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Position dependent phenomena during deactivation of three-way catalytic converters on vehicles

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Abstract

Mapping procedures have been developed to characterise some of the position dependent phenomena occurring in three-way catalytic converters. The activity of small samples for the removal of CO, NO, propene and propane from a simulated mixture under slightly lean conditions was measured in a flow system and correlated with surface area. Contamination was determined by particle-induced X-ray emission (PIXE) with XRD used to follow structural changes in the washcoat. The procedures have been used to investigate a substantial set of converters which had seen extensive use on vehicles. Three of these converters, taken from vehicles which had failed a standard emission test, are discussed here. In one case, loss of surface area and CO/hydrocarbon/NO activity was greater at the front and is associated with phosphorus deposition. XRD measurements showed that operating temperatures were sufficiently high to result in the formation of cerium orthophosphate at the front and substantial growth in ceria particle size throughout which also contributed to activity loss. A second converter showed substantial loss of NO activity alone which was traced to high levels of lead, concentrated towards the front but significant throughout. A third converter of the same type had undergone a lesser loss of activity for NO removal at the front due to lead but the deterioration in CO and propene was greater towards the rear of the converter. This was associated with a loss of surface area caused by a period of overheating under net reducing conditions with XRD measurements showing the formation of cerium aluminate and a cerium barium magnesium hexaaluminate which are characteristic of such conditions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic converter; Monolith; Contamination; Cerium aluminate; Cerium barium magnesium hexaaluminate; Ceria particle size

1. Introduction

Catalytic converters are central to the control of automotive emissions. The emission control system must maintain a set of conditions that ensures that the converter will function reliably over 80,000 km in Australia, and more recently, 160,000 km in US. Increased emissions can occur as a result of engine/control system component failure [1] and/or loss of catalytic converter performance [1–4]. In some instances component failure causes subsequent converter failure which can occur by a variety of chemical, thermal and/or mechanical processes [4].

Common causes of performance loss include contamination/poisoning [5–7], masking [6], pore-mouth plugging [8], washcoat sintering [9], platinum group metal (PGM) sintering [10,11], washcoat interactions, meltdown [4] and bypassing [4]. In some studies, thermal deactivation has been shown to be the principal cause of deactivation [12,13] while in others, contamination has been observed to play a major role [8,14]. It is difficult to determine the degree to which each

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process contributes to the loss of activity. This problem has been studied using leaching [12,14], abrasion [8] and outlet-end sample selection/treatment techniques [15].

It has been known for a long time that contamination is usually concentrated at the front of monolithic converters [16] but other processes can lead to more deactivation elsewhere. However, there have been relatively few studies which have attempted to measure catalytic activity as a function of position in converters [5,13,17–20]. Most recently, Beck et al. [18–20] have used measurements of that type to show that phosphorus deposition, rather than thermal degradation, is the major cause of performance drop-off over the life of some current generation catalysts.

The aim of the present work was to develop procedures for characterisation of the various types of position dependent phenomena and to use this information to explain the loss of performance in a set of converters recovered during a program which evaluated in-use emissions from a vehicle fleet.

2. Experimental

Three of the catalytic converters were recovered from vehicles which had marginally failed an Australian emission test (ADR37/00, equivalent to US 1975 standards) as part of a testing program involving more than 400 vehicles selected at random [21]. The fourth converter, intended as a reference, was removed from a wrecked vehicle which had travelled only a short distance. All four converters were manufactured in the same plant in the years 1990–1992 using ceria/alumina washcoats of similar CeO_2 content (17–20 wt.%) deposited on the same type of cordierite monoliths (62 cells/cm^2) but with different amounts of PGMs. Details of each converter are given in Table 1. PGM content, and the contaminant analyses given later, were performed using particle-induced X-ray emission (PIXE) with procedures described elsewhere [22]. This method is semi-surface giving signals which are largely confined to the outer 20–30 μm.

Table 1
Converter origin and PGM content, wt.% of washcoat

Designation	Vehicle	Distance	Pt	Pd	Rh
No. 51	Nissan, 1.8L	3,000 km	0.29	Nil	0.074
No. 33	Ford, 4.0L	104,560 km	0.11	0.55	0.088
No. 62	GM, 3.8L	70,758 km	0.48	Nil	0.055
No. 63	GM, 3.8L	103,544 km	0.48	Nil	0.055

The converters were cut from the outer canisters using a high speed band saw. Samples were obtained by dividing each monolith axially and transversely with a hacksaw to produce small pieces 7 cells square and 20 mm in length which were pared to a cylindrical shape with a penknife. Each sample had a mass of ∼1 g and a volume of 1.57 cm^3. For mapping experiments, samples were removed sequentially along the same central axis. The same samples were used for activity, surface area and XRD measurements with the PIXE analyses carried out on samples taken adjacently. Surface area measurements and XRD diffractograms were obtained as described previously [23] with ceria particle sizes calculated from X-ray line widths using the Scherrer equation with the instrumental line width determined by measurements on crushed quartz.

Activity testing was carried out with each sample placed centrally in a silica reactor tube, 450 mm in length and 13 mm OD, and resting on a sheathed K-type thermocouple. A small quantity of quartz wool was packed before and after the sample. The reactor tube assembly passed through an aluminium cylinder located at the centre of a tubular furnace and supported from a stainless steel flange resting on top of the furnace. The temperature during ramping was controlled from a second thermocouple located in the aluminium block. The test mixture (10,300 ppm CO, 490 ppm propene, 197 ppm propane, 2,680 ppm H_2, 1,040 ppm NO, 9,400 ppm O_2, balance He) was made by blending standard gas mixtures supplied by BOC (Australia) using Brooks 5850E mass flow controllers. The total flow rate was 205 cm^3/min giving a space velocity of ∼10,000 h^{-1} at STP. The above composition is slightly lean with a redox ratio (the ratio of oxidants required for total oxidation divided by that in the O_2 and NO supplied) of 0.98.

The output of the flow system was fed to a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and a Unibeads A, mesh 80/100, 1.8 m column for separation of propane and propene. The product stream leaving the column loop of the GC was diluted with nitrogen by a factor of ∼50 to bring the maximum concentration of CO and NO within the dynamic range of the analysers downstream.

Carbon monoxide was measured with a non-dispersive infrared photometric analyser (Monitor Labs type 9830) and NO using a chemiluminescent analyser (Monitor Labs type 9841).

Analogue signals from both analysers and the thermocouples were fed to a personal computer fitted with a PCL812 A/D input card which was used to ramp the furnace temperature and continuously monitor removal of NO and CO. The standard procedure for these light-off experiments was to allow He to flow over the sample at room temperature while the system stabilised for 1.5 h and the feed composition was measured on bypass. The reaction mixture was then switched over the sample and the system allowed to stabilise for 5 min before commencing the temperature ramp at 3°C/min from room temperature. The ramp rate was reduced to 1°C/min as soon as removal of CO and/or NO commenced and maintained there up to 500°C. Gas chromatographic analyses for propane and propane were made on a 8 min cycle during the ramp with a 3 min dwell period following each 5 min analysis.

3. Results and discussion

Fig. 1A shows the light-off curves for a sample taken from the rear of the little used converter designated No. 51. Nitric oxide, carbon monoxide and propene react in that order in close sequence with a considerable gap to propane. The fall in NO conversion after reaching a peak is characteristic of the slightly lean test mixtures used here and is a sensitive function of ageing [24]. Samples taken from front and centre positions of the same converter exhibited near identical behaviour to that in Fig. 1A with the temperatures required for 50% conversion (T_{50}) averaging 245 ± 4°C for CO, 248 ± 4°C for C_3H_6, 235 ± 4°C for NO and 387 ± 5°C for C_3H_8. Tests on samples taken from the rear of other little used converters with varying PGM contents all gave T_{50}'s for CO, C_3H_6 and NO of less than 250°C and hence the above values for the No. 51 converter are appropriate as measures of good performance.

The corresponding performances of front, centre and rear samples from the extensively used trimetallic converter No. 33 are shown in Fig. 1B–D, respectively. The temperatures required for the oxidation of CO and propene are all higher than the above criteria especially for propene at the front position. Propane removal is negligible while the maxima in NO removal are in the range 50–70% with pronounced fall-offs above the peak removal temperatures. Since 50% removal was not reached with propane, or with NO for many other samples, T_{50} is not a useable measure in these cases. A suitable is a mean conversion as used by Bart et al. [25] and defined here as the average conversion over the temperature interval 100–500°C. On this basis, a sample exhibiting a step-wise light-off to complete conversion at 200°C would have a mean conversion of 75%, while that for samples from converter No. 51, as in Fig. 1A, were 62 ± 2% for NO and 31 ± 4% for propane.

Fig. 2 shows the performances of seven samples taken end-on along the central axis of the trimetallic

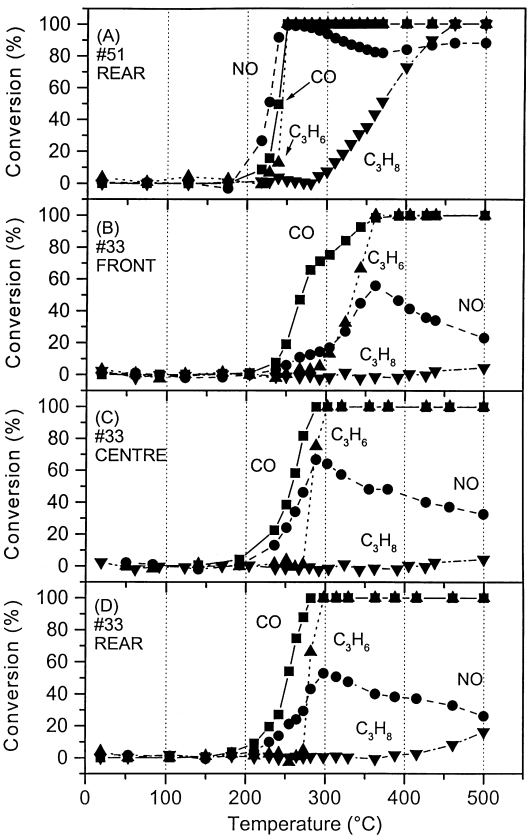

Fig. 1. Light-off curves for samples removed from used three-way catalytic converters: (A) reference converter No. 51 rear; (B) No. 33 front; (C) No. 33 centre; and (D) No. 33 rear.

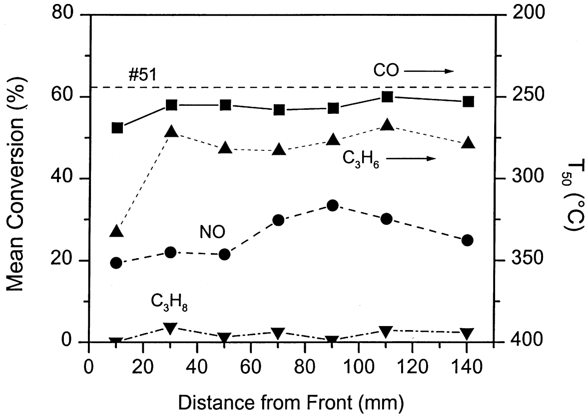

Fig. 2. Temperatures for 50% conversion (T_{50}) for CO and C_3H_6 and mean conversions for NO and C_3H_8 as a function of position for converter No. 33. The dashed line corresponds to the performance of the No. 51 reference converter for removal of CO, C_3H_6 and NO.

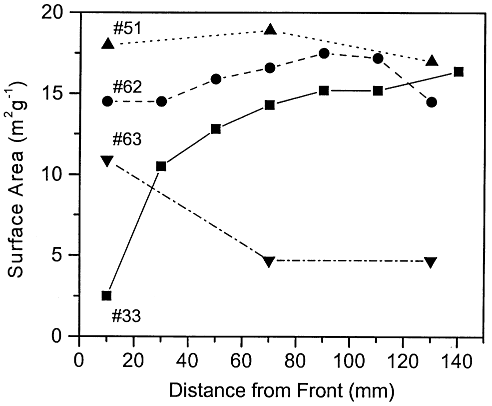

Fig. 3. Surface area as a function of position for the converters Nos. 51, 33, 62 and 63.

converter No. 33 in terms of T_{50}, for both CO and C_3H_6, and mean conversion, for NO and C_3H_8. Note that the scales have been chosen so that higher activity is upwards in both cases and so that the performance of the reference catalyst No. 51 (the dashed horizontal line) is near coincident for CO, C_3H_6 and NO (i.e. 245°C, 248°C and 62%, respectively). All samples from No. 33 exhibit less activity than that of the reference catalyst but the apparently larger activity loss for NO is not significant due to the different measure of performance used for NO and also the difference in catalyst formulation (Table 1). However the trend from relatively low performance at the front, to better performance further along, is significant especially for propene.

The surface areas of the same samples in comparison to the reference sample No. 51 and data for the two converters to be discussed later are plotted in Fig. 3. It is clear that the front-most sample from No. 33 has undergone a large loss of area, while the area of the rear samples approaches that of No. 51.

The corresponding map of contaminant concentrations is shown in Fig. 4. Phosphorus, attributable to combustion of dithiophosphate additives in engine oil [16], is present in the largest amount followed by potassium (present in some engine coolants), calcium and zinc (also both present in oil additives). Only the front sample contains significant lead, probably derived from fuel. Due to the semi-surface nature of the PIXE analytical method, the absolute concentrations are much higher than found by bulk analysis (typically <3% [26]) but are consistent with peak concentration reported using other spot methods [14,17]. The trend in total contamination along the converter is the inverse of the surface area map in Fig. 3 pointing to a link between them. Deposition of phosphorus usually follows a shell progressive model with blockage of fine pores and then eventual total coverage [27]. The increased diffusional resistance initially reduces ultimate conversion under mass transfer conditions and then performance as a whole. Zinc can contribute to this loss at low temperature through the formation of

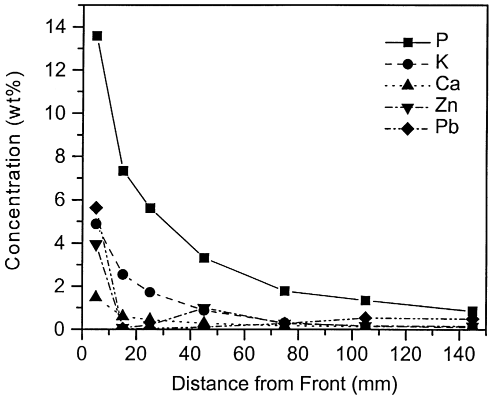

Fig. 4. Contaminant concentration (wt.% in washcoat) as a function of position for converter No. 33.

Table 2
CeO_2 particle sizes (nm) for front, centre and rear samples

Designation	Front	Centre	Rear
No. 51 (reference)	10	10	8
No. 33	26	22	21
No. 62	9	11	11
No. 63	∼22	∼22	∼22

glazes [6,28,29]. Hence it appears that contamination is a major cause of loss of area, and therefore of activity, especially at the front. However, given the relatively low loss of area, and low contamination, further into the converter it is unlikely to be the sole cause of activity changes.

Table 2 shows estimates for the size of CeO_2 particles in the various samples as measured by XRD line width analysis. All three samples from No. 33 have much larger particles than those in the reference sample No. 51 indicating considerable exposure to high temperatures. Under laboratory conditions extended ageing at 900°C or more would be required to produce the same degree of sintering [15,23]. Since ceria aids performance through a variety of factors including oxygen storage, stabilisation of PGMs and activity for the water gas shift reaction [30], increases in CeO_2 particle size with the associated loss of ceria surface area will lower performance overall. The XRD patterns also showed significant amounts of $CePO_4$ at the front of the converter which is not useable for oxygen storage [17]. The overall conclusion is that while much of the loss of performance at the front of No. 33 is attributable to the deposition of contaminants thermal degradation is an additional factor throughout.

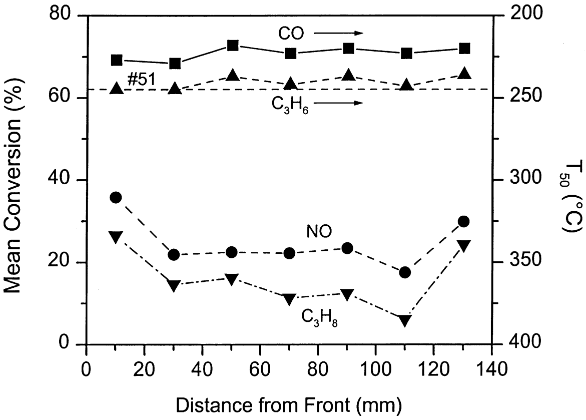

Fig. 5. Temperatures for 50% conversion (T_{50}) for CO and C_3H_6 and mean conversions for NO and C_3H_8 as a function of position for converter No. 62. The dashed line corresponds to the performance of the No. 51 reference converter for removal of CO, C_3H_6 and NO.

Fig. 5 shows performance as a function of position for converter No. 62 which has the same formulation as No. 63 discussed later. Its performance for CO and propene removal is as good or better than that of the reference converter No. 51, and much better than that of No. 63 (Fig. 7 subsequently), at all positions while its surface area (Fig. 3), and ceria particle size (Table 2), also indicate little change from new. Nonetheless, the performance for NO removal is well down against both the reference converter No. 51 and all samples from No. 63. The probable cause is lead since, as shown in Fig. 6, this is present at all positions in concentrations greater than that of any other contaminant and is known to be a more severe poison than phosphorus on an equal weight basis [29].

The deposition of lead is a complex process [31]. It may occur predominantly on the outer surface of the washcoat near the front of the converter, as with phosphorus, or penetrate the washcoat more extensively at all positions. It is the latter which causes PGM poisoning. Removal of NO, which requires rhodium, is affected much more than the oxidation of CO and hydrocarbons [32]. This is because platinum is much more active than rhodium for the oxidation of SO_2 to

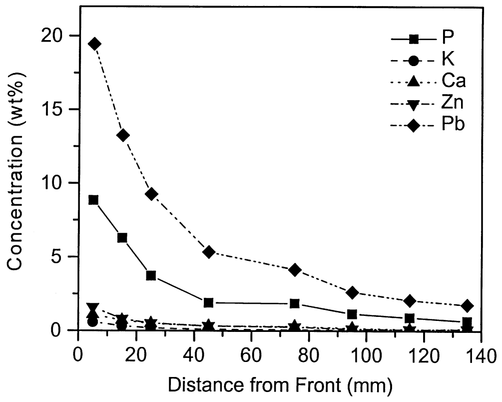

Fig. 6. Contaminant concentration (wt.% in washcoat) as a function of position for converter No. 62.

SO_3 which is to some extent protective through deposition of lead as its sulphate rather than as more deactivating lead oxide on the PGM [33,34]. Likewise co-deposition of phosphorus may lessen deactivation through formation of lead phosphate. This is the probable reason why the larger amount of lead at the front of the converter has a lesser effect on NO performance than the lower amounts of lead towards the rear. The overall conclusion is that the converter has loss of activity for the reduction of NO, but not the oxidation of CO or propene, due to lead poisoning presumably through a significant period of use of leaded fuel, either accidentally or deliberately. While the latter is illegal in Australia, and made difficult through smaller filler sizes, it is occasionally done by owners seeking the higher octane of leaded fuel.

Fig. 7 shows the performance of front, centre and rear samples from converter No. 63. Lead, which was present at the front in amounts less than in No. 62 but more than in No. 33, is a likely contributor to the lower activity for NO removal at the front. The activity for CO and hydrocarbon removal is also down on that of the matching converter No. 62. However the behaviour here is unusual in that activity is worse at the centre and rear positions than at the front. This unusual aspect is clearly related to the surface area which is much lower towards the rear (Fig. 3) although the front position has also lost substantial area relative to the reference catalyst as well. XRD measurements indicated a relatively large ceria particle size throughout (Table 2) and some unexpected phases as shown in Fig. 8. The front sample shows lines due to CeO_2, cordierite and a minor amount of $CePO_4$ with the alumina remaining amorphous. However both the centre and rear samples exhibit a strong line attributable to cerium aluminate ($CeAlO_3$) and two lines originating from a newly discovered cerium barium magnesium hexaaluminate phase, $CeBa_{0.13}Mg_{0.87}Al_{11}O_{17}$ [23]. Cerium aluminate has been reported previously in samples aged on an alternating rich and lean cycle at 950°C and above [35]. The hexaaluminate phase can also be produced by heating intact ceria/alumina/cordierite samples in the laboratory but only with hydrogen present and at

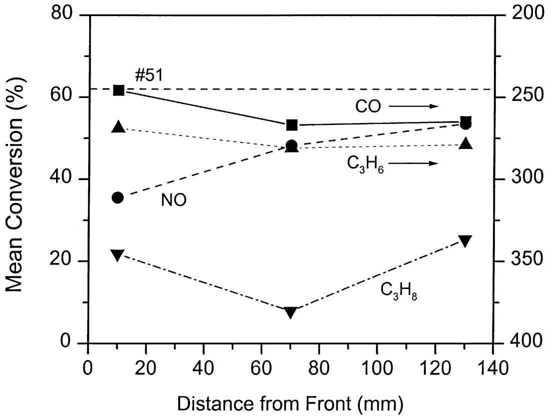

Fig. 7. Temperatures for 50% conversion (T_{50}) for CO and C_3H_6 and mean conversions for NO and C_3H_8 as a function of position for converter No. 63. The dashed line corresponds to the performance of the No. 51 reference converter for removal of CO, C_3H_6 and NO.

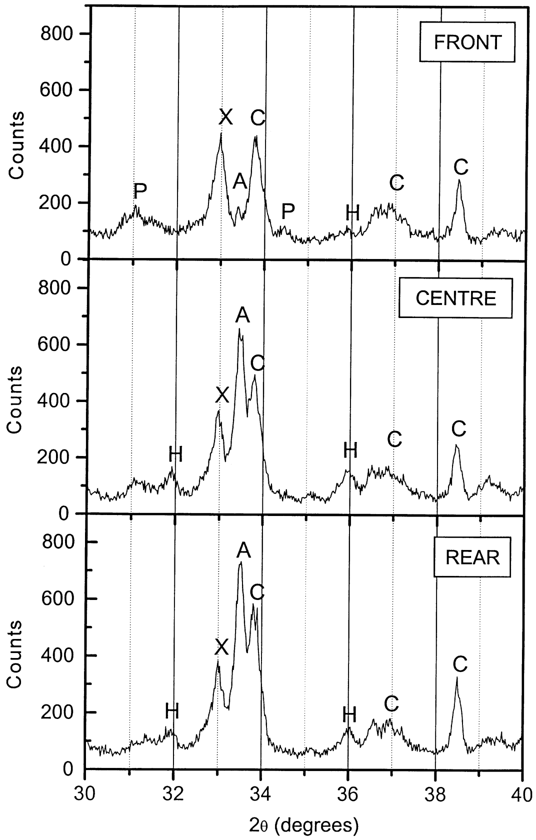

Fig. 8. Diffraction patterns of front, centre and rear samples from converter No. 63 (cordierite: C, ceria: X, cerium aluminate: A, cerium barium magnesium hexaaluminate: H, cerium orthophosphate: P).

high temperature, at least 1100°C for 24 h [23]. The presence of both phases in the No. 63 converter indicates prolonged exposure at high temperature during rich operation. Indeed the balance between CO, hydrocarbons and NO in the emission test on the vehicle from which the converter was taken were heavily weighed to the reduced species, possibly due to an oxygen sensor fault.

The hydrogen required for generation of the hexaaluminate is probably formed through the water gas shift and endothermic steam reforming reactions, which occur throughout the converter under conditions where heat generation is restricted by the low availability of oxygen. This leads to a higher hydrogen concentration, and more aluminate, at centre and rear positions. The tying up of cerium as $CePO_4$ may also restrict formation of $CeAlO_3$, which is a precursor to formation of the hexaaluminate, at the front position. The loss of ceria area through formation of the two reduced phases coupled with the growth in CeO_2 particle size is probably accompanied by sintering of the PGMs which becomes the reason for loss of CO and C_3H_6 activity at the centre and rear positions. Attempts to confirm this by TEM did indicate larger PGM particles than were present in the matching No. 62 converter but morphological differences arising from the presence of the additional phases prevented an accurate determination of the respective particle size distributions.

4. Conclusions

Deactivation of catalytic converters during long-term use on vehicles involves a set of complex processes. The determination of activity, in parallel with characterisation, on small samples taken sequentially along the converter can help resolve these issues. In the present set, one converter had lost performance through a combination of extensive phosphorus contamination at the front and high temperature exposure. Lead was the primary cause of activity loss in the second converter but its effect was largely confined to NO removal. The third converter was unusual with high temperature exposure under reducing conditions causing extensive reductions in area, and loss of ability for CO and hydrocarbon removal, at the centre and rear of the converter.

Acknowledgements

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References

[1] B.J. Cooper, W.D.J. Evans, B. Harrison, Stud. Surf. Sci. Catal. 30 (1987) 117.
[2] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control: Commercial Technology, Van Nostrand Reinhold, New York, 1995.
[3] K.C. Taylor, in: J.R. Anderson, M. Boudart (Eds.), Catalysis — Science and Technology, Vol. 5, Springer-Verlag, Berlin, 1984, p. 119.
[4] L.L. Hegedus, R.W. McCabe, Catalyst Poisoning, Marcel Dekker, New York, 1984.
[5] E. Jobson, M. Laurell, E. Högberg, H. Bernler, S. Lungren, G. Wirmak, G. Smedler, SAE Technical Paper 930937 (1993).
[6] W.B. Williamson, J. Perry, R.L. Goss, H.S. Gandhi, R.E. Beason, SAE Technical Paper 841406 (1984).
[7] D.R. Monroe, SAE Technical Paper 800859 (1980).
[8] G. Kim, M.V. Ernest, S.R. Montgomery, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 525.
[9] P. Nortier, M. Soustelle, Stud. Surf. Sci. Catal. 30 (1987) 275.
[10] R.A. Dalla Betta, R.C. McCune, J.W. Sprys, Ind. Eng. Chem. Prod. Res. Dev. 15 (1976) 169.
[11] S. Kim, M.J. D'Aniello, Appl. Catal. 56 (1989) 23.
[12] D. Liedermann, S.E. Voltz, P.W. Snyder, Ind. Eng. Chem. Prod. Res. Dev. 15 (1976) 172.
[13] E. Jobson, E. Högberg, K.H. Weber, G. Smedler, S. Lundgren, A. Romare, G. Wirmark, SAE Technical Paper 910173 (1991).
[14] T.N. Angelidis, S.A. Sklavounus, Appl. Catal. A 133 (1995) 121.
[15] R.K. Usmen, R.W. McCabe, G.W. Graham, W.H. Weber, C.R. Peters, H.S. Gandhi, SAE Technical Paper 922336 (1992).
[16] M. Shelef, K. Otto, N.C. Otto, Adv. Catal. 27 (1978) 311.
[17] G. Smedler, S. Eriksson, M. Lindblad, H. Bernler, S. Lundgren, E. Jobson, SAE Technical Paper 930944 (1993).
[18] D.D. Beck, J.W. Sommers, D.R. Monroe, C.L. DiMaggio, SAE Technical Paper 952416 (1995).
[19] D.D. Beck, J.W. Sommers, C.L. DiMaggio, Appl. Catal. B 11 (1997) 257.
[20] D.D. Beck, J.W. Sommers, C.L. DiMaggio, D.R. Monroe, D.A. Frank, SAE Technical Paper 972842 (1997).
[21] Federal Office of Road Safety, Report of the National In-Service Vehicles Emissions Study, Australian Government Publishing Service, Canberra, May 1996.
[22] D.E. Angove, N.W. Cant, G.M. Bailey, D.D. Cohen, Nucl. Inst. Meth. Phys. Res. B 109/110 (1996) 563.

[23] D.E. Angove, N.W. Cant, D.H. French, K. Kinealy, Appl. Catal. A 194–195 (2000) 27–34.

[24] N.W. Cant, D.E. Angove, D.C. Chambers, Appl. Catal. B 17 (1998) 63.

[25] J.M. Bart, M. Prigent, A. Pentenero, Stud. Surf. Sci. Catal. 96 (1995) 813.

[26] S.A. Culley, T.F. McDonnell, D.J. Ball, C.W. Kirby, S.W. Hawes, Auto. Eng. (1996) 39.

[27] L.L. Hegedus, K. Baron, J. Catal. 54 (1978) 115.

[28] H.S. Gandhi, W.B. Williamson, J.L. Bomback, Appl. Catal. B 3 (1982) 79.

[29] W.B. Williamson, J. Perry, H.S. Gandhi, J.L. Bomback, Appl. Catal. 15 (1985) 277.

[30] B. Harrison, A.F. Diwell, C. Hallett, Plat. Met. Rev. 32 (1988) 73.

[31] R.H. Hammerle, Y.B. Graves, SAE Technical Paper 830270 (1983).

[32] T. Tabata, K. Baba, H. Kawashima, Appl. Catal. B 7 (1995) 19.

[33] H.S. Gandhi, W.B. Williamson, E.M. Logothetis, J. Tabock, C. Peters, M.D. Hurley, M. Shelef, Surf. Interf. Anal. 6 (1984) 149.

[34] H.S. Gandhi, M. Shelef, Stud. Surf. Sci. Catal. 30 (1987) 199.

[35] S. Humbert, A. Colin, L. Monceaux, F. Oudet, P. Courtine, Stud. Surf. Sci. Catal. 96 (1995) 829.