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Commercial automotive catalysts: Chemical, structural and catalytic evaluation, before and after aging

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Abstract

This paper presents the effect of aging on a series of commercial three way catalysts, of the same supplier, by analyzing their chemical, textural, structural and catalytic properties. The catalysts were aged in a motor bench test, involving runs of 150 or 300 h and using gasoline with two sulfur levels: 400 and 700 ppm. The catalysts were characterized by X-ray diffraction (XRD) and fluorescence (XRF), surface area, pore volume and pore diameter. The catalytic activities were determined based on CO and propane conversions. After aging, a decrease in surface area and pore volume was observed, as well as an increase in mean pore diameter. Evidence of the presence of α-Al_2O_3, δ-Al_2O_3 and PdO phases was found according to XRD data, which can be attributed to a severe thermal deactivation of the catalysts. Some crystalline compounds containing fuel contaminants like cerium phosphate were also identified. The activity for CO and C_3H_8 oxidation presented a slight correlation with the surface area of the aged catalysts.

Keywords: Three way catalysts; Aging; Characterization; CO oxidation; Propane oxidation

1. Introduction

Among the proposed solutions to reduce environmental pollution, the automotive catalyst is one of the best-known technological applications to control vehicle emissions. Although well established, this technology is still in continuous development and has been adopted by the majority of the countries ruled by policies controlling emissions from vehicles.

Researchers and specialists in the field have been making stronger efforts to develop products and processes that meet stricter environmental regulations and attend the demand for high quality fuels (especially regarding the control of sulfur levels in gasoline), drastic reduction of vehicle emissions and longer durability of the automotive catalyst (100,000 km or 5 years). Not only does this development affect catalyst manufacturers but also automobile manufacturers and oil companies.

Thus, it is important to understand the phenomenon that happens on the catalyst when it is exposed to high temperatures and contaminants, especially from gasoline and lubricant oil, in order to achieve the required durability.

Sulfur compounds present in the gasoline forms SO_x after combustion which may interact with most of the catalytic material, since promoters and stabilizing agents like La_2O_3, BaO and ZrO_2, to major compounds like cerium oxide and alumina. SO_2 may also interact with CeO_2 forming cerium sulfates, spoiling the oxygen storage capacity (OSC) of the catalytic system. Besides, it interacts with noble metals' (NM) poisoning part of the main active sites on the catalyst. It is known that this poisoning is more significant at low temperatures, it enhances from oxidizing to stoichiometric conditions and in the presence of hydrocarbons in the exhaust gas. It's partially reversible from 500 to 700 °C and much less pronounced in operations at higher temperatures [1]. During reducing cycles, SO_2 stored as sulfate species decomposes

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producing H_2S. The use of NiO in the automotive catalyst formulation significantly reduced this effect through "gathering" of the H_2S formed, originating nickel sulfide, and later regenerating the oxide phase during the oxidizing cycle [2].

Another important aspect concerning automotive catalysis refers to thermal resistance that directly affects the catalyst durability. Thermal deactivation is a natural aging process but engine troubles like bad tune-up and incomplete burning may accelerate this process. As a consequence, the automotive catalyst operates at a higher temperature and, in some cases, self-ignition in its interior may even occur, damaging all its structure. These events promote sintering of the catalytic material leading to active area loss [3]. The sintering rate of a metal supported on an oxide of high surface area depends on the interaction between them and metal mobility, which is related to the partial pressures of the species on the surface. Thus, the sintering of palladium particles at high temperatures will be faster in reducing conditions because metallic palladium vapor pressure is higher than that of palladium oxide [4]. This kind of active area loss may occur in normal driving conditions including temperature peaks from 900 to 1000 °C. Thermal aging may also cause loss of OSC through sintering, leading to the loss of close contact between cerium particles and the metallic sites. This contact is necessary for oxygen transport [5].

Aged commercial catalysts were analyzed with the aim to study thermal and chemical deactivation effects. The catalysts were aged in an engine bench in diverse conditions, simulating severe catalyst operation. Several papers with the same emphasis were already published, but with focus on different characterization techniques [6–8]. In this paper, the main focus is the study of catalytic performance in relation to CO and propane oxidation and attempt to correlate these results with the data obtained from XRF, XRD, surface areas, and finally the emission tests performed before and after aging.

2. Experimental

2.1. Aging procedure of the commercial catalysts

The catalysts were exposed to an aging process in chassis dynamometer during 150 or 300 h tests. The test temperature ranged from 500 °C (average), in the mildest operation, and above 1000 °C in the most drastic one. In order to analyze their performance, fresh and aged catalysts were evaluated based on the emission test results, which consisted of the determination of CO, NO_x, hydrocarbon and aldehyde levels in the exhaust gas, according to Brazilian regulations ABNT NBR6601 and ABNT NBR 12026.

Eight commercial catalysts designated A, B, C, D, E, G, H and I were studied. Catalysts from A to G underwent a 300 h aging process, except for catalyst C, aged for 150 h. The aging of catalysts A, B and C involved more drastic conditions, while catalysts D, E and G were aged in milder conditions. In spite of the division into two distinct groups, the aging conditions were not identical within the same group. For one single group, alterations in the maximum temperature values and time of exposure at these temperatures may occur in the aging cycle used, which involves several temperatures. These values are not available as these alterations resulted from simulations of engine trouble. Other information like fabrication year, sulfur level in the used gasoline and emission test results are shown in Table 1.

Table 1
Commercial automotive catalysts identification, aging conditions and emission tests data

Catalyst	Fabrication (year)	Aging (h)	Surpassed emission limits	S level in gasoline (ppm)
A	98	300	Yes	700
B	99	300	Yes	700
C	99	150	Yes	400
D	00	300	Yes	400
E	00	300	No	700
G	00	300	No	700
H	00	Fresh	–	–
I	00	Fresh	–	–

2.2. Sampling and physico-chemical characterization

The catalysts were subdivided into three sections: inlet, middle and outlet, in relation to the exhaust gas flow. Each part was separately analyzed through several techniques.

X-ray fluorescence spectrometry (XRF) was performed in an S4_Explorer (rhodium tube) from Brucker-AXS. The samples were fused with lithium tetraborate, in a 1:5 dilution and the results were obtained through the semiquantitative scanning method. Several spots on the catalysts were analyzed, particularly in the inlet, middle and outlet regions. This procedure enabled the comparison of the catalysts concerning their homogeneity in relation to the diverse components present in the washcoat.

Nitrogen adsorption and desorption isotherms were obtained in an ASAP 2400 V3.07 analyzer. From this data, it was possible to determine surface area, pore volume distribution, establish the average pore diameter (BJH method), and consequently infer about a probable sintering process. In this case, the sampling of the commercial catalysts consisted in taking small fractions of the monolith without grinding them.

The XRD patterns of the samples, obtained through the powder method, were collected in a Bruker-AXS equipped with Goebel mirror for parallel X-ray beam, in the following operating conditions: Co Kα radiation (35 kV/40 mA); goniometer velocity of 0.02° 2θ per step with count time of 1.0 s per step and collected from 5 to 80°. Qualitative interpretation of the spectra was done by means of comparison with standards stored in PDF02 data bank in Bruker DiffracPlus software.

In order to perform the catalytic tests, fractions from the inlet, middle and outlet were grounded and homogenized. This procedure ensured that the fraction taken was representative of the whole. With the aid of a CARVER press, model 4332, approximate pressure of 3500 psi, pellets were prepared from the powder. These pellets were ground and sieved in steps, in a way that three granulometry ranges were obtained: 20–40, 40–60 and 60–80 mesh. To evaluate diffusional effects on the catalyst bed, tests were made with each range of particle diameter. These results led the analysis to the selection of the fraction which ensured the absence of internal diffusional effects. The catalyst bed, in the chosen granulometry, was diluted with silicon carbide in a massic ratio of 1:3. This procedure contributed for the test reproducibility as it minimized the formation of hot spots inside the reactor.

The equipment utilized in the catalytic tests consisted of a U-type reactor made of Pyrex glass, 6.6 mm internal diameter, a vertical furnace with PID temperature control and an Agilent 6890N gas chromatograph to analyze reactants and products. The reacting mixture, which simulated exhaust gas, was composed of approximately 1% of CO, 9.3% of CO_2, 0.33% of H_2, 1.30% of O_2 and 0.12% of propane (balance with He). A space velocity of 35,000 h^{-1} was applied during a 2 °C/min temperature ramp from room temperature to 450 °C. Samples were taken regularly each 15 min during the temperature ramp.

3. Results and discussion

Fig. 1 presents specific surface area, pore volume and average pore diameter of the catalysts. These values were obtained from the arithmetic mean of the measured values on the inlet, middle and outlet sections.

Catalysts H and I are fresh and show a surface area above 25 m^2/g. Significant differences are noticed among the fresh catalysts, from the same fabrication year, in relation to surface area (27 and 35 m^2/g, respectively) and pore volume (0.063 and 0.090 cm^3/g, respectively). Pore diameter was the same for both samples (approximately 100 Å).

Catalysts A, B and C are part of the group that underwent more drastic aging conditions, and the results obtained confirm this fact as this group presented the lowest surface areas (Fig. 1(a)) and pore volumes (Fig. 1(b)) when compared to the others. Catalyst C presented the lowest surface area, in spite of having been the only catalyst aged for 150 h. This is the first fact that may indicate this catalyst was exposed to such higher temperature aging that the thermal effect surpassed the effect of total aging time.

Another explanation is that catalyst C may have been exposed to higher temperatures for a greater time, compared to the others, in spite of its shorter total aging time. All of the catalysts from this group failed the emission tests. Catalysts D, E and G, aged in milder conditions, could keep their respective surface areas and pore volumes better. Within this group, catalysts E and G passed the emission tests but catalyst D failed it. The results of surface area and pore volume for this latter catalyst are much lower than the ones from catalysts E and G. Besides, its pore diameter is the biggest of all, indicating partial sintering (phase coalescence, Fig. 1(c)). If we consider that aging temperatures in this group were milder, a possible explanation for this would be that catalyst D may have been exposed during a longer time at the highest temperature applied in the whole group.

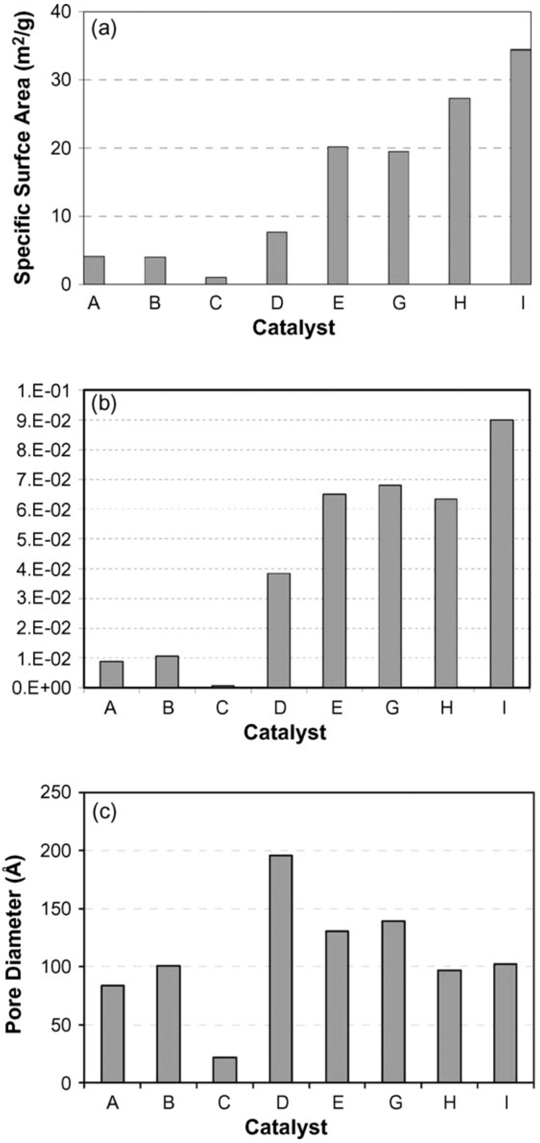

Fig. 1. (a) Specific surface area, (b) pore volume and (c) diameter of the catalysts.

The results from textural analysis also indicated that the catalysts presented practically no micropores, since only adsorption isotherms of type IV, typically from mesoporous solids, were observed [9].

Chemical analysis results (XRF) of the catalyst washcoat, calculated by subtracting cordierite contribution, indicated a similar composition, with alumina, cerium oxide, zirconium oxide, nickel oxide and lanthanum oxide contents in the ranges of 50.0–55.0, 27.0–29.0, 9.5–11.3, 4.3–5.0 and 1.7–2.0%, respectively. Catalyst E was the exception as it was only catalyst containing barium oxide (2.0%), a higher content of alumina (65.8%), lower contents of cerium, zirconium and nickel oxides (16.4, 5.4 and 2.9, respectively) and absence of lanthanum oxide.

As cited in the characterization item, analysis in the inlet, middle and outlet of each catalyst was done in order to verify the homogeneity in washcoat. Thus, it was possible to evaluate the distribution of the components along each catalyst studied.

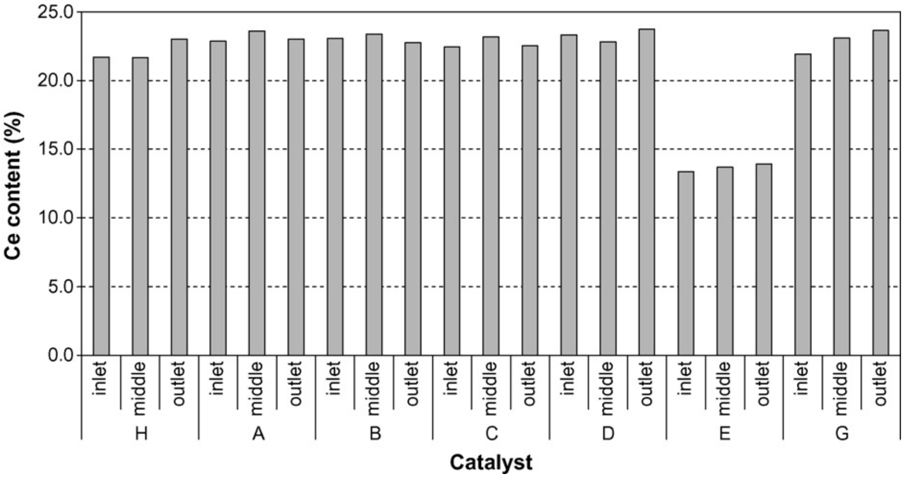

Fig. 2. Cerium distribution along the catalysts.

In relation to the typical components present in the automotive catalyst, an excellent homogeneity was observed. Fig. 2 presents, as an example, cerium distribution. There is good accordance, not only for each catalyst individually (when inlet, middle and outlet are compared) but also for practically all of the studied catalysts, with cerium level ranging around 22 and 24%. Very similar graphs indicating noticeable homogeneity were obtained for the other typical constituents of the automotive catalyst. As mentioned before, results from catalyst E did not follow the tendency and reached approximately 14% in cerium in the three analyzed regions.

By analyzing the overall composition, that is, including the cordierite contribution, it was able to evaluate possible material losses from the catalysts to the environment, by detachment of fragmented parts of the washcoat, as indicated by SEM in a previous work [8], especially for the samples A, B and C. Fig. 3 shows the alumina average composition in the catalysts.

The results show that the observed differences in Al_2O_3 contents, which is the most important catalyst component (approximately, 50% of the washcoat), are not meaningful. Apparently, it does not have significant losses of washcoat to the environment. Thus, previous SEM and XPS results [8,10] together with these XRF ones, we must consider that the deep cracks observed in the severely aged catalysts (that even exposed cordierite phase leading to the detection of SiO_2 through XPS analysis) may also be due to a strong agglomeration of catalytic material and not only its loss.

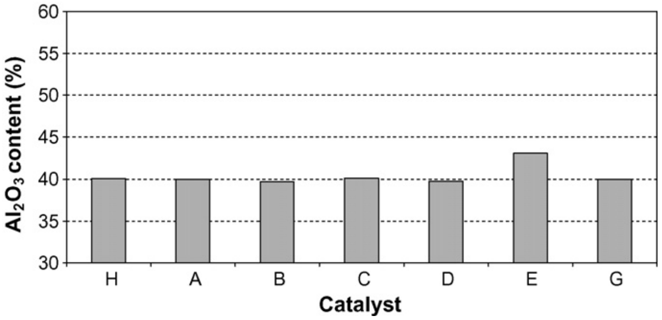

Fig. 3. Alumina distribution in the catalysts (cordierite computed).

In spite of this conclusion, the washcoat loss by abrasion needs to be studied with more details. The abrasion can occur in very small extension and cannot be detected by the XRF analysis, because experimental errors would probably be higher than the quantities lost by this phenomenon. Moreover, the aging procedure in chassis dynamometer had a maximum duration of 300 h and simulated the thermal and chemical impact at the catalyst after 80,000 km. In fact, this procedure does not simulate the damages by erosion. For information about compounds emissions from automotive catalyst to environment there are other studies that include chemical analysis of soil, dust and particulates with focus on platinum metals group [11–14].

Besides comparing the compositions of the typical components of the automotive catalysts, the analysis of the contaminants distribution on the aged catalysts also brings important information. Gasoline presents many organosulfur compounds that, when burned, emit SO_2 and SO_3. Fig. 4 presents sulfur distribution along the aged catalysts.

There is no defined tendency concerning sulfur distribution. Apparently, sulfur acts in the whole catalyst, reaching it from the inlet to the outlet parts, in an almost uniform distribution. SO_2 and SO_3 interact with the present oxides like CeO_2, Al_2O_3, NiO and metals like Pd, Pt and Rh, possibly forming sulfates or other sulfur-based compounds. This interaction is better noted at low temperatures and depends on the aging atmosphere. At elevated temperatures (above 700 °C), decomposition of these compounds occurs and the catalytic activity is, at least, partially restored [1]. If one considers that catalysts A, B, C and D underwent a greater thermal treatment, one can infer that the low sulfur levels observed occurred due to this phenomenon. Following this approach and analyzing catalysts E and G, which kept surface areas similar to the fresh catalysts (lower temperature treatment), much higher sulfur levels could be observed. Even though the results are consistent with the argumentation about temperature influence in this kind of system, one should not ignore that sulfate decomposition also depends on the gas composition. As the aging process was done in engine bench, the only information known is that the system ranged from oxidizing to reducing atmosphere.

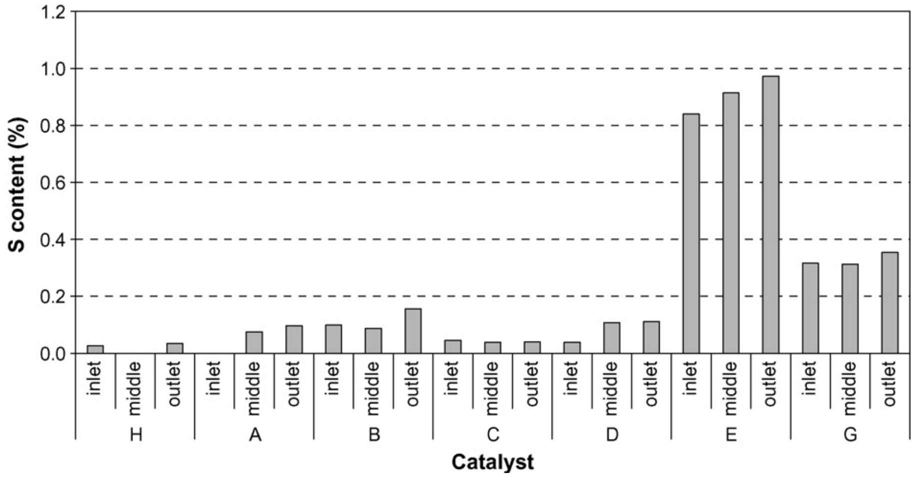

Fig. 4. Sulfur distribution along the catalysts.

Another aspect to be considered is the difference observed in terms of the sulfur level of catalyst E that is far above the mean value, approximately eight times higher.

To justify the higher affinity of catalyst E for sulfur, its composition must be analyzed. As mentioned before, this catalyst has a different composition: it is the only one that has barium oxide, no lanthanum and significantly lower cerium oxide and nickel oxide contents.

Barium presence, according to Klingstedt et al. [15], confers a greater resistance to sulfur poisoning. Sulfur trapping, normally attributed to nickel oxide, can be also performed by barium oxide. Thus, the higher sulfur level found in catalyst E may have been occasioned by the presence of these two components acting simultaneously to remove SO_2 and/or SO_3 from the medium, normally through the formation of sulfates or any other sulfur compound on the surface of these oxides.

Contamination by phosphorous is also very common and is present in major part of the aged catalysts. Differently from the homogeneity of sulfur contamination along the catalysts, in case of phosphorous, it occurs predominantly in the inlet part, presenting a noticeable tendency of reduction in the outlet direction, as observed in Fig. 5. Phosphorous compounds originate from poisoning by lubricant oil components like zinc dialkyl dithiophosphate (ZDDP), an additive used for wear protection and to reduce oil oxidation. This compound adsorbs on the catalyst surface, affecting gas diffusion inside the pores of the catalyst [16]. This tendency was observed for all aged catalysts.

Fig. 6 presents the XRD patterns of some catalyst samples. The graphs refer to the inlet region, selected for normally being the most affected one. All the XRD patterns present evident cordierite peaks in 12, 25.3, 30.8, 33.3 (overlaps cerium oxide) and 34.3. Cerium oxide peaks are also noticeable in 33.3, 38.8, 55.8 and 66.5 in all catalysts, especially fresh catalysts H and I. As Ce–Zr mixed oxide (CZ) compositions containing 100–67% in ceria show practically the same XRD patterns, it is not possible to affirm whether the catalysts present pure ceria, CZ or both.

Comparing the XRD of fresh catalysts (H and I) with the aged (A to G) catalysts, significant changes are observed. There are signs of the presence of α-Al_2O_3 and δ-Al_2O_3 crystalline phases and clear formation of PdO [17]. These phases are

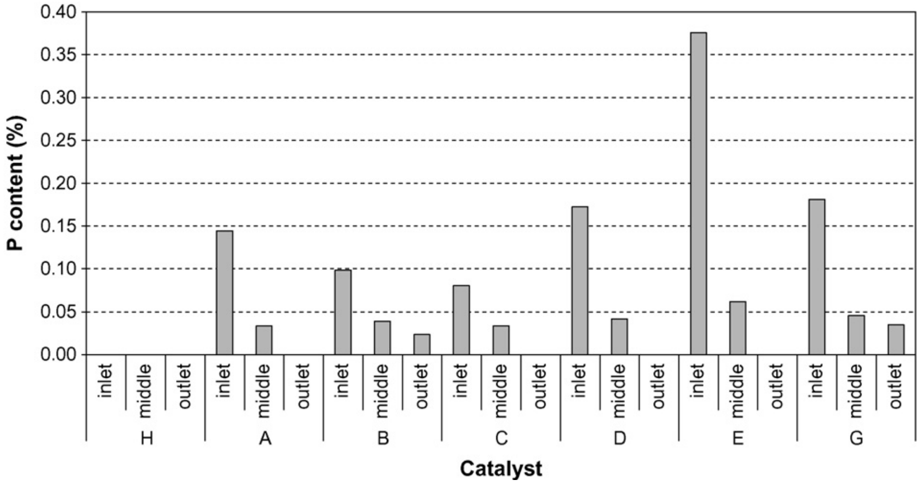

Fig. 5. Phosphorous distribution along the catalysts.

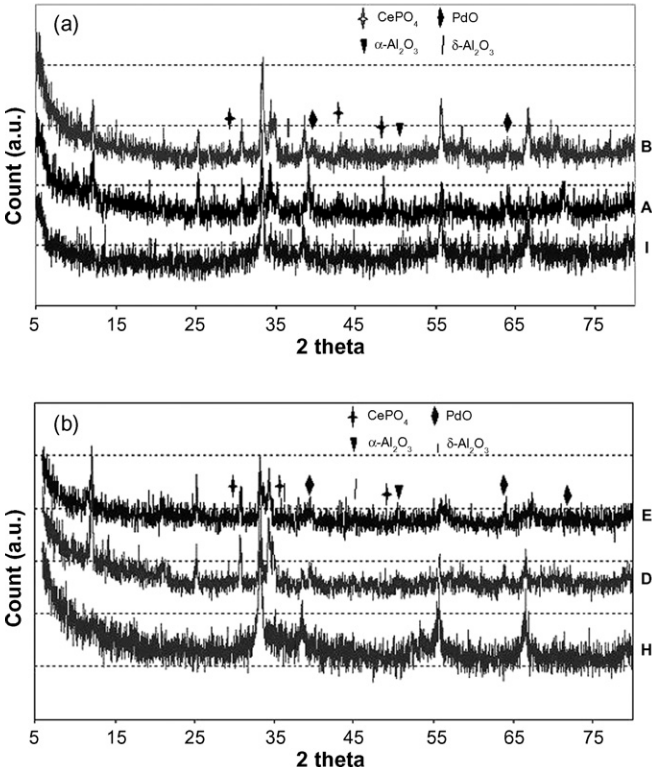

Fig. 6. XRD results from the catalysts. (a) Catalysts A, B and I and (b) catalysts D, E and H (inlets).

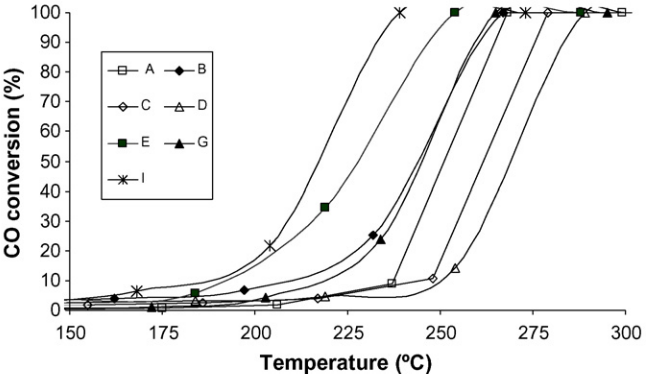

Fig. 7. CO *light-off* curves of the catalysts (inlets).

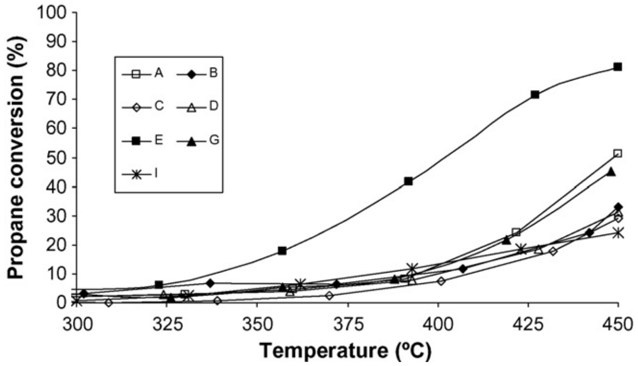

Fig. 8. Propane *light-off* curves of the catalysts (inlets).

indicated in the XRD patterns of Fig. 6. The formation of these phases is associated to thermal aging. δ-Al_2O_3 and α-Al_2O_3 formation is related to active area loss and may promote Pd particle agglomeration, which become visible through XRD. There are also indications of the presence of $CePO_4$ [18], which are consistent with XRF results.

For most severely aged catalysts like A and B, the presence of peaks in 2θ 35 and 59° can be attributed to a new mixed oxide phase. This can be due to the segregation of CZ upon aging leading to the formation of a phase rich in zirconium. According to the literature, this phase probably has 16% in zirconium [19].

The results of the catalytic tests are presented through the *light-off* curves, obtained from CO and propane conversions during a temperature ramp applied to the catalyst (2 °C/min, up to 450 °C). The *light-off* curves of catalysts A, B, C, D, E and G, inlets, are represented in Figs. 7 and 8. Activities are compared through *light-off* temperatures (T_{50}), that is the temperature in which the catalyst reaches 50% CO or C_3H_8 conversions. The *light-off* temperatures are shown in Table 2. The indices *a* indicates that 50% conversion was not reached. Thus, the values presented refer to $T_{20,}$ or the temperature in which 20% conversion was reached.

The choice to test inlets samples is due to the fact that this region is the most affected during natural or engine bench aging, as also observed by Angove and Cant [20]. In general, the *light-off* temperature tends to enhance as surface area decays. For CO oxidation (Fig. 7), it was showed that the best performance was attained with fresh catalyst I, as expected. A fresh catalyst is normally present with its components in an optimized condition, as compared to the aged catalyst, considering that the noble metals particles are well dispersed and in adequate interaction with the support and the other components.

In general, after aging it is observed a reduction performance for the CO oxidation in agreement with previous papers [17,21–23]. The characterization results show BET surface areas, for all the catalyst, decreasing neatly from the value obtained for the fresh one. XRD data indicate clear phases evolution after aging, including δ-Al_2O_3, α-Al_2O_3 formation and probably $CePO_4$. A segregation process of Ce–Zr mixed oxide phases was also observed for all the catalysts. According to Nibbelke et al. [24], that studied CO oxidation by O_2 over a Pt/Rh/CeO_2/γ-Al_2O_3, one of the reaction pathway steps involves the reaction between CO adsorbed on the noble metal surface and oxygen from ceria at the noble metal/ceria interface. This

Table 2
Light-off curves of the fresh and engine bench aged catalysts (inlets)

Catalyst	T_{50} CO (°C)	T_{50} C_3H_8 (°C)
A	250	450
B	240	420[a]
C	265	440[a]
D	270	430[a]
E	225	400
G	240	450
I	220	420[a]

[a] 20% conversion temperature.

explains the importance of this contact which is improved in dispersed metals systems. Then, the decrease of activity can be associated, basically, to the drop of the active sites number at the catalyst surface and the reduction of the interaction between palladium and CZ.

For propane conversion, the same tendency was basically observed. The exception was the fresh catalyst I. For this reaction, its performance was as bad as catalyst B. Probably the explanation is related to the presence of chloride ions (~0.15%), which was detected in the fresh catalyst but not in the aged ones, as indicated by chemical analysis results. Actually, previous works [25–27] have comment that the removal of residual chlorine present at the catalyst is ineffective by oxidative treatments and, according to Gélin and Primet [28], ions chloride originating from the metal precursor are not completely removed by conventional activation treatments (calcination in oxygen followed by reduction in hydrogen).

Although a specific study about the residual chlorine effects in these oxidation reactions was not carried out in the present work, there are some references in the literature about this subject. Roth et al. [27] analyzed this effect using NM/Al_2O_3 catalyst in the methane oxidation and observed a strong deactivation for Pd/Al_2O_3. Cant et al. [25] also studied this influence in Pt, Pd and Rh supported catalysts prepared with chlorinated precursors for oxidation of hydrocarbons others than methane, as isooctane, benzene, toluene and hexane. For all of them, the activity increased when the tests were repeated, that is, when the catalysts were submitted subsequently at high temperatures under the selected gas mixture. Cant et al. [25] attributed this activity gain to the removal of residual chloride ions. Thus, it is possible that the same could have happened with the catalyst I, the only one that had chloride ions detected by chemical analysis. Thus, after aging, this contamination would be eliminated and the catalytic activity would increase.

About the performance of the other catalysts studied in propane oxidation, the catalyst E stood out in relation to the others, proved by the gas emission tests results (Table 1) and the catalytic performance (Fig. 7), in spite of the presence of typical thermal aging phases in the XRD results. Probably, this superior behavior may include the sustenance of a high specific area after aging, what possibly can be explained by its different composition that comprises components as barium oxide. According to Klingstedt et al. [15], which investigated the promotional effect of barium oxide in Pd/Al_2O_3 catalysts, this compound presents a series of advantages: improves hydrothermal stability, confers better sulfur resistance and allows operation in a wider air/fuel ratio window. These aspects may justify, for example, the absence of lanthanum oxide in catalyst E, as barium oxide also confers thermal stability. The effect of sulfur storage in barium and nickel discussed previously is also very favorable because it reduces the tendency of interaction between sulfur and the noble metals. Besides, a wider air/fuel ratio window certainly favors catalyst performance.

The worst performance for propane oxidation was observed with catalyst C, which also failed the emission test. This behavior can be associated to the characterization results, since this catalyst presented the lower specific surface area and the presence of phases associated to thermal aging in XRD data.

Concerning the sulfur impact on the catalyst activity, the observed behavior was not the one expected. In either the group of the most sintered catalysts (A, B and C), or the group of the most thermally preserved (D, E and G), catalysts C and D, which were aged with a gasoline of lower sulfur level (400 ppm), presented the worst performance. However, other effects like sintering and contaminants deposition are present contributing for the lower performance of these samples.

4. Conclusions

The characterization results from a group of commercial automotive catalysts, engine bench aged, showed that the catalysts exposed to higher aging temperatures presented a decay in surface area and pore volume and an enhance in the pore diameter, besides the indication of the presence of δ-Al_2O_3, α-Al_2O_3 and PdO phases. In inlet regions, it seems that crystalline compounds containing contaminants like cerium phosphate are formed. CO and C_3H_8 conversion activities were consistent with the surface area of the aged catalysts, provided residual chloride ions are not present.

Even though there is no precise information concerning the aging conditions which simulated engine troubles, there are strong indications pointing that the major contribution to catalyst deactivation comes from thermal effects.

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