, that combines catalyst and HC-trap on a single substrate. Here the thermal problems associated with separate units were overcome, and the model predicted good performance on a vehicle. The computer model should permit design of optimised systems in the future. Nissan (2000-01-0892) presented results for systems comprising a closed-coupled TWC followed by underfloor two-layer catalysed hydrocarbon traps. These had a lower layer HC absorber, and a top TWC layer, and the overall system demonstrated potential for SULEV applications.

Vehicle Demonstrations

Volvo (2000-01-0894) discussed three SULEV approaches: hydrogen (H_2) injection onto the catalyst when starting, a rich start-up with rapid temperature rise and air injection, and storing start-up HCs in a canister until the catalyst is operating.

Each has the potential of providing SULEV requirements, but the most attractive is the second, requiring least modification to current designs. By bringing together several different technologies on vehicles, emissions below the SULEV levels can be achieved. Nissan (2000-01-0890) described the combination of ultra thin wall (2 mil) substrate coated with low light-off catalyst, and a two-stage catalysed HC-trap, on an engine with tight air:fuel ratio control. The cold start HCs from the engine were minimised by incorporating an electronically actuated swirl control valve, and a high-speed starter. The resulting vehicle emissions were exceptionally low, as they also were from a car described by Honda (2000-01-0887). Honda used 1200 cpsi (2 mil walls) substrates made possible by a new canning method, which overcomes strength problems. However, to meet SULEV standards it was necessary to adjust the spark timing to decrease the time to reach catalyst light-off temperature, and to control intake air (early lean operation), and use an advanced secondary oxygen sensor feedback system. This identifies different catalyst models in real time and predicts the post-catalyst sensor output, so eliminating emissions that would be released while the control system adjusted to the actual secondary sensor signal.

NOx-Traps for Lean-Burn Gasoline Engines

The new generation of direct injection, lean-burn gasoline engines offers potential improved fuel economy, but requires NOx emissions to be trapped when running lean, and periodic regeneration under rich conditions to release the stored NOx as nitrogen (N_2). This developing NOx-trap technology, which uses platinum and rhodium, suffers from sulfur poisoning, and NOx-traps need to be purged of sulfur periodically. Both regeneration conditions require careful engine management to achieve the desired effects without affecting driveability, but desulfation is the more difficult because of the higher temperatures involved.

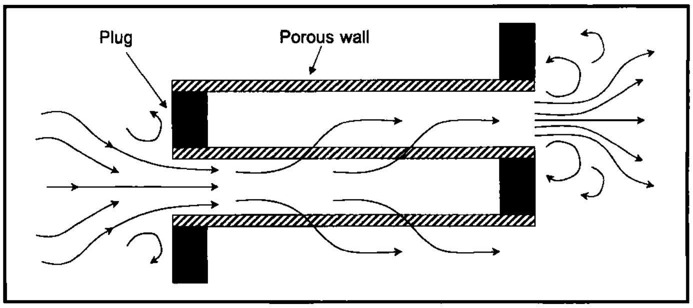
Ford (2000-01-1200) described a novel way of sustaining high catalyst temperature by rapid air:fuel ratio fluctuations. The oxygen storage components in the NOx-trap respond to this and generate isotherms of around 300°C, without being overall rich. Toyota (2000-01-1196) investigated ways of restricting the amount of accumulated sulfur, and found that incorporating titania and zirconia into the formulation was beneficial. Honda (2000-01-1197) also reported formulation work, and found addition of "mixed metal oxides" of different types improved performance.

Diesel Aftertreatment

Control of Diesel Particulate Emissions

Diesel soot, formed by incomplete combustion of fuel, is a potential health hazard and it is desirable to minimise soot emissions into the environment (3). It comprises a high surface area carbon core with adsorbed HC, partially oxidised species like aldehydes, carboxylic acids, etc., with water, sulfur compounds (including sulfuric acid), and some nitric acid derived from nitrogen oxides. Over recent years improved fuelling, better combustion system characteristics, and enhanced engine management have contributed to a reduction of soot. However, the introduction of finer fuel spray from new injector nozzles, made possible by higher-pressure fuel systems, was probably the single most important advance (4). The development of the high performance modern high speed diesel engine also provided means of reducing exhaust pollutants, and additional benefits are now coming from use of increasingly-available ultra low sulfur fuel with low polyaromatic content which produces less soot than conventional diesel fuel (5).

Johnson Matthey (2000-01-0479) described a procedure to lower particulate emissions from older American diesel buses (built before 1994) by 25%, or to below 0.1 g bhp^{-1} h^{-1}, by replacing some engine components, and fitting a platinum oxidation catalyst to provide additional particulate



Exhaust gas flow patterns through a wall-flow diesel particulate filter. Contributions to pressure drop across an empty filter include entry and exit effects, and the most important factor, flow through the porous walls. The overall pressure drop goes up as increasing amounts of soot cover the inner walls, highlighting the value of the continuously regenerating trap (CRT™) concept reduction. Platinum oxidation catalysts can remove some organic components from soot, but usually significant amounts of carbon are not oxidised.

Diesel Particulate Filters

Future legislation demands much lower particulate emissions than are made possible by engine modifications and oxidation catalysts, and a particulate filter, of which there are several kinds, will have to be used. Corning (2000-01-0184) derived and experimentally verified a pressure-drop model for clean cordierite wall-flow filters. Agreement between predicted and measured pressure drop was excellent. The approach is being extended to filters loaded with soot, and preliminary data for lightly loaded filters were presented: lower cell densities are appropriate for longer filters, and higher cell densities for short ones. Extension of this work should permit prediction of optimised filter length, volume, and cell density for particular applications. Ibiden and Peugeot (2000-01-0185) studied the characteristics of silicon carbide wall-flow filters along similar lines, and concentrated on the thermal durability and high temperature resistance. Their model for a loaded filter assumed a uniform soot layer, with ash collecting at the end of the channels forming an inert zone.

The Continuously Regenerating Trap

For continued operation it is necessary to remove trapped soot from a diesel particulate filter, and several ways of doing this have been investigated. Johnson Matthey (2000-01-0480) reviewed heavy-duty diesel experiences with a successful approach which uses nitrogen dioxide (NO_2) to combust trapped soot at temperatures much lower than it burns in air. The required NO_2 is obtained by oxidation of nitric oxide (NO) over a platinum catalyst before the filter, this also oxidises HCs and CO. Under most operating conditions soot is continuously removed, so the system is referred to as a continuously regenerating trap (CRT™). Over six years more than 6000 of these have been utilised in European countries where the necessary low sulfur fuel was promoted – Sweden, Germany, the U.K., and to a lesser extent in several other countries. A selection of CRTs which had been used for up to 600,000 km was tested under laboratory conditions. There was virtually no deterioration of performance, confirming the robustness of this system in actual use. A lighter duty application of the CRT™ was described by AVL (2000-01-0181) who have developed a diesel engine for Sports Utility Vehicles (SUVs) which meets the American Tier 2 emissions levels.

Peugeot (2000-01-0473) used a CRT configuration of a platinum oxidation catalyst in front of a silicon carbide wall-flow filter on a European diesel car which should soon be in production. Strategies are incorporated to increase exhaust gas temperature through post combustion fuel injection, and the fuel is dosed with a cerium additive to facilitate soot combustion. Faurecia (2000-01-0475) discussed cordierite and silicon carbide wall-flow filters, and proposed an oxidation catalyst in front of the filter in a CRT configuration that included an electrical heater close to the filter to increase gas temperature when appropriate.

Control of Diesel NOx Emissions

Lean-NOx Catalysts

Diesel exhaust contains low levels of reductant (CO, HC) in the presence of a vast excess of oxygen, and most of the reductant is oxidised by the oxygen over platinum oxidation catalysts. Little reductant remains to reduce NOx (and only over a small temperature range), so normally only a relatively small amount of NOx is removed by what are called lean-NOx catalysts under normal conditions, and this can be somewhat increased if additional reductant is added to the exhaust.

Selective Catalytic Reduction

To achieve significant direct NOx reduction additional reductant that selectively reduces NO in the presence of oxygen must be introduced – a process called selective catalytic reduction (SCR). Ammonia is an excellent reductant in SCR systems, and although at present it appears inappropriate to use PGM-based SCR catalysts, platinum catalysts are used in two different roles in these systems. Urea is potentially a convenient source of ammonia, and Degussa (2000-01-0189) described a urea-based SCR system for heavy-duty diesel applications. This had a platinum pre-oxidation catalyst, a hydrolysis catalyst and a vanadium-based SCR catalyst, followed by a platinum guard catalyst to prevent traces of ammonia from escaping into the environment by oxidising it to NO which is environmentally less sensitive. Using a simple urea dosing strategy a NOx reduction of 77% was recorded in the ESC test procedure (European Stationary Cycle, a heavy-duty diesel test cycle).

Mack Truck and Siemens (2000-01-0190) reported results for an American 12 litre heavy-duty diesel engine, and a Class 8 truck equipped with a vanadium SCR system. This returned NOx reductions averaging 65% in road tests, with a urea solution consumption of a little less than 100 mpg, and with another catalyst 140 mpg based on OICA test cycle data (Organisation Internationale des Constructeurs d'Automobiles, a heavy-duty diesel test cycle).

Johnson Matthey (2000-01-0188) described a urea-based SCR unit integrated with a CRT™. Combined particulate and NOx control was evaluated on several engines over a number of different test cycles. Simultaneous NOx conversions of 75–90% and particulate control up to 90% on current engines in both American and European test procedures were measured. A platinum oxidation catalyst was used before the particulate filter, SCR catalysts after ammonia injection for NOx reduction, and a platinum oxidation catalyst to control ammonia slip. The platinum pre-catalyst significantly enhances low temperature SCR performance by converting some NO to NO_2 which reacts faster, perhaps via reactive surface species of a N_2O_3 type. Although many challenges have to be overcome, SCR systems have demonstrated high efficiencies for NOx reduction, and in combination with particulate control capability, the way towards ultra clean diesel engines is being defined.

Conclusions

Emissions of exhaust pollutants from internal combustion engines in automotive applications have been dramatically reduced over recent years. This trend continues, and new technologies are being successfully developed to meet increasingly demanding requirements. The Detroit 2000 SAE Congress provided a focus for discussion about these developments, and confirmed the critical role PGM-containing catalysts have in this important area.

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References

1 "Diesel Exhaust Aftertreatment 2000", SP-1497; "General Emissions Research", SP-1506; "LEV-II Emissions Solutions", SP-1510; "Advanced Catalysts Substrates and Advanced Converter Packaging", SP-1532; "Exhaust Aftertreatment Modeling and Gasoline Direct Injection Aftertreatment", SP-1533. These and individual technical papers are available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096, U.S.A. See also: http://www.sae.org

2 M. V. Twigg, *Platinum Metals Rev.*, 1999, 43, (3), 119

3 "First International Conference on Health Effects from Vehicle Emissions", London, 16–17 February 1999; see also J. P. Warren, *Platinum Metals Rev.*, 1999, 43, (2), 71

4 See papers in: "In-Cylinder Diesel Particulate and NO Control 2000", SAE SP-1508 (2000)

5 In the U.K. diesel fuel typically now contains less than 50 ppm sulfur

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HEALTH EFFECTS OF VEHICLE EMISSIONS

A REVIEW FROM THE SECOND INTERNATIONAL CONFERENCE

The Second International Conference on Health Effects of Vehicle Emissions was held in London from 23rd to 24th February, 2000. Some 165 delegates from 16 nations, and a variety of industrial, environmental, government and academic backgrounds, met to discuss issues concerned with reducing the environmental impact and health risks associated with vehicle emissions.

J. Wallace (Ford, U.S.A.) summarised some U.S. steps with respect to vehicle emissions. Since 1966 vehicle emissions have been reduced by a factor of 25. Hydrocarbon emissions have decreased by