Exhaust Emissions Control Developments

A SELECTIVE REVIEW OF THE DETROIT 2001 SAE WORLD CONGRESS

The Society of Automotive Engineers' (SAE) Detroit World Congress in the Cobo Center (5th–8th March) was a great success, with some 50,000 delegates, and about 1300 technical presentations. There were many well-attended sessions on the control of engine exhaust emissions, and this selective review focuses on papers concerned with platinum group metal (pgm) catalysts. Platinum oxidation catalysts are used in selective catalytic reduction systems which use ammonia or urea, but these are not discussed here. The reference numbers of papers mentioned are given, most being available in SAE "Single Publications" (1).

Three-Way Catalysts

With conventional gasoline engines, the first objective in obtaining the very strict legislated hydrocarbon (HC) emissions requiring 99% conversion is to have the catalyst operating (light-off) within seconds of starting the engine. To achieve this a low-temperature light-off catalyst and an engine start-up procedure that rapidly heats the catalyst are required. It is essential to minimise heat losses, and computer models are used to understand the interplay between various components.

Volkswagen (2001-01-0940) described a simulation package for calculating gas/solid heat and mass transfer in exhaust systems. They studied the effects of conventional single-wall exhaust pipes, pipes with air-gap insulation, flanges, and flexible couplings. Their results indicated that conserving heat is essential for reducing catalyst light-off times and HC emissions during the crucial first seconds. Excess oxygen was beneficial with standard catalyst heating strategies (lean operation of the catalyst), and having oxygen stored in the catalyst was important.

Volvo (2001-01-1311) reported a new lean start-up strategy for five- and six-cylinder engines. They described how the 99% conversion/lambda window gradually decreased with time. Partial zero emission vehicles (PZEVs) require 150,000 miles durability. Heat losses and catalyst warm-up time are minimised by placing the catalyst close to the exhaust manifold. But in this 'close-coupled' position, it can be subjected to exhaust gas pulsation, poor mixing and high-temperature excursions which could be detrimental to performance.

Nissan (2001-01-0943) modelled the gas flow and heat transfer for a close-coupled catalyst configuration, and concluded that during low engine-load conditions, for example during catalyst warming, it is difficult to concentrate the gas flow in the centre of the catalyst and this can delay light-off. The difficulty in obtaining SULEV emissions was illustrated by projects that failed to achieve them (2001-01-1313, 2001-01-1314).

Threshold catalysts (deactivated so emissions are outside the legislative limits by a prescribed amount) are needed to calibrate on-board diagnostic (OBD) systems. The catalysts are often made by very high-temperature treatments that can degrade the substrate. Shell, DaimlerChrysler and Emitec (2001-01-0933) reported that a high-temperature vacuum treatment can achieve required activation without causing substrate deterioration.

The price of palladium (2) has been an incentive to develop high performance TWCs based on Pt/Rh rather than Pd/Rh. A paper by DaimlerChrysler and dmc^2 (2001-01-0927) described a durable two-layer Pt/Rh catalyst that at reduced pgm loadings could replace close-coupled and underfloor Pd/Rh catalysts on engines that rapidly warm the catalyst. On engines with less rapid heating strategies Pd-based catalysts were favoured in close-coupled positions due to a better HC performance. Probably for similar reasons, ASEC (2001-01-0923) in some two-catalyst configurations, favoured a Pd-only front catalyst followed by a Pt/Rh catalyst. Light-off of the front catalyst was improved if it did not contain ceria, and had only a small oxygen storage capacity (OSC).

Ford and the Kunming Institute of Precious Metals (2001-01-0225) confirmed that relatively low-loaded pgm TWCs containing appropriate oxygen storage components can be used for emission control in emerging markets. If carbureted Chinese cars were retrofitted with catalysts, emissions could be significantly reduced.

NOx-Trapping Catalysts

Catalysts that store NOx as nitrate (NO_3^-) under lean conditions, via nitric oxide (NO) oxidation over Pt to nitrogen dioxide (NO_2), and which are reacted with a pulse of reductant (CO and HCs) to give N_2, are called NOx-traps or NOx-absorbing catalysts. These are being developed for use on lean-running gasoline and diesel engines. Temperatures below 550°C are required for efficient NOx removal, so NOx-traps are usually located underfloor.

Mitsubishi and ICT (2001-01-1300) discussed catalyst systems for direct injection gasoline engines, comprising a close-coupled TWC, an underfloor NOx-trap followed by a second TWC. The close-coupled TWC controls start-up HC (a Pd/Rh formulation was originally used). The OSC was minimal because stored oxygen increases the amount of fuel consumed during NOx-trap regeneration. Several Pt/Rh catalysts were evaluated in the close-coupled position. A single layer Pt/Rh catalyst had poorer HC oxidation performance under lean conditions than a Pd/Rh catalyst. Performance was substantially improved when the Pt and Rh components were in separate layers.

Toyota (2001-01-1297) modelled the duration of the rich pulse during NOx-trap regeneration. They confirmed that regeneration rate increases as the duration of the rich pulse increases, and that heat produced during regeneration (and by reduction of stored oxygen) heats the downstream part of the NOx-trap causing NOx to be released. These effects are taken into account when designing and sizing NOx-traps. NOx-traps react with sulfur dioxide (SO_2) in exhaust gas, storing it as sulfate (SO_4^{2-}). This gradually decreases the NOx capacity of the trap. To overcome this a NOx-trap must be periodically desulfated under rich conditions at temperatures higher than needed to remove stored NOx. Mild desulfation gives SO_2, but rapid desulfation requires high temperatures and more strongly reducing conditions and may lead to undesirable H_2S formation.

Ford (2001-01-1299) addressed this problem and described two methodologies to minimise H_2S production; one used a 'H_2S getter', such as a nickel compound that forms a stable sulfide; the second involved the use of short lean pulses during high-temperature rich desulfation. This was sufficient to re-oxidise sulfide to SO_2. The combination of both methods should be interesting.

Alkali metals form stable nitrates, so could be used in NOx-traps. However, they are mobile at high temperatures in the presence of steam, and react with cordierite substrate causing loss of the NOx storage component, and deterioration of substrate properties. Mitsubishi, ITC and NGK (2001-01-1298) reported three approaches to overcome these problems. The first was to retain alkali in the washcoat by reaction with an acidic component: a zeolite was chosen. The second approach was to protect the substrate with a silica pre-coat, and the third was to minimise sulfur accumulation by incorporating titania in the washcoat. Combining all three modifications afforded a NOx-trap with improved overall thermal resistance.

Diesel NOx-Traps

Diesel NOx-traps have special demands: diesel engines operate at cool temperatures and are specifically designed to run lean, so obtaining rich regeneration conditions is a challenge. ASEC (2001-01-0508) described work confirming that NOx-traps can be desulfated at 650°C and at an air:fuel ratio ~ 13. A programme involving FEV, National Renewable Energy Laboratory, MECA, Battelle, Ford, ASEC and Detroit Diesel examined desulfation of NOx-traps in diesel applications; finding NOx conversion efficiency could be restored. A NOx-trap aged for 250 hours running on 30 ppm sulfur fuel had its NOx conversion efficiency fully restored by a single desulfation. However, with repeated desulfations performance gradually decreased. The reason for this is unclear, but may be due to the regeneration procedure.

Diesel Particulate Filters

Diesel engines run lean and have excellent fuel economy, but removing particulate matter (PM) from the exhaust gas is difficult. Over recent years the amount of soot has been lowered dramatically through higher injector pressures, better fuel atomisation, and by improved fuel management and combustion control. However, it is generally thought that 'clean diesel' requires a Diesel Particulate Filter (DPF), and the most common DPF is a ceramic wall flow filter.

Understanding the fluid dynamics of DPFs was extended by presentations from Michigan Technological University, CERTH/CPERI and Corning (2001-01-0908, 2001-01-0909, 2001-01-0911) describing three flow mechanisms which contribute to pressure drop: filtration inertia losses, channel inlet contraction and channel exit expansion loses. Exit losses are dominant, being about twice those at the filter inlet. The models estimate filter pressure-drop as a function of loading and agree well with observations. The influence of inlet radial non-uniformity can lead to partial regeneration near the periphery. The practical challenge is to burn trapped soot without high temperatures damaging the filter.

One successful approach used low-temperature oxidation of soot with NO_2 obtained by oxidising NO in the exhaust gas over a Pt catalyst. In heavy-duty applications the temperature of the exhaust gas is usually high enough for this to occur. This system is known as the Continuously Regenerating Trap (CRT), or Continuously Regenerating Diesel Particulate Filter (CRDPF) and many thousands are installed on buses and trucks. Japanese/Finnish work (2001-01-1256) resulted in a procedure for increasing exhaust gas temperature at low engine speed for CRT operation without fuel penalty.

Experience with a test fleet of heavy-duty diesel vehicles fitted with CRTs in Southern California was reported by Johnson Matthey, National Renewable Energy Laboratory, BP and West Virginia University (2001-01-0512). The fleet included school buses, fuel trucks, and delivery and transit vehicles. The CRTs worked well and reduced PM, CO and HC in the exhaust by 90 to 99%. No measurable impact on fuel economy was noted. New York Environmental Conservation, Johnson Matthey, Environment Canada, Equilon Enterprises and Corning (2001-01-0511) reported the performance and durability of CRTs on diesel buses at New York City Transit. In this successful programme PM, CO and HC were reduced by over 90%, carbonyls by more than 99%, polyaromatic hydrocarbons (PAHs) by more than 80%, and nitro-PAHs by more than 90%.

NGK reported a computer simulation for high temperature regeneration of wall-flow filters, and performed 2D thermal stress analysis for different filter designs. Their results showed that the maximum temperature during soot combustion is moderated if the filter has high thermal mass and high thermal conductivity. These properties are larger for silicon carbide (SiC) than for cordierite, and explains why SiC is gaining popularity in potential light-duty diesel applications. Light-duty diesel vehicles have cooler exhaust gas than heavy-duty ones, and achieving high temperatures for DPF regeneration has an undesirable impact on fuel consumption, so the reaction of soot with NO_2 at moderate temperature is very beneficial. The regeneration of catalytic DPFs was discussed by Peugeot Citroën, dmc[2] and the University of Siegen (2001-01-0907). They showed that having catalyst in the DPF can have a small benefit in reducing the soot combustion temperature.

Conclusions

The integration of new advanced pgm-based catalysts into total systems for emissions control is achieving extremely low tail-pipe emissions levels. Currently it appears that the role of platinum is becoming relatively more important. This trend could well continue. M. V. TWIGG

References

1 "Advanced Catalytic Converters and Substrates for Gasoline Emission Systems" (SP-1573), "Advances in Combustion 2001" (SP-1574), "Diesel Exhaust Emissions Control: Developments in Regulation and Catalytic Systems" (SP-1581), "Diesel Exhaust Emissions Control: Diesel Particulate Filters" (SP-1582), "Direct Injection SI Engine Technology 2001" (SP-1584), "Emissions Measurements and Test Methods" (SP-1588), "General Emissions Technology" (SP-1590), "Emission Control Modeling" (SP-1605)

2 "Platinum", Johnson Matthey, London, 2000 and www.platinum.matthey.com for details of platinum and palladium prices

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