Modification of a three-way catalyst washcoat by aging: A study along the longitudinal axis

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Abstract

This work reports the research carried out by studying aliquots extracted at different axial coordinates from Three Way Catalyst (TWC) monoliths aged under real traffic conditions. Our study focused on the catalytic properties and on several chemical and physical effects caused in the Front and Rear monolith washcoat surfaces by vehicle aging after 60,000 km. Regarding the catalytic properties, all the used aliquots showed poorer activity than their corresponding fresh counterparts. The strongest deactivation was detected for NO and hydrocarbon conversion. CO conversion was less affected and the Rear monolith was as deactivated as the Front one. The characterisation techniques (TXRF, N2 adsorption–desorption isotherms, XRD and H2-TPR) detected – (i) the deposition of P, Zn and Pb; (ii) the formation of CePO4 on account of the Ce from the washcoat; (iii) thermal sintering; (iv) inhibition of the reducibility of Ce oxides – as the main effects brought about by vehicle aging conditions. The deactivation observed at the beginning of the Front monolith was the result of a combination of the former effects. When moving downstream to higher axial coordinates, Pb accumulation and the loss of specific area appeared to be the only probable sources of deactivation.

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1. Introduction

Since the early 1970s, automotive catalysts have been continuously improved from the point of view of design, although mainly that of composition. Current TWCs are designed to comply with the different norms concerning the purification of exhaust gases for around 100,000–150,000 km. However, the decay in catalytic activity starts from the very beginning of use, and from the practical point of view it is certainly necessary to gain greater insight into the deactivation processes operating in TWCs under real aging conditions. Most studies refer to thermal deactivation [1–5]. The high temperatures reached by TWCs as a result of hot exhaust gases and the exothermal reactions that take place at the surface of the catalysts can produce sintering, noble metal alloying, metal–support interactions, metal losses, etc. Another source of deactivation may arise from the deposition of foreign elements carried by the exhaust gases and generated by different additives present in the fuels and in lubricants. Elements such as S and Pb contained in fuels or Zn, Ca, P and S present in lubricant additives are retained as contaminants by the catalyst cartridge [6–8].

One of the approaches that may help to estimate the impact of the probable causes of deactivation in the catalytic properties is cross-comparison of the characterisation results with the catalytic properties of samples taken along the main symmetry axis of vehicle-aged TWC converters. Since there is a strong axial profile in the deposition of contaminants [9,10] (the radial gradient is not that intense) this approach can shed some light on the discrimination of the effect of contaminant deposition versus other deactivating causes such thermal sintering. To our knowledge, so far only limited work following this strategy has been published [10–12].

Thus, in an attempt to map the effects that working conditions may bring about in TWCs, the methodology used here involved the sampling of aliquots at different locations along the longitudinal axis of a vehicle-aged TWC and the exhaustive
physico-chemical characterisation of such aliquots using a variety of suitable techniques (chemical analysis by Total Reflection X-Ray Fluorescence, X-Ray Diffraction, Temperature Programmed Reduction and textural measurements). A fresh TWC (0 km) of the same kind as the vehicle-aged device was used as a relative contrast. This fresh catalyst cannot be used for quantitative comparative purposes. The monoliths were supplied by the same catalyst manufacturer and the specifications of the catalyst were similar in all the catalytic cartridges supplied. Despite this, the industrial manufacture of TWC catalysts cannot ensure complete reproducibility of the composition and chemical properties from one monolith to another. Nevertheless, the axial dependence of the catalytic activity and the characterisation results of the used catalysts was compared with those of a 0 km catalyst and with themselves in the reasonable expectation that such information might provide certain insight into the causes of deactivation and their impact on catalytic activity.

Our approach was different from other studies exploring monolith cores (25–50 mm long) drilled out from the main bricks [11–14]. In the present work, small pieces of used catalyst were gently separated from the monolith and introduced in a plug flow reactor. A high flow rate (high GHSV) was used for the activity measurements. Thus, considering that the catalytic reaction occurs in the thin layer of the porous washcoat deposited on the cordierite particles, the external and internal diffusion restrictions are expected to be minimized (at least at low and medium conversion levels). In this way emphasis is placed on the chemical causes of deactivation that affect the rate-determining steps of the chemical reactions.

2. Experimental

2.1. Sample selection and manipulation

The fresh and used TWC (60,000 km) were provided by Ford Spain S.A. The converters contained Pd and Rh as noble metals and corresponded to a gasoline-fuelled engine (Ford Fiesta 1.4) with an urban driving pattern. The catalysts consisted of two monolithic substrates; the Front (F) and the Rear (R) pieces placed upstream and downstream, respectively. The two monoliths were cut into pieces designated FI, Front Inlet; FO, Front Outlet; RI, Rear Inlet and RO, Rear Outlet (Fig. 1). I and O also refer to the upstream and downstream positions. Small pieces were separated from the monolith around a certain point defined by two coordinates \((r, h)\) \((r\) is the distance from the axis, in cm and \(h\) is the distance from the entrance, in cm) by crushing the honeycomb structure under gentle pressure. Further treatment of the sample is critical for its characterisation: an optimal physical shape (pieces of monolith wall or powder obtained by grinding the pieces) must be selected depending on the characterisation technique employed. Accordingly, the physical shape will be stated clearly below when describing the equipment used for characterisation purposes.

2.2. Characterisation techniques

Quantitative and semi-quantitative chemical analyses by TXRF were performed on a Seifert EXTRA-II spectrometer (Rich Seifert & Co). Further details of the methodology can be found elsewhere [9,15]. For the quantitative analysis, acid digestion was performed for dissolving those elements that were quantified. Undigested solid remains indicated that other elements (Ce, Al and Sr) have not been fully dissolved. These elements can only be analysed semi-quantitatively (expressing the mass ratio with respect to Si from the cordierite).

Nitrogen adsorption–desorption isotherms were recorded at the temperature of liquid nitrogen (77 K), using a Micromeritics ASAP 2000 apparatus. Prior to the determination of an adsorption isotherm, the sample in the form of a fine powder was degassed at 413 K for 12 h.

Powder X-ray diffraction (XRD) patterns were recorded by scanning between 10° and 80° in the scan mode (0.02°, 2 s),
using a Seifert 3000 XRD diffractometer equipped with a PW goniometer with Bragg-Brentano $\theta/2\theta$ geometry, an automatic slit, and a bent graphite monochromator. The samples were used as powders resulting from finely grounded aliquots.

The patterns of Temperature Programmed Reduction with hydrogen (H$_2$-TPR) were acquired by placing 100 mg of sample in a U-shaped quartz reactor, whose exit was connected to a Baltzer Prisma$^\text{TM}$ quadrupole (QMS 200) Mass Spectrometer (MS). The sample consisted of particles between 0.6 and 0.8 mm, resulting from gently crushing the monolith. Before the H$_2$-TPR experiments, the samples were calcined for 1 h at 773 K (heating rate 10 K/min) under a 5% O$_2$/He flow. Further details of the experiments can be found elsewhere [15,16].

2.3. Microactivity tests

Activity tests were carried out in a conventional fixed-bed flow reactor at atmospheric pressure. Activity runs were performed typically using 1 cm$^3$ of sample obtained by gently crushing the sample (particle size 0.6–0.8 mm) diluted with SiC to a total volume of 3 cm$^3$. Propene is representative of the unburned hydrocarbons found in a typical exhaust gas. A gas mixture was continuously cycled (frequency of 1 Hz) from a lean ($A/F = 15.07$) to a rich ($A/F = 14.19$) composition around the stoichiometric value (10% CO$_2$, 10% H$_2$O, 900 ppm NO, 900 ppm C$_3$H$_6$, 0.4–1.6% CO, 1.37–0.77% O$_2$, 0.13–0.53% H$_2$, and argon to balance). The temperature was raised to 773 K at a rate of 3 K/min and the GHSV was $10^5$ h$^{-1}$. Further details of the equipment and the determination of the components concentration are detailed elsewhere [15,16].

3. Results and discussion

3.1. Elemental analysis

Fig. 2 shows the axial distribution, with error bars, of some of the constituent elements. Zr, Pd, and Rh were selected because they are included in the formulation of the active phase of the TWC (washcoat and noble metals). Pt was also selected for reasons discussed below. Based on Zr distribution, it appeared that the fresh and used catalysts were not identical, as was indeed expected considering their industrial origin. Regarding the Zr content of the F-monoliths, the value of the used catalyst was higher than that of fresh catalyst, whereas in the R-monoliths it was similar. For the fresh samples, the Ce/Zr ratio obtained by TXRF was close to 0.45 for both the F- and R-monoliths whereas for the used samples the values were 0.28 and 0.45, respectively. This indicates that the Ce content is fairly similar in both samples.
In any case, the Ce content of the used sample is not lower than that of the fresh sample. All together suggests the absence of washcoat loss during operation.

The Pd concentration was one order of magnitude higher than the Rh content and the F used catalyst displayed higher Pd concentrations. This can be explained by the unavoidably heterogeneous composition of TWCs during fabrication; namely, that the fresh and the original fresh catalyst subsequently vehicle-aged have different Pd content. The axial profiles, taken separately for the F- and R-monoliths indicate that, apparently, no loss of noble metals occurs after aging. The presence of Pt – which is not in the formulation of the TWCs investigated (manufacturer’s reference, and Fig. 2) – in the Front used catalyst was interesting. Ruling out an error by the manufacturer in providing a TWC with different specification, the only source of Pt would be the fuel, which may contain traces of Pt arising from attrition due to the reforming catalyst used in refineries [17,18]. It may be also valid that other type of Pd containing catalysts used in refinery can also explain the highest Pd concentration in the F used monolith. In any case it must be stressed that total noble metal loading in used samples is higher that in the fresh catalyst.

Several elements accumulate on TWCs during functioning, the most concentrated ones being P, Zn, Pb, Ca, Fe and Ni. Their origins are explained elsewhere [8,9,15]. Fig. 3 shows the axial distribution of other deposited elements such as P, Zn and Pb. Other less concentrated elements such as Ca, Ni and Cu are not represented for the sake of simplicity, but their trends were similar to those of P and Zn. In the used samples, a high concentration of phosphorus in the first millimetres of the F-monolith was observed, while the axial profile was constant and similar to that seen in the fresh counterparts in the R-monolith (Fig. 3). The concentration of deposited Zn was smaller than that of P; it decreased axially and it was three times higher in the F-monolith with respect to the R-monolith. The Zn concentration decreased continuously along the longitudinal axis and at the end of the second monolith seemed to be higher than in the fresh sample. This suggests that Zn might not be fully retained by the monolith and may be emitted by the exhaust pipe. The axial distribution of Pb, reported to be the main element responsible for Pd poisoning [19,20], points to the accumulation of Pb on both monoliths. The Pb concentration was higher in the FI-monolith and became fairly constant after the first half of the F-monolith. The somewhat high value reached in the RO-monolith suggested that Pb was also emitted in the exhaust gases.

3.2. XRD measurements

The XRD profiles of the fresh and used catalysts from the first monolith (FI- and FO-samples) and second monolith (RI-sample) are shown in Fig. 4. The fresh samples displayed very similar profiles regardless to their position. Accordingly, for sake of simplicity only one is shown in the figure. Cordierite diffraction peaks were clearly detected in the fresh monolith sample, and a tetragonal ZrO₂ oxide peak was detected as a shoulder of cordierite peak at 2θ ca. 30°. No reflections of Ce oxides were detected. Two reasons can be invoked to explain this: either (i) ceria–zirconia is well dispersed as small crystallites or (ii) since the Ce/Zr ratio is 0.45, the amount of ceria is so low that the most intense reflection at 2θ = 28.5° could be overshadowed by the intense peak at 2θ = 28.5° of the cordierite. No other secondary reflection lines of ceria or ceria–zirconia mixed oxides were detected at higher diffraction angles (not shown in Fig. 4 for the sake of clarity). The very weak diffraction peak at 2θ = 25.16° (labelled as (x)) corresponds to anatase (TiO₂), an additive of commercial TWCs.
In the patterns of the used FI-samples – namely, FI (1, 0.5) and FI (4, 0.5) – the detection of diffraction peaks at 2\(\theta\) = 26.96° and 31.90°, labelled as (\(^*\)) in Fig. 4, were assigned to CePO\(_4\). A more in-depth discussion of this assignment can be found elsewhere [15, 21]. The radial distribution of phases was also checked in Fig. 4 and no difference was observed, pointing to a uniform impact of exhaust gases on the whole section of the monolith. The peak at 2\(\theta\) = 23.00° can be assigned to the most intense peak of the Sr(PO\(_3\))\(_2\). Sr is one of the basic additives that can be used in the manufacture of TWCs to stabilise the textural properties of the alumina. Sr was also detected by TXRF.

Diffraction peaks from Zr-rich Ce\(_{1-x}\)Zr\(_x\)O\(_2\) mixed oxide became visible in the used samples, whereas tetragonal ZrO\(_2\) signals disappeared. It seems that Zr-rich ceria–zirconia may grow at the expense of ZrO\(_2\) through a solid-state reaction between the ZrO\(_2\) and CeO\(_2\), driven by the high temperatures reached by the catalyst under running conditions.

In the FO samples, the diffraction peaks of Ce\(_{1-x}\)Zr\(_x\)O\(_2\) mixed oxide were narrower and more intense with respect to those found in the FI samples (cordierite is considered to remain unaltered under working conditions), suggesting a higher degree of sintering. This points to the idea that the temperatures reached at the end of the first monolith would, on average, be higher than those at the beginning. The P concentration is low and Ce phosphate reflections cannot be detected.

In the RI-sample shown in Fig. 4, peaks assigned to Ba\(_2\)P\(_2\)O\(_7\) were detected (chemical analysis by TXRD revealed that Ba instead of Sr was used as a basic additive in the R-monolith). It is also possible, as stated above, that these peaks might not be due to P contamination (in fact, P deposition was less pronounced in the R-monolith); instead it could be related to sintering and a higher degree of crystallisation of other phases present in the catalysts. It is worth noting that the sintering of the Ce\(_{1-x}\)Zr\(_x\)O\(_2\) mixed oxide was less intense (the R-monolith was subjected to lower temperatures) as can be deduced from the lower width of the peak at 2\(\theta\) = 30.07° as compared with the patterns of the F-used samples.

### 3.3. Textural measurements

Table 1 summarises the specific areas of the used samples and of the corresponding fresh counterparts. The data clearly show that the specific surface of used catalysts is smaller than those of the fresh samples. This loss of specific area can be assigned to the sintering of the washcoat components. Concerning porosity, the pore-size distribution obtained using the BJH method reveals that all samples had interparticle mesoporosity (defined as void spaces in the agglomerates of very small metal oxide particles of the washcoat; Al\(_2\)O\(_3\) and Ce–Zr mixed oxides) [22]. Mean pore diameter increased from 7–9 nm in the fresh samples to 12–15 nm in the used samples. The interparticle mesopores become larger when sintering develops larger crystals of oxide particles (in agreement with XRD patterns).

### 3.4. H\(_2\)-TPR–MS

Both the fresh and used catalysts were investigated by means of the H\(_2\)-TPR–MS. Fig. 5 shows the \(m/z = 18\) (H\(_2\)O) trace relative to that of \(m/z = 40\) (Argon) for the used and fresh samples collected at different axial locations from the F- and R-monoliths. In the \(m/z = 18\) profiles shown in Fig. 5, a low-

| Table 1: Specific area and mean pore diameter for fresh and used samples |
|------------------|------------------|------------------|
| Sample location | Surface area (m\(^2\)/g) | Mean pore diameter (nm) |
| Fresh samples   |          |                    |
| FI (1, 0.5)     | 35       | 9                  |
| FO (1, 5)       | 34       | 9                  |
| RI (1, 5.5)     | 38       | 7                  |
| RO (1, 10)      | 30       | 8                  |
| Used samples    |          |                    |
| FI (1, 0.5)     | 6        | 12                 |
| FO (1, 5)       | 9        | 13                 |
| RI (1, 5.5)     | 15       | 15                 |
| RO (1, 10)      | 15       | 15                 |
temperature zone (up to 600 K) and a high-temperature zone (above 600 K) can be distinguished. It should be noted that a definitive assignment of the peaks is complicated owing to the proprietary nature of the samples. Nevertheless, the results indicate that the TPR profiles from different fresh aliquots were quite different, even though they had been extracted from the same fresh TWC but at different axial positions. The reason may be due to the inhomogeneity in the composition of the samples, as observed from the chemical analyses.

Deposition on a support, the nature of the support, and the surface area affect the TPR profiles to a dramatic extent [23,24]. Noble metal oxides and ceria oxide (or Ce from Ce–Zr mixed oxides) are the only metal oxides that can be reduced in the real samples studied in this work. It is generally accepted that low temperature processes account for the reduction of noble metals and the reduction of the surface of Ce oxide (however, a reduction of part of the bulk cannot be discarded). The hydrogen spillover is considered responsible for the surface reduction at lower temperature with respect to pure ceria [25,26]. The peaks at the higher-temperature region can be attributed to reduction processes occurring in the bulk of the Ce oxides [25,26].

A higher degree of H2O formation was detected in the fresh F-samples, especially in the FO-aliquot. This trend is consistent with the chemical analyses: a higher Ce loading was found in the FO monolith. A tentative explanation for the shift of the low-region peak in the FO-sample is the higher amount of Rh (Fig. 2), which might be responsible for an increase in hydrogen spillover. The higher amount of Rh, observed by TXRF, could also be linked to the shift to lower temperature of the high-temperature reduction peak in the fresh F-monolith with respect to the fresh R-monolith. The high concentration of Ce in the F-monolith can be viewed as a strategy of the manufacturer to provide better catalytic properties to the frontal monolith, which first enters into contact with the exhaust gases. However, the most visible difference between the fresh and used aliquots was that the total amount of water produced in the TPR experiments in the used samples decreased dramatically in comparison with the corresponding fresh catalysts. This effect was more intense in the used F-samples than in the R-samples. This cannot be due to a loss of cerium or noble metal by attrition since it was not shown up in the chemical analyses. The reason can only be related to an inhibition of the reducibility of the species that can in fact be reduced.

Fig. 5 (right) shows relative identical reduction profiles for the used samples. The most striking feature of the TPR profiles in the used samples is the absence of the high temperature peak. This seems to indicate either that no Ce4+ exists in the samples or, more likely, that bulk ceria is not accessible to hydrogen owing to the formation of a protective superficial layer of CePO4. At the same time, the dramatic decrease in the intensity of the low temperature peak supports the above assumption, owing to the fact that only noble metals can be reduced.

3.5. Catalytic activity

Figs. 6 and 7 show the typical light-off curves obtained for the three main pollutants – CO, NO and C3H6 (as model hydrocarbon) – on samples from different axial positions of the fresh and used F- and R-monoliths. Comparison of the light-off curves between the fresh and used samples unequivocally shows that the used samples are deactivated. The comparison is only qualitative because, unfortunately, the characterisation techniques suggested composition differences between the fresh catalyst and the original composition (fresh state) of the used catalyst. Moreover, the axial composition does not seem to be uniform, even in the fresh catalysts (Figs. 6 and 7, the empty symbols). However, despite these observations, the chemical
analysis showed that the concentrations of active elements in the used monolith are not lower than those of the fresh catalysts (Fig. 2). It may thus be proposed that the lower conversion observed for the used samples must be assigned to the deactivation brought about by vehicle aging.

With respect to CO oxidation, the results indicate that the deactivation was not so intense for F- and R-monoliths. There was practically no variation between light-off curves of the fresh and used F-monolith whereas a slight shift to a higher temperature was observed in the used R-monolith with respect to the fresh counterpart, indicating a low degree of deactivation. In the FI (1, 0.5) aliquot (the part closest to the engine), the deactivation observed for the NO reduction was very important: NO conversion scarcely reached 30% in the used FI section. In the used FO sample the light-off curves of the fresh and used samples are very similar. This means that the deactivation is not as intense as in the forwardmost aliquots.

In the used RI-sample (Fig. 7), NO conversion at 773 K reached 72.4%, a value clearly lower than that recorded for the corresponding fresh RI (100%), while in the case of RO conversion was 84.2% with respect to 100% for fresh RO. In both cases, the light-off curves of the used samples were shifted to higher temperatures than those of the fresh RI- and RO-samples, indicating that the Rear catalyst is less effective in the removal of NO.

Regarding propene oxidation, the light-off curves for the FI- and FO-samples clearly show that they were deactivated (Fig. 6). However, comparison of the light-off curves of the used FI- and FO-samples indicates that the degree of deactivation for the propene oxidation reaction in the FO sample is not as intense as that of the FI sample (for NO conversion the differences between the FI and FO sections were much more remarkable). In the case of the used R-monolith axis, the deactivation of propene oxidation was also evident, taking into account the shift to higher temperatures of the light-off curves.

3.6. Discussion

The loss of specific surface is one of the thermal effects detected in the used samples studied in this work. Although the real consequences caused by high temperature-aging in TWCs are still a matter of debate, thermal effects such as the alloying
of noble metals, strong interactions with the support, or the oxidation of metal particles are not thought to play a major role [2,27,28]. Regarding the effect of the sintering of washcoat components there is increasing evidence to suggest that the loss of specific surface has a minor effect on catalytic performance in the last generation of TWCs that contain Ce–Zr mixed oxide in the washcoat [29]. The extraordinary resistance of the Oxygen Storage Capacity (OSC) of Ce–Zr mixed oxides to inhibition after high-temperature sintering is widely recognised [30–32]. In fact, Pd–Rh-based TWCs, such as the ones investigated in this study, have been reported to undergo a very low degree of deactivation due to thermal aging [33].

Another effect detected was the retention of contaminants. Pb can poison TWCs through different pathways, especially by forming less active alloys with Pd [19,20]. Pb was detected along the whole of the catalyst bed and its concentration was very high, the Pb level being axially constant starting to the half of F-monolith (Fig. 3). The presence of Pb in gasoline has been considerably reduced if not banned. Thus, in European Union countries the maximum Pb concentration in commercial gasoline has been set at 5 mg/L for beyond 2000. An estimation assuming this level for an average consumption of gasoline of 7 L/100 km and running for 60,000 km gives a theoretical deposition of a few grams of Pb on the monolith. This amount is of the same order of magnitude as the noble metal loading in the TWC. It is very likely that the Pb concentration in gasoline is lower than 5 mg/L, but the estimation stresses the importance of the accumulation of Pb in used TWC. The retention of Pb in the monoliths does not only depend on its concentration in gasoline. Flow and temperature gradient fields in the monolith bed also play a role. The significant vapour pressure of Pb oxides and the presence of scavengers in the gas exhaust have been claimed to enable its transportation along the catalyst bed [10]. Thus, the even distribution of Pb in the F- and R-monolith is readily easily understood. It is the result of an equilibrium between two competitive phenomena: deposition and volatilisation. Different variables as the temperature, the flow rate, the flow pattern, the presence of scavengers, etc. may have an influence on the volatilisation and deposition rates but the even distribution suggests that the rate of deposition equals the rate of volatilisation. Similar equilibrium processes can be proposed for other contaminants such as Zn, which show practically no gradient in concentration along the axial position in the R-monolith.

The other contaminants, such as P and Zn, were mainly retained in the F-monolith. These contaminants (together with Ca—not shown in Fig. 3) are concentrated in an impervious crust on the washcoat [6,15,34]. This crust is formed by phases resulting from the reaction between contaminants and washcoat components or between the contaminants themselves, such as AlPO₄, CaZn₂(PO₄)₂, Ca₃(PO₄)₂, Zn₃(PO₄)₂ or Zn₂P₂O₇ [6,34], which plugs the pores and therefore hinders the access of gaseous molecules to the active sites. Their presence in our TWCs cannot be discarded although they may be present only as amorphous phases.

CePO₄ phase formation has been proposed to be responsible for the poorer reducibility observed in the TPR experiments for all the aliquots assayed. CePO₄ is a very stable Ce³⁺ phase; it cannot be oxidised and may lock the Ce³⁺/Ce⁴⁺ active couple [15,21]. The remarkable depletion of H₂O desorption observed in the TPR profiles of the used samples suggested that an important fraction of Ce³⁺ has not been oxidised in the calcination step that preceded the TPR experiments. In fact, the lowest amount of Ce⁴⁺ (less intense H₂O evolution) was detected at the entrance of the F-monolith, in agreement with the detection of a higher phosphorus concentration (Fig. 3) and with the formation of crystalline CePO₄ (Fig. 4). It must be recalled that good TWC performance under rich and poor O₂ concentration oscillations in the composition of the exhaust gas is based on the buffering effect that the rapid Ce³⁺/Ce⁴⁺ redox couple, with the subsequent rapid O-exchange, supplies. If part of the available Ce⁴⁺ cations are transformed in Ce³⁺ present in CePO₄, the OSC becomes seriously damaged and so do the catalytic properties of the catalysts. It has been shown that a small amount of CePO₄ is able to lock the Ce⁴⁺/Ce³⁺ pair so extensively because the CePO₄ phase covers the Ce–Zr oxide particles, thus hindering oxygen transfer [35]. However, it must be admitted that thermal aging could also account for the large differences between the TPR patterns of the fresh and used samples. Further research on this issue is required.

In the case of the F-monolith, the concentration of contaminants, especially Pb and P, displayed a very marked axial gradient. CePO₄ was detected by XRD only at the beginning of this first monolith. The strong degree of deactivation of the catalytic properties for propene oxidation and for NO reduction at the beginning of the F-monolith must be a consequence of a joint combination of all the effects detected, although it is clear that the high concentration of Pb retention, and the locking of the Ce⁴⁺/Ce³⁺ redox pair by CePO₄ must lie at the origin of the strong degree of deactivation. However, the latter effects, which caused strong deactivation in propene and NO elimination, are inefficient for the deactivation of CO oxidation: the degree of deactivation is very similar both at the beginning and at the end of the first monolith. This kind of behaviour for CO has been reported previously [4] and associated with less demanding thermodynamics, i.e. a lower reaction temperature and/or with a low dependence on the catalyst structure for CO oxidation.

Only Pb deposition and the loss of specific surface due to sintering of washcoat components were clearly detected in the R-monolith. The other effects were practically negligible with respect to the F-monolith. Assuming that the loss of specific surface area has a limited effect on the deactivation of the TWC, it can be proposed that the Pb deposition in the R-monolith is the main cause of deactivation. Since Pb has a limited effect on the deactivation of Rh-based TWC [16] it may be deduced that the deterioration must be due to the formation of Pd–Pb alloys [17,20].

4. Conclusions

In an attempt to map the effects of working conditions on a commercial TWC, the methodology used here involved the sampling of aliquots from different locations along the main
axis of the monoliths. The overall picture that emerged from the measurements of the catalytic activity of the different aliquots is that propene conversion and especially NO conversion are seriously deactivated in both the first and second monolith. CO oxidation, although affected after vehicle aging, was not as seriously hindered as in the case of NO and propene. Pb oxidation, although affected after vehicle aging, was not as seriously deactivated in both the first and second monolith. CO is that propene conversion and especially NO conversion are measured in the catalytic activity of different aliquots of the upstream region. The former results highlight the importance of CePO₄ and the deposition of Pb as the main causes of inhibition.

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