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Thermal deactivation of Pt/Rh commercial automotive catalysts

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ABSTRACT

The influence of thermal ageing effects on catalytic activity was analyzed for a Pt/Rh three-way catalyst. Characterization techniques such as X-ray fluorescence (XRF), N_2 physisorption, X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption of H_2 (H_2-TPD) and scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX) revealed deep textural, structural and physicochemical changes in the catalyst washcoat caused by exposure to high temperatures (900 °C and 1200 °C). The catalytic activity was evaluated in terms of CO and propane oxidation and the reduction of NO by CO. In general, the conversions were lower after the ageing. The exception was the catalyst aged at 900 °C for 12 h. This catalyst presented a better propane conversion than the fresh Pt/Rh catalyst. It is likely that the well-dispersed Pt in the fresh catalyst was more susceptible to oxidation. A short-time ageing would increase the size of Pt particles, which are harder to oxidize, contributing to an improved activity. On the other hand, the NO reduction showed lower conversions after ageing, probably related the rhodium to being the most sensitive metal towards sintering at high temperatures under exhaust gas conditions.

1. Introduction

A lot of research has been performed in order to elucidate and improve automotive catalyst operation. The modern commercial catalyst formulation consists of a combination of various metal oxides that contribute to better catalytic performance such as barium, nickel, lanthanum, titanium and the traditional ones that build the basis of the catalyst such as cerium, zirconium and aluminum. Concerning the noble metals, platinum group metals such as Pt, Pd and Rh are mostly employed because they are less susceptible to poisoning or thermal deactivation [1].

Catalyst deactivation is usually a complex phenomenon, mainly involving commercial catalysts, due to the presence of many components playing diverse roles in the entire catalytic system [1–5]. Thermal effect is one of the most frequent causes of automotive catalyst deactivation. The driving force of this process is the surface energy that is reduced with the transport, growth and coalescence of the particles, and pore elimination, causing noble metal agglomeration and sintering of the main oxides in the washcoat, such as Ce/Zr mixed oxides and alumina [6].

It is known that the sintering rate depends on the temperature, but the ageing atmosphere is also important. According to Moulijn et al. [7] and Bartolomew [8], sintering is more severe in oxidizing than in reducing atmospheres. This is probably because catalytic behaviour is affected by different metal oxidation states. For example, for a CO oxidation reaction, PdO is the most active form of palladium, whereas Pt works in its reduced form [9].

Fernandes et al. [10] verified the influence of ageing temperature and the atmosphere when they studied the activity of Pd/Rh commercial catalysts. Alumina and Ce/Zr phase transitions and clear textural modifications were visualized, which demonstrated that thermal ageing may cause severe changes in the commercial catalyst properties. Regardless of these changes, the catalyst still presented good activity in CO and propane oxidation.

Thus, the aim of this work was to continue studying automotive catalyst behaviour towards thermal ageing, but with a focus on a Pt/Rh commercial catalyst from different supplier, but also employed in Brazilian vehicles. According to González-Velasco et al. [11], that studied model catalysts containing Pt and Pd, ther-

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Table 1
Contents of the main compounds of catalyst washcoat.

Compound	Means and standard deviation (% *m*/*m*)					
	Middle (A + B + C)	Border (A + B + C)	A (middle + border)	B (middle + border)	C (middle + border)	Global
Al_2O_3	42.2 ± 1.4	42.1 ± 2.2	42.2 ± 3.0	43.1 ± 1.0	41.0 ± 1.0	42.1 ± 2.0
BaO	1.42 ± 0.18	1.39 ± 0.16	1.60 ± 0.2	1.29 ± 0.06	1.34 ± 0.06	1.40 ± 0.16
CeO_2	18.5 ± 0.7	17.8 ± 1.6	18.4 ± 2.3	17.7 ± 0.7	18.1 ± 0.4	18.0 ± 1.3
Fe_2O_3	0.65 ± 0.05	0.84 ± 0.14	0.79 ± 0.20	0.78 ± 0.13	0.76 ± 0.13	0.78 ± 0.15
HfO_2	0.46 ± 0.05	0.44 ± 0.06	0.40 ± 0.07	0.46 ± 0.04	0.48 ± 0.04	0.45 ± 0.06
La_2O_3	0.70 ± 0.05	0.69 ± 0.07	0.71 ± 0.10	0.70 ± 0.03	0.67 ± 0.03	0.69 ± 0.06
NiO	3.04 ± 0.29	3.06 ± 0.26	3.28 ± 0.31	2.97 ± 0.14	2.90 ± 0.13	3.05 ± 0.26
Pr_6O_{11}	2.23 ± 0.13	2.10 ± 0.27	1.94 ± 0.27	2.17 ± 0.15	2.31 ± 0.12	2.14 ± 0.24
TiO_2	1.05 ± 0.06	1.32 ± 0.11	1.18 ± 0.16	1.26 ± 0.17	1.23 ± 0.17	1.23 ± 0.16
ZrO_2	28.5 ± 1.3	28.8 ± 3.0	25.9 ± 2.3	29.9 ± 0.8	30.3 ± 1.3	28.7 ± 2.6

mal ageing affects the performance of Pd/Rh and Pt/Rh catalysts differently. This study aims to analyze this aspect, now considering commercial systems, which are much more complex as they involve several additives and stabilizers.

2. Methods and materials

A Brazilian Pt/Rh commercial catalyst, termed catalyst G, which is designed for 1.0 engines and is updated with PROCONVE (National Program to Control Vehicular Emissions) phase III was employed. Its chemical homogeneity was analyzed using XRF, following the same procedure as described in Fernandes et al. [10].

Samples of catalyst G were subjected to two types of thermal ageing. One was stoichiometric, under simulated exhaust gas flow (1.0% CO, 0.33% H_2, 1.27% O_2, 9.3% CO_2 and 0.12% C_3H_8, in helium, named the MPP1 mixture) at 13.5 L/h. The ageing was carried out at 900 °C for 12 and 108 h. The catalyst was also aged in air with no gas flow (static) at 1200 °C for 12 and 72 h.

The catalytic evaluation and characterization techniques employed such as N_2 physisorption, X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX) and TPR experiments were carried out according to Fernandes et al. [10]. The MPP1 mixture was used to evaluate the catalytic activity on propane and CO oxidation. NO reduction by CO was also investigated, but with a stoichiometric gas mixture of NO and CO (1.0% CO and 1.0% NO, in helium, named the MPP mixture).

The studied reactions (CO oxidation, propane oxidation and reduction of NO by CO) are all highly exothermic and therefore adequate procedures were employed to minimize the interference of heat and mass transfer during the catalytic test. Temperature gradients in the catalytic bed were minimized by using small reactor diameter and by mixing the catalyst with silicon carbide in the 1:3 weight ratio.

According to Duprat [12], the typical test to evaluate intraparticle diffusional limitations involves performing experiments with different sizes of catalyst. The test of external mass transfer limitations involves measuring the conversion at constant space–time but varying flow velocity by adapting the amount of catalyst. These tests were performed using one of the most active commercial automotive catalysts available in our laboratory (catalyst E in Fernandes et al. [5]), aiming to guarantee the validity of the tests for all of them. The catalyst particle size and catalytic test flow rates used in the present work were chosen in such a way that heat and mass transfer were not limiting the catalytic processes.

Both the fresh and aged catalyst G samples were submitted to temperature programmed desorption of H_2 (H_2-TPD) to evaluate the platinum dispersion (see Lambrou et al. [13]). The procedure was carried out in a temperature programmed multipurpose unit. The catalyst samples were ground and homogenized before insertion into the reactor. The samples were pretreated at 600 °C in 5% O_2/He for 1 h, 1.61% H_2/Ar for 1 h and pure Ar for 1 h. After cooling to 25 °C in an Ar flow, hydrogen was chemisorbed for 30 min with the same H_2/Ar gas mixture, followed by the desorption of physisorbed hydrogen in pure Ar. This procedure was performed twice. Finally, H_2-TPD was initiated in an Ar flow with a heating rate of 30 °C/min up to 600 °C. The gas flow was adjusted to 30 mL/min for all of the steps. A fixed weight of 1000 g of catalyst was used.

3. Results and discussion

The contents of the main compounds of catalyst G washcoat are presented in Table 1. The chemical composition of the samples was similar over all of the catalysts; therefore, it was considered homogeneous. The maximum standard deviation obtained was 3.0% for all of the elements found. Concerning the noble metals content, ICP-OES analysis of the catalyst indicated 236 mg/kg of Pt and 428 mg/kg of Rh, which is equivalent to 1.2 μmol Pt/g and 4.2 μmol Rh/g.

The adsorption isotherms obtained for the fresh catalyst were of type IV, typical of mesoporous solids [10]. Table 2 presents the textural characterization results after ageing at 900 °C. The loss of surface area reached 50% for samples aged for 12 h or more, while the pore volumes decreased and the pore diameters increased, as expected. Ageing at 1200 °C severely affected the catalyst texture after 12 h. Thus, the increase in ageing temperature from 900 °C to 1200 °C and the change to the oxidizing atmosphere caused an almost total loss of surface area and other textural properties, as observed in the literature [1].

Table 2
Textural properties of the catalyst.

Catalyst G	Ageing time (h)	BET area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
Fresh	0	46	0.112	103
Aged at 900 °C stoichiometric	12	23	0.097	137
	108	23	0.099	146
Aged at 1200 °C oxidizing	12	0	n.d.	n.d.
	72	0	n.d.	n.d.

n.d., not detected.

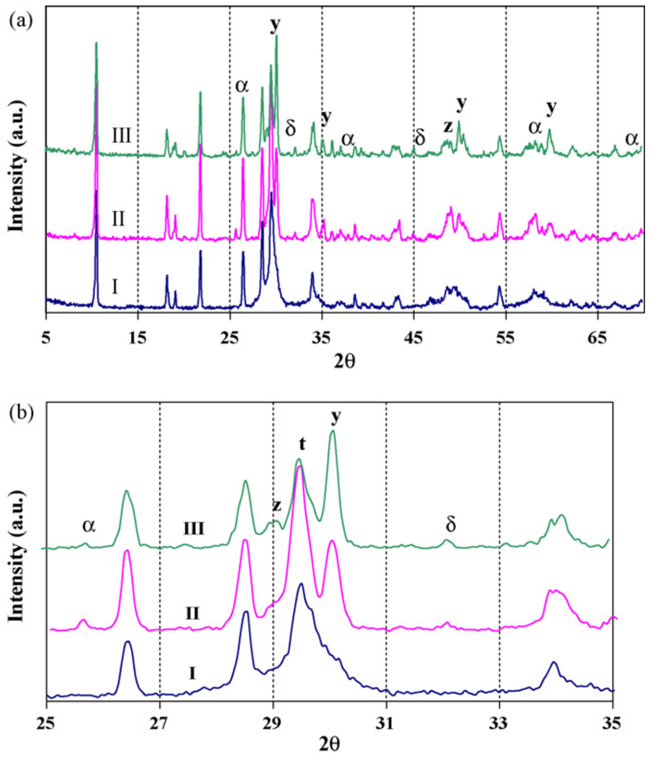

Fig. 1. (a) XRD of fresh and aged catalyst G at 1200 °C in oxidizing conditions, (b) enlargement of the 25–35 (2θ) range. (y) Zr-rich phase, (t) intermediary Ce/Zr phase and (z) Ce-rich phase. (I) fresh, (II) 1200–12 h, (III) 1200–72 h.

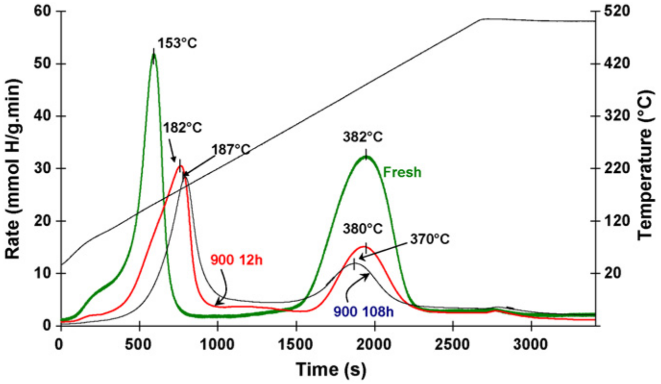

Fig. 2. TPR profiles for fresh and aged catalyst G at 900 °C in stoichiometric conditions.

The diffractogram of the fresh sample is presented in Fig. 1(a). Most of the peaks were attributed to the cordierite that is the material of the monolith. Its diffraction lines can be found in the literature (Larese et al. [14] and Martín et al. [15]). Indeed, it was not possible to observe any γ-Al_2O_3 peaks in the fresh catalyst diffractogram. The XRD profile of pure γ-Al_2O_3 can be seen in Paglia [16].

The samples aged at 900 °C had a diffractogram (not shown) that was very similar to the fresh one. The ageing at 900 °C under stoichiometric conditions did not cause any structural change that could be detected by this technique; therefore, it can be inferred that this ageing was not enough to produce significant thermal deactivation.

However, important changes were observed for the catalyst aged at 1200 °C (Figs. 1(a)). Alumina, the major washcoat component, is used for its high surface area and thermal stability. After 12 h, some diffraction lines corresponding to different alumina phases were identified: δ (32°; 45°), θ (37°) and α (26°; 57.5°; 68°), according to Wu et al. [17] and Iglesias-Juez et al. [18]. Pure γ-Al_2O_3 starts its transition to lower area phases at around 800 °C, but only above 1000 °C is the non-porous α-Al_2O_3 phase is formed [5,18]. When stabilizers such as Ce/Zr mixed oxides (CZ), lanthanum oxide and/or barium oxide are present, this phase transition is delayed until higher temperatures [16,19,20]. Considering La, Ba and CZ are present in catalyst G, as identified by the chemical analysis, retaining high surface areas after ageing at 900 °C is justified. However, the catalyst could not stand drastic conditions such as the oxidizing ageing at 1200 °C. Thermal treatment under these conditions caused an almost total loss of surface area, and many diffraction peaks observed were attributed to the transition phases of the alumina oxides.

A phase segregation of mixed Ce/Zr oxides was also verified after ageing at 1200 °C. Fig. 1(a) presents the diffraction peaks of a Zr-rich tetragonal phase, named y, whose intensity increased with ageing time. These peaks appear at approximately 30°, 35°, 50° and 60° 2θ. A peak at 29° 2θ may be related to a Ce-rich mixed oxide phase, named z. This phase was identified as $Ce_{0.83}Zr_{0.17}O_2$, according to Bozo et al. [21]. This phenomenon has already been reported by other authors [21–23]. Fernandes et al. [10] also observed this when studying Pd/Rh commercial automotive catalysts [24].

The evolution of the diffraction peaks in 28–30° 2θ range can be better observed by an enlargement of this region, shown in Fig. 1(b). These peaks are associated with what is reported in the literature as Ce/Zr mixed oxide demixing, and was observed only after ageing at 1200 °C. The intermediary phase, named t, occurs at 29.5°, and according to Bozo et al. [21], corresponds to $Ce_{0.47}Zr_{0.53}O_2$. When the ageing was prolonged, the t phase decomposed into the Ce-rich phase (z), evidenced by a new line at 29° after 72 h of ageing, and the Zr-rich phase (y).

No $CeAlO_3$ phase was found in the diffractograms. According to Larese et al. [14], the reaction between Ce^{+3} and alumina leading to cerium aluminate formation was not found when using Ce/Zr mixed oxides in the place of CeO_2, since the insertion of Zr into the cerium oxide lattice minimizes this interaction. Indeed, Yue et al. [24], who prepared $Ce_xZr_{1-x}O_2/Al_2O_3$ with different Zr contents, did not observe $CeAlO_3$ formation in samples calcined at 1000 °C for 2 h.

Fig. 2 presents the TPR profiles for the fresh sample of catalyst G and for the samples aged at 900 °C under stoichiometric conditions. Three peaks were observed at the temperature ranges 90–100, 150–190 and 330–390 °C. According to the literature [25–28], noble metal oxides are usually reduced at low temperatures. In their study about the catalytic performance of rhodium supported on ceria–zirconia mixed oxides, Haneda et al. [29] observed a reduction peak at around 100 °C that was ascribed mainly to the reduction of nearby CeO_2-ZrO_2, which strongly interacts with rhodium. According to Lambrou et al. [13], who studied commercial automotive catalysts (Pd and Rh as precious metals), Rh reduction was attributed to the first peak of TPR (70 °C), and the peak at 125 °C was related to palladium reduction.

Concerning the second peak, Fan et al. [30] analyzed the influence of the oxidative/reductive treatments on the activity of a $Pt/Ce_{0.67}Zr_{0.33}O_2$ catalyst. They observed a peak at 150 °C and correlated it to a possible reduction of Pt oxide. Fornasiero et al. [28] studied the interaction of molecular hydrogen with a $Pt/Ce_{0.6}Zr_{0.4}O_2/Al_2O_3$ three-way catalyst and observed an intense peak at 180 °C in the fresh sample, which was associated with the reduction of the Pt oxide and $Ce_{0.6}Zr_{0.4}O_2$ mixed oxide. [28]. Liotta et al. [31] also observed a similar peak at 160 °C during the TPR of a $Pt/Ce_{0.6}Zr_{0.4}O_2$ catalyst with approximately 1% Pt. According to the authors, this peak is likely due to a concomitant reduction of highly dispersed PtO_x crystallites and ceria.

Thus, both peaks at 92 °C and at 150 °C found during the TPR of fresh catalyst G may be associated with noble metal reduction, which can simultaneously involve the reduction of superficial cerium oxide. It is well-known that the noble metals have the capacity to anticipate cerium oxide reduction due to H_2 spillover from the metal to the Ce/Zr support, facilitating its reduction [25–27,30].

The decomposition and integration of the TPR peaks [3] showed a consumption of 12 μmol H/g for the peak at 92 °C, and 153 μmol H/g for the peak at 150 °C. According to the ICP-OES results, the amount of hydrogen necessary to reduce the rhodium (as Rh_2O_3) in the catalyst would be 12.6 μmol H/g. Therefore, the peak at 92 °C in the TPR profile is probably related to the reduction of Rh. Consequently, the second peak would be attributed to the reduction of Pt oxide. If only PtO_2 was formed during the oxidizing step, the calculated H_2 intake would be of 4.8 μmol H/g; if PtO was formed instead of PtO_2, the intake would be of 2.4 μmol H/g, according to the Pt content in the catalyst as determined by ICP-OES. The calculated H_2 intake obtained from the integration of the second peak (153 μmol H/g) was much higher than the H_2 necessary to reduce the noble metals. Thus, the simultaneous reduction of noble metals and the mixed oxides at 150 °C is clear.

The peak observed at 382 °C was investigated based on the discussion presented in the literature. High-temperature reduction peaks are generally related with bulk mixed oxide reduction, which occur at 400 °C and higher when supported on alumina [26,32–34]. Fornasiero et al. [32] observed bulk reduction at temperatures higher than 600 °C when they studied the redox behaviour of high surface area Rh-, Pt-, and Pd-loaded $Ce_{0.5}Zr_{0.5}O_2$ mixed oxide. In this work, considering the presence of NiO, it is also possible that its reduction occurs below 500 °C. TPR results from Takeguchi et al. [35], obtained for $NiO/Ce_{0.25}Zr_{0.75}O_2$ catalysts, confirmed NiO reduction at 340 °C (for 12.4 wt% NiO supported on CeO_2-ZrO_2) and higher for lower nickel concentrations. Therefore, NiO may be reduced in this temperature range. The NiO content was determined by ICP-OES, and 0.84% NiO was found in catalyst G. This amount of NiO demands 224 μmol H/g for its reduction, which is quite close to the result of the high-temperature peak integration (217 μmol H/g). Thus, the peak at 380 °C is likely due to the reduction of NiO, although the reduction of bulk mixed oxides may occur at higher temperatures, as reported by the literature [26,32–34].

After ageing at 900 °C, the TPR results (Fig. 2) show that the first peak was shifted to a higher temperature, whereas the second was not. A decrease in the peak area was also observed, indicating the presence of sintered particles, which are harder to reduce. The shape of the peaks did not change with longer ageing times, indicating that the catalyst structure is stable, meaning that prolonged ageing is not enough to cause any significant interactions among the washcoat components. Fornasiero et al. [28] also observed a shift of the TPR peak (lower temperature) to higher temperatures. According to the authors, the formation of bulk Pt oxide or a phase like Pt-O-Ce may have occurred, and these phases demand higher temperatures for reduction. Thus, these phenomena may justify the changes in the reduction profiles of the catalysts aged at 900 °C.

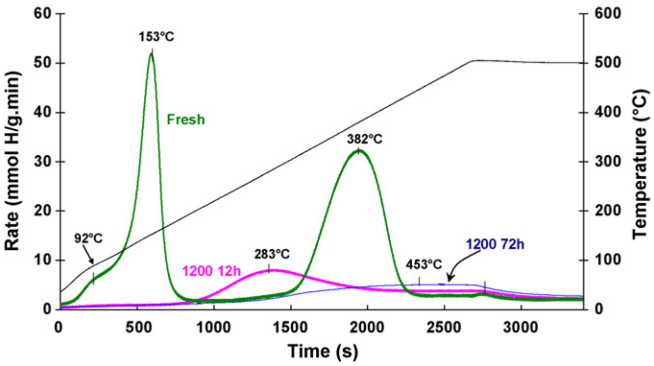

Fig. 3. TPR profiles for fresh and aged catalyst G at 1200 °C in oxidizing conditions.

After oxidizing ageing at 1200 °C, the reduction profiles presented low and broad peaks, as observed in Fig. 3. After 12 h, the reduction peak was centred at 283 °C, whereas after 72 h, a little H_2 intake was observed in a peak centered at 453 °C. The total H_2 intakes obtained from the TPR up to 500 °C of the fresh and aged catalysts are presented in Table 3.

The total H_2 intakes obtained for the fresh catalyst were much higher than for the aged catalysts; therefore, the fresh catalyst presented a larger reduction capacity, as expected. Ageing at 900 °C affected the catalyst redox properties to a lower extent when compared to ageing at 1200 °C. After 12 h at 900 °C, the H_2 intake decreased 31% compared to the fresh catalyst. After 108 h, the H_2 intake was 39% lower. The decrease in H_2 intake reached 70% and 82% after 12 and 72 h of ageing at 1200 °C, respectively. These observations are in agreement with the textural analysis results and lead to the conclusion that the first 12 h of ageing are responsible for the major changes in the redox catalyst properties.

SEM-EDX analysis of fresh catalyst G (Fig. 4) revealed the presence of several elements such as Ce, Zr, Pr, Nd, Hf and Ni (Point 1). After ageing at 1200 °C for 72 h, the non-homogeneity of the washcoat was clear. Fig. 5 shows Points 1 and 2 that correspond to parts of the washcoat surface, and when compared, the differences are visible. These results are in agreement with the XRD profile of this sample (Fig. 1), which suggests phase segregation and some transition phases. The ageing at 1200 °C strongly affected the catalyst structure, as also happened to the commercial catalyst studied in the previous work by Fernandes et al. [10]. The high temperature caused the washcoat sintering, and consequently affected the adhesion to the cordierite support. A significant area of cordierite was exposed after the severe ageing conditions, as observed in Fig. 6.

No agglomerated Pt or Rh was found in any of the micrographs for both the fresh and aged samples, likely indicating a very high dispersion of Pt and Rh on the catalyst G washcoat.

The catalytic activity was evaluated through the light-off curves (Fig. 7) of fresh and aged catalyst G samples for CO and propane oxidation and NO reduction. The T_{50} values, the temperatures at which the catalysts reach 50% conversion, are presented in Table 4.

Table 3
Total H_2 intakes (μmol H/g) during TPR up to 500 °C.

Ageing time (h)	H_2 intakes (μmol H/g)[a]		
	Fresh	Furnace at 900 °C in stoichiometric conditions	Furnace at 1200 °C in air (static)
0	408	–	–
12	–	280	119
72	–	–	72
108	–	248	–

[a] Obtained by integration of the complete profiles.

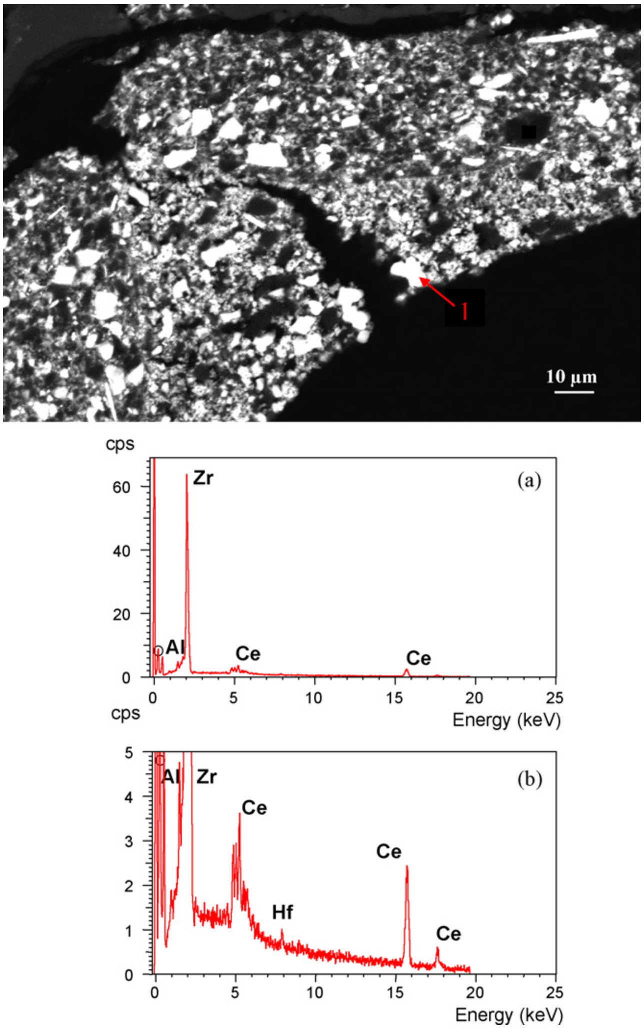

Fig. 4. Washcoat of fresh catalyst G with EDX chemical analysis of Point 1 (a), with a scale enlargement in (b).

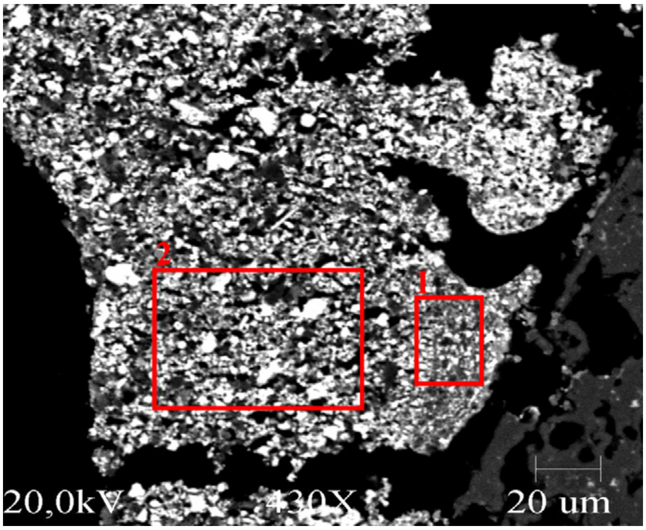

Fig. 5. Washcoat of catalyst G aged at 1200 °C for 72 h.

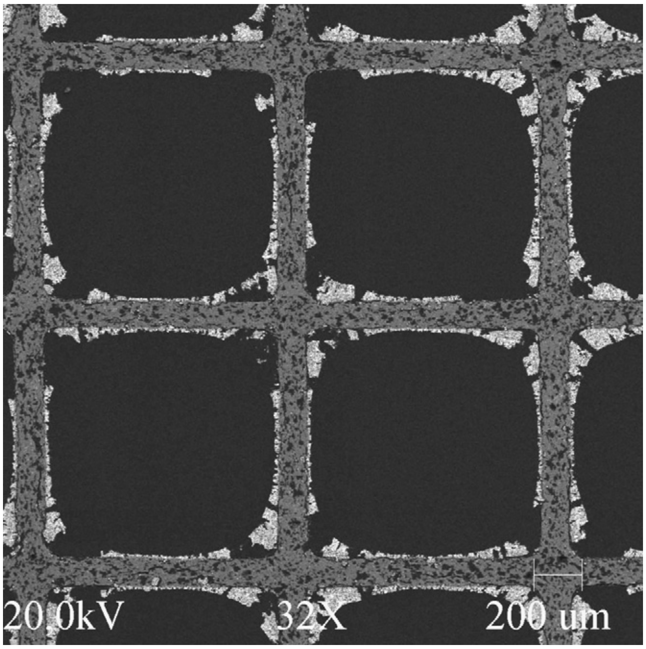

Fig. 6. Catalyst G aged for 72 h at 1200 °C.

According to Fig. 7(a), ageing for 12 h at 900 °C affected CO conversion to a very low extent. After 108 h of ageing, the T_{50} shifted from 265 °C to 295 °C, which is an increase of 11%. Ageing at 1200 °C for 12 h in an oxidizing atmosphere increased T_{50} from 265 °C (fresh catalyst) to 410 °C. After 72 h, T_{50} was shifted to 440 °C for CO oxidation. Wu et al. [26] also observed deactivation in a 2% Pt/$Ce_{0.67}Zr_{0.33}O_2$ catalyst after oxidizing ageing for 20 h at 950 °C; the T_{50} for CO conversion increased 105°C. Despite the different catalyst compositions and ageing conditions employed in this work when compared to Wu et al., the shift in T_{50} for CO conversion was of the same order of magnitude.

Another aspect to highlight is the high activity of CO conversion of catalyst G after ageing at 1200 °C for 12 or 72 h. This performance was observed in spite of the intense modifications to its textural and structural properties, including the demixing phenomena. Hietikko et al. [36] also observed good performance of real catalysts (Pd-Rh) after thermal ageing. The samples were aged in the range of 800–1200 °C in a static air atmosphere (oxidizing) and under other conditions. Light-off temperatures of CO oxidation increased

Table 4
Light-off temperatures for CO, propane and NO conversions.

Catalyst	Ageing time (h)	CO oxidation (T_{50})	Propane oxidation (T_{20}[a])	NO reduction (T_{50})
Fresh	0	270	455	280
Aged at 900 °C stoichiometric	12	265	315	355
	108	295	485	380
Aged at 1200 °C oxidizing	12	410	n.d.	n.d.
	72	440	n.d.	n.d.

n.d., T_{20} or T_{50} was not reached until 500 °C.
[a] T_{20} was reported as T_{50} was not reached for the studied temperature range.

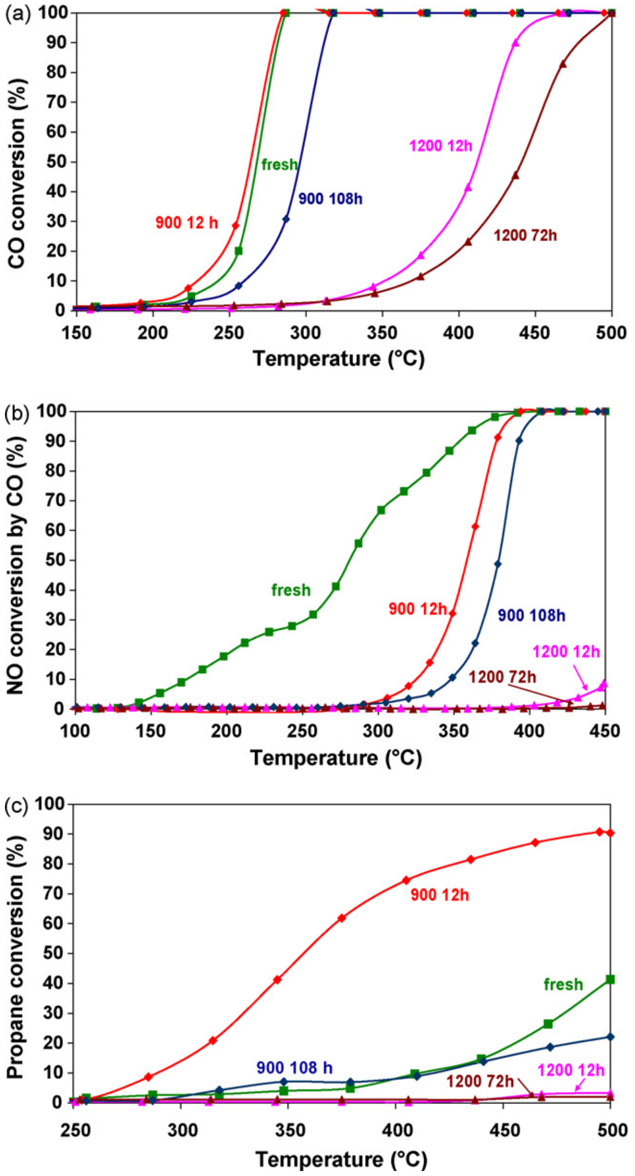

Fig. 7. Light-off curves for CO (a), NO (b) and propane (c) conversions.

systematically as a function of ageing temperature, but even after ageing at 1200 °C, the high catalytic activities still remained.

NO reduction by CO was also investigated for catalyst G. In Fig. 7(b), the light-off curves show the expected behaviour. The T_{50} was higher for the fresh catalyst, and decreased with ageing at 900 °C under stoichiometric conditions (Table 4). Oxidizing ageing at 1200 °C severely affected the catalytic activity for NO reduction, and neither T_{50} nor T_{20} could be detected. This behaviour is probably related to rhodium, as it is the most sensitive metal towards sintering at high temperatures under the exhaust gas conditions. This leads to poor activity, especially for NO_x reduction [37].

Propane conversion, presented in Fig. 7(c), showed an uncommon behaviour when compared to the other reactions. The activity for propane conversion for the fresh catalyst was much lower than that obtained for the sample aged for 12 h at 900 °C. The fresh catalyst did not reach 50% of the conversion at 500 °C. This behaviour was not expected, considering the aged samples presented a significant decrease in surface area and pore volume. Furthermore, the TPR profiles presented a decrease in total H_2 intake when the catalyst aged for 12 h was compared to the fresh one (Table 3). The catalytic tests indicated that ageing at 900 °C for 12 h activated the catalyst in spite of the losses in textural and redox properties. Therefore, the explanation for this behaviour may be associated with other structural modifications during this thermal treatment.

C–H bond activation in saturated hydrocarbons is a crucial first step in the combustion of these compounds. The rate of activation of C–H bonds on metal catalysts depends on the choice of hydrocarbon, the metals involved, its dispersion and interaction with the support, as well as the reaction conditions. Under oxygen-rich conditions, one may consider that the metal may be fully covered with oxygen due to the strong adsorption of activated oxygen species as compared to saturated hydrocarbons [38]. Another important factor in C–H bond activation on metal catalysts is its inhibition by reaction products such as CO_2 and H_2O. Previous studies have shown that the rate of methane oxidation on Pt increases up to a maximum value as the catalyst is exposed to a methane/air mixture. The optimum activity occurs when the Pt is partially oxidized [in 38], and the fully oxidized form is less active. In contrast, the combustion of methane on Pd increases steadily as the Pd is progressively and fully oxidized to PdO [in 38]. This is probably the explanation of why in our previous work [10] a commercial Pd catalyst still showed some activity for propane oxidation, even after oxidizing ageing at 1200 °C, unlike the Pt catalyst G tested in this work.

Carlsson et al. [39] studied propane oxidation on Pt-Al_2O_3 catalysts at low temperature (250 °C), with a Pt content in the range of 1–10% *m*/*m* and different ageing conditions. The results showed that the ageing atmosphere strongly influenced the catalytic activity. The higher conversions (almost 100%) were reached when the gas composition was close to stoichiometric conditions. Lean gas mixtures (high air/fuel ratio) led to a worse catalytic performance, probably due to Pt oxidation, forming a less active catalytic phase.

Another aspect to be considered is the dispersion of the metal particles. Otto et al. [40] studied propane oxidation on several Pt/Al_2O_3 catalysts with different dispersions and concluded that the reaction is structure sensitive. The low activity observed for highly dispersed samples was explained considering that small Pt particles are more susceptible to oxidation than large ones, thereby deactivating faster. Fan et al. [41] studied Pt catalysts supported on Ce/Zr/La mixed oxides and, in a group of three catalysts prepared under the same conditions, found higher propane conversions for the catalyst with the lower Pt dispersion. In the same report, an additional decrease in the activity for these reactions after ageing at high temperatures (1050 °C) was attributed to metal encapsulation in the support. Similarly, Gélin and Primet [42] reported that complete methane oxidation can be structure sensitive. For example, Hicks et al. [43] measured the catalytic activity of supported Pt and Pd catalysts under slightly oxidizing conditions. TOFs were calculated using the initial dispersion determined by chemisorption of hydrogen on the reduced samples before exposure to reaction conditions. The mean steady-state TOFs at 335 °C were found to vary as follows for the different catalysts: dispersed phase of platinum, TOF = $0.005\ s^{-1}$, crystalline phase of platinum; TOF = $0.08\ s^{-1}$, small particles of palladium; TOF = $0.02\ s^{-1}$, large particles of palladium; TOF = $1.3\ s^{-1}$.

In this work, H_2 temperature programmed desorption was used for estimating the noble metal dispersion, as proposed by Lambrou et al. [13]. The results are presented in Fig. 8. The contents of Pt (1.2 μmol/g) and Rh (4.2 μmol/g) determined by ICP-OES were lower than the desorbed hydrogen from the fresh catalyst (19 μmol/g), assuming a 1:1 stoichiometry between hydrogen and the active sites. These results show that the H_2-TPD technique suggested by Lambrou et al. [13] does not reflect the hydrogen exclusively associated with the metallic sites, probably due to the H_2 capacity to spill over the Ce/Zr support. Nevertheless, the results indicate that ageing strongly influences hydrogen chemisorption. Stoichiometric ageing at 900 °C for 12 h caused a slight decrease

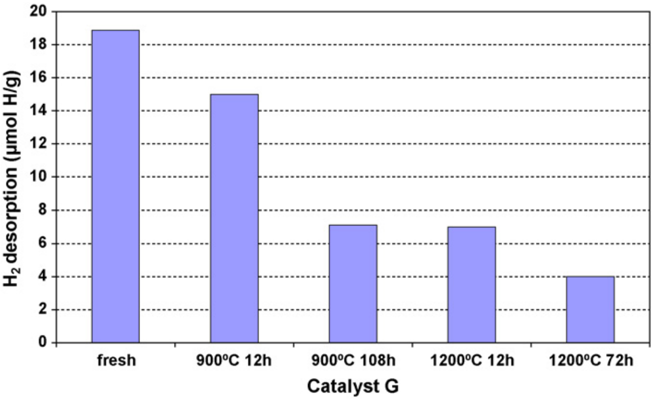

Fig. 8. Total hydrogen desorbed for fresh and aged catalyst G.

in H_2 desorption (19 µmol/g to 15 µmol/g), whereas 108 h of ageing was enough to drop the H_2 desorption almost three times lower (7 µmol/g). The same effect was obtained after oxidizing ageing at 1200 °C for 12 h. After 72 h, the H_2 desorption dropped to 4 µmol/g.

Thus, this concept may explain what was observed in this work. The catalyst ageing at 900 °C under stoichiometric conditions probably caused an increase in Pt particles, followed by a decrease in dispersion, which must be very high for the fresh catalyst, as already indicated by SEM-EDX analyses. This mechanism may have favoured propane oxidation for the catalyst aged for 12 h. However, after 108 h, T_{20} was shifted from 455 °C to 480 °C, indicating that prolonged ageing increases catalyst sintering, probably surpassing the optimum Pt particle diameter required for propane oxidation.

Additionally, the presence of Rh in the catalyst formulation and its interaction with Pt may significantly change the catalytic activity for propane oxidation, as shown in the literature [44] with Pt-Rh/Al_2O_3-CeO_2 catalysts. Pirault et al. [44] observed that when Pt and Rh were in separated domains (after ageing at 900 °C), catalyst activity was increased. In contrast, catalysts containing Pt and Rh in close interaction (fresh catalyst) presented lower activity.

Thus, the uncommon behaviour observed towards propane oxidation, meaning an increase of catalyst activity after ageing at 900 °C for 12 h, was also observed by other authors in the literature, but further research is required to explain this phenomenon. As this study was based on a commercial catalyst and its preparation and pretreatment procedures are unknown, it is not possible to affirm that the poor propane oxidation is due to a unique aspect of the catalyst. Variations in Pt dispersion and the Pt oxidation state, as well as interactions with Rh may contribute to this behaviour.

4. Conclusions

It was shown that thermal deactivation causes a negative impact on automotive catalyst activity, changing its textural, structural and redox properties. However, certain activation was observed after 12 h of ageing at 900 °C under stoichiometric conditions. The aged catalyst was more active than the fresh one for propane oxidation, while the oxidation of carbon monoxide was apparently not affected. However, NO reduction suffered an important deactivation after ageing, probably due to sintering of the rhodium particles. For propane oxidation, the low activity for the fresh catalyst probably occurred due to its high Pt dispersion. Small Pt particles are more susceptible to oxidation, and oxidized Pt particles are not active in the conversion of propane. It is possible that the thermal treatment at 900 °C for 12 h provided the optimum Pt particle size, minimizing its oxidation.

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