Emission Control Technology at Detroit

A SELECTIVE REPORT FROM THE 1997 SAE ANNUAL CONGRESS

Traditionally, the main annual Congress of the Society of Automotive Engineers (SAE) takes place each year in Detroit during the last week of February. This year it was held from 24th to 27th February, inclusive, and the scale of the event can be judged from the 800 exhibiting companies in the "exposition" areas, and the 45,180 officially registered participants, drawn from all the countries concerned in the manufacture of cars or their components. In total 1008 papers were presented, covering all aspects of automobile technologies; each day there were sessions dealing with exhaust emission control. Within this area a wide range of topics was considered. Most of the papers are available in SAE "single publications" SP1227, SP1238, SP1246, SP1248 and SP1260.

Here, a selection of these papers has been chosen to illustrate the changing roles that platinum group metals have in the important area of exhaust aftertreatment, and the direction that catalyst technology is taking. The SAE reference numbers of the original papers are given in parentheses.

The main emphases in emissions control this year, as last year, included cold start strategies and three-way catalysts (TWCs) for conventional gasoline engines. Additionally, there was a high level of interest in the treatment of exhaust gases from diesel and other lean burn engines.

Cold Start Strategies

Electrically Heated Catalysts

Last year several reports were presented on the use of electrically heated catalysts (EHC) for dealing with cold start emissions (1). This year Alpina, BMW and Emitec (970263) gave an update on the only European production car fitted with EHCs. Of the 100 vehicles produced, each was started on average four times per 100 km, and more than a third of them were cold starts where the coolant temperature was below 40°C. The EHCs worked well and had good mechanical durability during the first year of service. However, with the present combination of a 110 Ah^{-1} battery and 150 A alternator, the EHC system is not capable of dealing with low temperature starting, for example, at −7°C, mainly due to the high internal resistance of the battery under these conditions. Clearly, further developments are needed in this area before EHC technology is capable of being introduced more generally. A paper by the Polish company Bosmal (970740) emphasised that low ambient temperatures are common during winter in much of Eastern Europe and many parts of North America, and described the effects this has on the initial emissions.

A rich-start strategy with secondary air injection, and an EHC for rapid increase in the temperature of a low light-off catalyst, was discussed in a paper by Nissan (971022). Nissan noted that the volume of exhaust gas increases as the alternator load rises, which has the disadvantage of reducing the rate of the desired exothermic reactions over the catalyst. It was concluded that it is preferable to supply electric power for the EHC from a battery, but no comments were made on low-temperature starting. Interestingly, a correlation between fuel distillation temperature and exhaust gas temperature was observed, which suggested that fuel composition could influence the performance of the cold start catalyst.

Hydrocarbon Traps

Development of hydrocarbon trap technology to minimise cold start emissions for ULEV (Ultra Low Emission Vehicles) applications continues, and Johnson Matthey (970741) described how *in situ* mass spectrometry techniques showed that hydrocarbon traps are effective for trapping aromatic species, C_4 and higher alkanes and alkenes, but ineffective for the very volatile methane, ethane and ethylene constituents. The trapping performance for C_3 to C_5 hydrocarbons is improved when competition with water is minimised by using a "water trap" upstream of the hydrocarbon trap. Hydrocarbon trapping efficiency then increases from about 40 to 60 per cent during the first 10 seconds of a cold start.

Three-Way Catalysts

Promoters

Several papers discussed the roles of promoters, stabilisers and other components in autocatalyst formulations containing platinum group metals; these included an explanation of the chemistry of the NOx trap. A highlight was two entire sessions devoted to the uses of zirconia in emissions control applications, ranging from oxygen sensors to autocatalysts. A contribution from MEL Chemicals (970460) provided a useful general overview. The chemical inertness and refractory properties of zirconia have been exploited in high temperature chemical process catalysts in the past, and over recent years zirconia has been used both as a support for platinum group metals in autocatalysts to impart improved thermal resistance, and in oxygen storage components in combination with other oxides. N. E. Chemcat (970466) reported on the effects of dopants on the thermal stability of the surface area of zirconia – barium, calcium and lanthanum being the most effective dopants. They measured the oxygen storage properties of various ceria/zirconia mixed oxides. This was also a topic covered by other papers, for example, Rhône-Poulenc (970463) focused on the characterisation of cerium-rich ceria/zirconia mixed oxide phases.

A contribution from the University of Pennsylvania and W. R. Grace (970461) pointed out that conventional characterisation studies, such as X-ray diffraction, of these mixed oxides can result in misleading conclusions. This is because it is not the bulk structure of defective oxides that is important in controlling surface reactions, but rather local structure at the atomic level.

Sulfur Poisoning

In meeting emission requirements, high conversions of pollutants take place over modern TWCs, but even small changes in performance can affect tail-pipe emissions. Factors such as catalyst poisoning are therefore important. In fact, two papers from Johnson Matthey were concerned with poisoning due to sulfur. One paper (970739) concluded that the performance of standard palladium-only catalysts is more sensitive to sulfur poisoning than platinum/rhodium, palladium/rhodium, or platinum/palladium/rhodium catalysts. Also, controlling interactions between the palladium and cerium-containing components in the washcoat is critical for the achievement of high catalyst activity at high sulfur levels. However, optimised palladium-only catalyst is more active than standard palladium-only catalysts in the presence of relatively high sulfur levels, and recovers activity more quickly as sulfur levels are lowered.

This paper, and a second one (970737) showed, as expected, that palladium-only catalysts generally have superior hydrocarbon performance under all conditions, and that sulfur affects carbon monoxide and NOx conversions more adversely over palladium-only catalysts, than over formulations containing rhodium. A paper from the University of Dundee and MEL Chemicals (970468) suggested that the addition of zinc to palladium-only TWC formulations can have advantages when operating in the stoichiometric to lean-burn range.

NOx Traps

The main engine exhaust component of "NOx" is nitric oxide (NO) and, although thermodynamically it is unstable compared with nitrogen and oxygen, its dissociation is virtually impossible under normal engine exhaust conditions. Therefore, NO is most conveniently treated by reducing it catalytically to nitrogen, and water or carbon dioxide, depending on the reductant concerned. One of the most demanding challenges for catalytic emission control is thus the removal of NOx under lean conditions. Such conditions exist in diesel engine exhaust, and will become increasingly commonplace as lean-burn gasoline engines are introduced for improved fuel efficiency.

One means of treating NOx under lean conditions is to adsorb it in a "NOx trap" as a surface nitrate species. When the trap is saturated it is purged with a short, concentrated pulse of reductant to reduce the adsorbed NOx. All of the NOx traps so far described contain platinum and rhodium, and the main objective of this technology is to remove NOx without deterioration of vehicle driveability, or significant fuel penalty. In a paper from N. E. Chemcat (970745), the thermodynamics of the processes involved in NOx traps were discussed. Under lean conditions NO is oxidised to NO_2 over platinum, which then reacts with alkaline metal carbonate in the trap to form nitrate species. When conditions are reducing, the nitrate species are unstable, and decompose to the metal oxide and NO_2. The latter is reduced to nitrogen over platinum/rhodium, and the metal oxide reacts with carbon dioxide to reform the carbonate.

In a joint paper, Mercedes-Benz, Daimler-Benz and Degussa (970746) concentrated on the modes of deactivation of NOx traps. They stressed the need for low sulfur fuel to prevent sulfate formation, and showed that high temperature treatment can even improve stoichiometric three-way performance, but NOx storage features are irreversibly lost. This was identified as being due to the NOx absorption components reacting with washcoat components to form stable compounds, such as aluminates, zirconates and titanates. A second deactivation mode involves sintering of the platinum and rhodium (as well as the absorbent species) and leads to loss of surface area, thus significantly reducing the interface between these two materials, with the result that the rate of NO_2 spillover from the active metal, where it is formed, is markedly lowered.

Diesel Aftertreatment

In an update of global trends in diesel emissions control, Michael Walsh (970179) pointed out that the number of diesel engined light duty vehicles is steadily increasing in many parts of the world. This can result in positive environmental benefits: lower fuel consumption (reduced CO_2 emissions), reduced hydrocarbon and carbon monoxide emissions (enhanced by using platinum oxidation catalysts), and very low evaporative hydrocarbons, when compared to their gasoline counterparts. However, diesel engines have relatively high NOx and particulate emissions, but new advanced engine design and catalytic aftertreatment strategies are improving the situation. A related paper from Mitsubishi (970753) reviewed the global situation with heavy duty diesel vehicles, and had similar conclusions.

Sun Electric (970748) described a potentially versatile 90° backscatter measurement of particulates using a red laser that could be developed and refined for on-board applications using small solid state devices. Comparisons were made with opacity methods, and the advantages and disadvantages were discussed. Soot is a problem, with heavy duty diesel engines in buses and other vehicles used in inner cities for delivery and collection duties. A joint paper from Engine Control Systems, Environment Canada and the Ontario Ministry of Transportation (970186) reported the results of retrofitting platinum oxidation catalysts on heavy duty diesel vehicles. They concluded that oxidation catalysts can reduce particulate matter – mainly soluble organic fraction – and can significantly lower carbon monoxide and hydrocarbon emissions without increasing fuel consumption.

A joint paper from Johnson Matthey, HJS Fahrzeugtechnik, Eminox, Swebus and PESAG (970182) described extensive successful experiences of Continuously Regenerating Traps (CRTs) in heavy duty applications. The CRT removes a high proportion of carbon monoxide and hydrocarbons, and eliminates soot emissions by using the NO_2 formed over a special platinum catalyst to burn soot retained in a filter; this is a combustion process that takes place at relatively very low temperatures (2).

Conclusions

The Detroit conference this year has again shown that the platinum group metals have key roles to play in the technologies that enable vehicles to comply with increasingly stringent legislative demands. M.V. TWIGG

References

1 M. V. Twigg, *Platinum Metals Rev.*, 1996, **40**, (3), 110

2 P. N. Hawker, *Platinum Metals Rev.*, 1995, **39**, (1), 2