Advanced Three-way Catalysts

Optimisation by targeted zoning of precious metal

Three-way catalysts have been used to control gasoline-fuelled vehicle emissions for over twenty years, during which time significant advances have been made in performance. Nevertheless catalyst manufacturers strive for continual improvements, and further reduction of system costs remains a key target. This article summarises paper 2005-01-2158 given at the 2005 SAE Brazil Fuels and Lubricants Meeting.

Rhodium can be used exclusively in the rear of the catalyst for NO_x conversion with reduced precious metal loadings

One area of catalyst system design which has received relatively little attention is the method of application of precious metal, specifically with regard to its positioning in the catalyst. Recent advances in catalyst coating technology have enabled both washcoat and precious metals to be distributed inhomogeneously (zoned) along the length of a catalyst monolith. With the option of zone coating now available, it is important to assess what precious metal is appropriate in which position on the catalyst. It is also important to know how much or, from a cost point of view, how little needs to be applied in order to ensure regulatory compliance and cost-competitiveness. To evaluate the role of zoning in cost reduction, Johnson Matthey scientists have carried out detailed studies.

Background to testing

Two different state-of-the-art catalyst formulations were aged over a bench ageing cycle and then tested on vehicles. The first was 118.4 x 127 mm in size with a total platinum group metal (pgm) loading of 35 g/ft^3, a platinum:palladium:rhodium (Pt:Pd:Rh) ratio of 0:6:1 (known as "35/0:6:1"), cell density of 400 cells per square inch (cpsi) and wall thickness of 6.5 mil. This was evaluated over the MVEG-B cycle in the close-coupled position on a 1996 Model Year 1.25L Euro 2 compliant vehicle. It was also evaluated after having been cut in half and only the front portion replaced on the vehicle. Further catalysts tested on this vehicle were zoned catalysts with a front half loading of 35/0:6:1 and rear half loadings of 25/0:4:1, 15/0:2:1 and 5/0:0:1 (Rh-only).

The second catalyst measured 101.6 x 152.4 mm Pt/Rh, with a cell density of 600 cpsi, wall thickness 4.3 mil and a loading of 15/2:0:1 g/ft^3. This was also evaluated over the same cycle in the close-coupled position, this time on a 2001 Model Year Ford Focus 1.6L Euro 3 compliant vehicle. A length of 25.4 mm was then cut from the rear of the catalyst, and it was re-evaluated with a non-pgm (washcoat only) piece of catalyst replacing the portion removed, in order to ensure constant backpressure. The catalyst was further cut down in 25.4 mm stages and evaluated at each stage.

Vehicle testing

The results for the Pd/Rh catalyst, both full size and front half only are shown in Figure 1. Carbon monoxide (CO) emissions are barely affected by cutting it in half, hydrocarbon (HC) emissions have increased by only about 10% but emissions of oxides of nitrogen (NO_x) have nearly doubled, and are now outside the Euro 4 limit of 0.08 g/km. This suggests that the front half of the catalyst performs the vast majority of oxidation of HC and CO, but that the full volume is necessary for maximum reduction of NO_x.

To reduce the NO_x emissions whilst avoiding inclusion of the clearly unnecessary 30 g/ft^3 of Pd in the rear half of the catalyst, further full size

Vehicle testing

Figure 1: Comparison of emissions from full size and half size catalysts

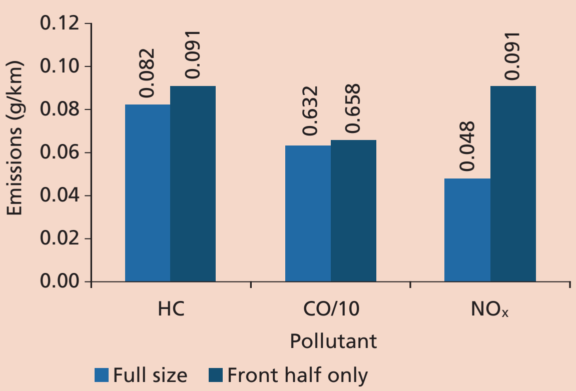
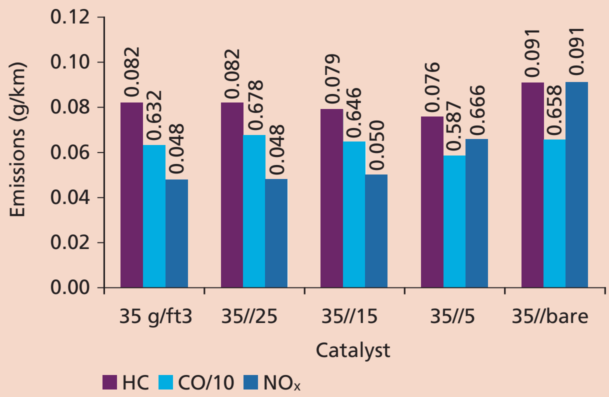


Figure 2: Comparison of emissions from homogeneous and zone coated catalysts



catalysts were tested with rear half loadings of 25/0:4:1, 15/0:2:1 and 5/0:0:1. The emissions results for these catalysts are shown in Figure 2.

Figure 2 shows that there is no significant difference between the homogeneously coated 35/0:6:1 catalyst and those with 25 and 15 g/ft³ i.e. 35//25 and 35//15 rear loadings for any of the pollutants. In other words the removal of most or all of the palladium from the rear half has not had any adverse impact on HC or CO emissions. A small increase in NO_x is seen when the rear half contains only rhodium, but the emissions remain well within Euro 4 limits. Only when all the Pd and Rh is completely removed from the rear half do the emissions exceed the NO_x limits. Furthermore, the coating method used enables the different pgm loadings to be present on a single catalyst rather than two smaller ones – a considerable cost saving over the possible alternative of using two differently loaded catalysts.

In order to investigate this phenomenon further, a 101.6 mm diameter catalyst was aged and tested at lengths from 152.4 mm down to 25.4 mm, in 25.4 mm increments on a Euro 4 compliant 1.6 L vehicle. The results are shown in Figure 3.

The results show that emissions increase in a non-linear fashion, indicating differing contributions to the overall conversion from each separate 25.4 mm portion. NO_x emissions increase throughout the length of the catalyst, and far more than CO and HC as the catalyst is cut down in size.

Vehicle testing

Figure 3: Comparison of emissions from catalysts of different lengths

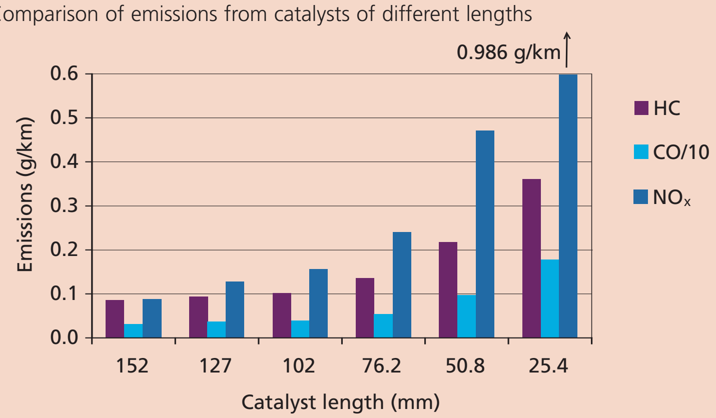
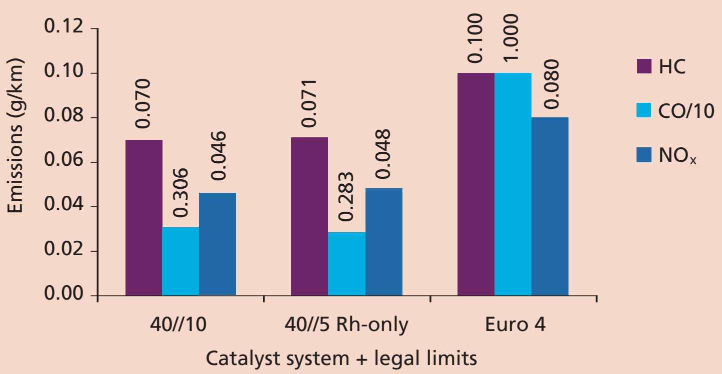


Figure 4: Comparison of Pd/Rh and Rh-only rear catalysts



Example of optimised zoned system

This work has led to several applications of the cost saving potential of the zoning strategy. One such is the case of a 40/0:7:1 catalyst, which had previously been used as a Euro 4 solution on a 1.6 L vehicle. Two possible cost saving strategies were tested, both based on zoning. The first was to reduce the pgm loading of the rear half of the system to 10/0:1:1, and the second was to replace the rear half with a single Rh-only formulation specifically developed for NO_x conversion, with a loading of 5 g/ft³.

Figure 4 shows that both of the aged catalyst systems are giving results well within the legal limits for all three pollutants. Furthermore the Rh-only system is showing equivalent performance to the 40//10 system.

The overall washcoat loading and backpressure of the catalyst with a Rh-only rear half have been significantly reduced as a result of the need only to apply multi-layer technology to the front half, and this can be achieved with no loss of performance. Both these solutions represent significant pgm cost saving (over $5 per catalyst at average 2004 prices) over the original system.

Conclusions

Systematic studies of emissions as a function of catalyst length have shown that pollutant conversion efficiencies along the length of a three-way catalyst are non-uniform. NO_x emissions are reliant on having the largest catalyst volume available, whereas CO and HC are overwhelmingly converted on the front portion of a catalyst system.

It is possible to coat different quantities of pgm throughout a catalyst system; in particular to apply less Pt or Pd to the rear. This has been shown to have little or no adverse impact on overall emissions performance. In essence, pgm can be applied only where it is needed, whilst retaining virtually all the activity of a homogeneously coated catalyst. This simple yet effective approach can result in very significant cost savings.