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Self-Regeneration Effect of Three-Way Catalysts during Thermal Aging Procedure

Evgeny A. Alikin 1, Sergey P. Denisov 1, Konstantin V. Bubnov 1 and Aleksey A. Vedyagin 2,*

1 Research & Development Department, Ecoalliance Limited Liability Company, Novouralsk 624131, Russia; alikin@eco-nu.ru (E.A.A.); denisov@eco-nu.ru (S.P.D.); bubnov@eco-nu.ru (K.V.B.)
2 Department of Materials Science and Functional Materials, Boreskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russia
* Correspondence: vedyagin@catalysis.ru

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Abstract: One of the most important features of the three-way catalysts is their long-term stability. However, quite often, promising catalytic compositions with excellent activity become deactivated after a relatively short period of exploitation due to various reasons. Therefore, a study on the onboard regeneration of the deactivated three-way catalysts remains its actuality. The present work is mainly focused on the self-regeneration effect of the rhodium-containing component. Aging of the catalysts in the standard and model engine braking regimes revealed the difference in the catalytic performance. Deactivated rhodium species turned to the active state as a result of rapid cooling in air flow from 1200 to 600 °C. The regenerated catalyst shows improved activity towards NOx reduction and, therefore, widened operation window, which indicates higher accessibility of the rhodium species. X-ray diffraction analysis of the aged catalysts does not reveal any noticeable phase changes. Contrary, significant changes in the Rh oxidation state were registered by X-ray photoelectron spectroscopy. The observed effect opens new horizons for the development of the onboard purification systems with prolonged exploitation lifetime.

Keywords: three-way catalysts; rhodium; engine bench; high-temperature aging; self-regeneration

1. Introduction

In modern life, automobile transportation represents the main source of air pollution contaminants, thus facing the most actual environmental problem. Therefore, within the constituents of modern cars, a three-way catalyst (TWC) is irreplacably applied to diminish the harmful emissions from the gasoline engines [1]. TWC accomplishes a function of simultaneous transformation of unburnt hydrocarbons (HC), CO, and NOx into CO2, water, and nitrogen. Traditionally, the composition of TWC is considered to include secondary support—modified aluminum oxide and ceria-containing system, and active components—metals of platinum group (Pt, Pd, and Rh) [1–3].

According to the ecological standards Euro 5+, acting in Russia in the present, TWC for passenger cars should provide efficient neutralization of exhaust gases over a period corresponding to 160,000 km. Thereby, a question of the long-term stability of TWCs is of great importance and actuality. The efficiency of the catalyst is most commonly examined by testing the exact automobile on the roll test rig in accordance with the normalized driving cycle.

In general, the world practice in the estimation of the TWC’s lifetime shows that the faster and most informative way is the forced aging of TWC under various drastic conditions [4–10]. Such an approach allows the researchers to study the reasons and mechanisms of the catalysts’ deactivation process [11–16]. During the last few decades, palladium was the most commonly studied precious metal, since the concept of Pd-only three-way catalyst was of high attractiveness. Therefore, the
deactivation and regeneration behavior of the Pd-containing catalysts was investigated in more detail. The deactivation processes can be divided onto two groups connected mainly with the transformation of the active species (change of the Pd oxidation state, sintering, and formation of large agglomerates) or with the strong interaction of the active metal with the support (formation of core-shell structures, near-surface diffusion, encapsulation and formation of joint phases) [17]. The regeneration effect is first attributed to the features of the thermal transitions “PdO→Pd”, which, for instance, results in re-oxidation of metallic palladium with the formation of active palladium oxide at cooling from 1000 to 700 °C in the presence of oxygen [18]. This mechanism explains the regeneration of the catalysts at consecutive aging in a neutral medium and then in an oxygen-containing atmosphere. Secondly, the changes in the Pd dispersion reasonably take place at repeated transitions “metal-oxide” [19–23].

Since Pt-containing catalysts are also of typical use, their high-temperature behavior is of great importance as well. Deactivation of platinum catalysts at elevated temperatures is mainly connected with the recrystallization of Pt particles leading to a decrease in the active surface. It is known that the sintering rate grows along with the temperature rise. This rate is noticeably higher in an oxygen-containing atmosphere than in hydrogen or inert media. The growth of platinum crystallites can occur via one of two mechanisms: (i) surface migration and agglomeration of particles [24,25]; (ii) oriented migration of Pt atoms towards the immobile crystallite (Ostwald ripening) [26–28]. The (i) route is preferable for the oxidative medium, while the (ii) route predominates in the case of the reductive medium [29]. The coefficient of the metal particles’ surface migration increases with a decrease in their size. The aging in the dynamically changing oxidative-reductive atmosphere actuates some additional migration mechanisms. All this results in a transfer of the metal particles from alumina to a ceria-rich component, where platinum can be stabilized due to the strong interaction with the support. It should be emphasized that the CeO$_2$ phase is required for such a strong interaction [30]. Therefore, the aging under the oxidative conditions does not facilitate the surface stabilization of Pt or Pt-Rh species since the CeO$_2$ phase predominates. Contrary, the aging under reductive conditions does not actuate the migration mechanisms, and both metals stayed on alumina. In the case of oscillation of reductive and oxidative conditions only, all the requirements are met, and the agglomerated Pt-Rh particles can be found on the ceria surface. Any oxidative high-temperature regeneration of such deactivated catalysts regrettably worsens the activity for the mentioned reasons.

In the case of the rhodium-containing component of TWC, the situation seems to be more complex. Rhodium, conventionally responsible for the reduction of nitrogen oxides [3], interacts with supports more intensively. As recently reported [31], rhodium ions rapidly diffuse into the bulk of alumina at elevated temperatures, where become irreversibly encapsulated within the corundum phase being formed. The doping of alumina with lanthanum affects the diffusion routes and preferable location positions of Rh ions, thus making the deactivation process reversible [32,33]. Rh also interacts with ceria and cerium-zirconium mixed oxides, causing the local compaction of the support, but in a less dramatic manner [34,35].

The present research is aimed to reveal the contribution of rhodium species behavior to the effect of the TWC regeneration under the high-temperature aging conditions. Recently, we have already reported that the model fuel-cut regime results in the catalyst reactivation, which is assigned to the re-dispersion of agglomerated rhodium particles serving as a source of the active rhodium species [36]. Here, the main focus is placed upon rhodium behavior at a model engine braking regime. Characterization of the aged samples was performed using X-ray diffraction analysis and X-ray photoelectron techniques. The effect of the catalysts’ reactivation was examined by testing the light-off performance and width of the operation window.

2. Results and Discussion

One of the mandatory measures for developing and commissioning the commercial automobile catalysts is the implementation of the forced aging procedures. The full-scale mileage tests of such catalysts within the composition of a real car are rather complicated from as financial as temporal
reasons. Therefore, various methods of forced aging of the honeycomb catalysts installed into a bench unit with a target engine are applied in world practice. All the existing specialized methods are based on the general accomplishment principles—the catalyst in the exhaust system is subjected to the aging in a flow of engine exhaust gases at a temperature above 1000 °C with periodic cooling to 600–800 °C and cycling of the gas mixture composition near the stoichiometry (Regulation No 83 (type V test) of the UN/ECE). The singularities of the exact approach can be assigned to the choice of the nominal temperature (800–1150 °C), the time parameters of the cooling-heating cycles, the deviation amplitude from the stoichiometry, and the total duration of the aging procedure. In accordance with the mentioned regulation, the lower the temperature, the longer the aging procedure. Thereby, from the economic points of view, the manufacturers prefer higher temperatures and shorter procedures.

A long-standing practice revealed the non-singular facts of a step-by-step improvement of the catalyst’s activity after the performing of such aging tests. Thus, for instance, Figure 1 demonstrates a decrease in the NOx emission during the consecutive roll emission tests on the automobile with installed OBD catalyst preliminary aged at a temperature of 1200 °C for 10 h. The role of the OBD catalyst is to be stable during the tests and meet the onboard diagnostic system (OBDS) standards. It should be mentioned that the level of NOx emission is one of the most strictly regulated characteristics. As was already mentioned, rhodium in the composition of three-way catalysts is responsible for nitrogen oxides reduction. Therefore, progressive improvement of the catalyst’s efficiency towards NOx allows supposing that the observed regeneration of the catalyst is connected with the changes in rhodium state. It is important to note that the similar facts of the catalyst regeneration were also registered immediately during the forced aging procedures on the engine bench.

![Figure 1](image1.png)

**Figure 1.** Results of the consecutive roll emission tests on Lada Vesta automobile with a rapidly aged OBD catalyst.

Figure 2 shows the vehicle speed regime during the driving cycle and the corresponding temperature of the exhaust gases. As seen, for the stages of acceleration to 16, 32, and 50 km/h with subsequent braking, the temperature values averagely vary in a range of 400–600 °C. An acceleration of the vehicle up to 120 km/h increases the temperature to 800 °C, and the following braking stage diminishes the temperature on ~350 °C. The latter driving stage was empirically found to make the maximal contribution to the catalyst regeneration process.
As evident from Table 1, after the model engine braking regime, the performance of the catalyst is characterized by the lower temperature values of 50% conversion ($T_{50}$) of hydrocarbons, CO, and NOx. The conversions of THC and NOx at 400 °C are also significantly intensive in the case of MEBR sample, while the intensity of the possible reflection of RhO2 phase is less presented in Figure 4b indicates that the reflections assigned to Rh2O3 phase \[37\] are less.

Table 1. Light-off parameters for the aged samples of Rh/(Al2O3-CeZrO2) catalyst.

| Aging Conditions                      | $T_{50}$, °C | Conversion at 400 °C, % |
|---------------------------------------|--------------|-------------------------|
|                                       | THC          | CO          | NOx        | THC | CO         | NOx   |
| Standard aging regime (StAR)          | 336          | 290         | 280        | 66  | 99         | 89    |
| Model engine braking regime (MEBR)    | 313          | 285         | 276        | 97  | 98         | 100   |

Figure 2. The speed and temperature profiles for the driving cycle (roll tests) of the monolith-supported catalysts.

In order to investigate the observed regeneration phenomenon more precisely, the monolith-supported Rh/(Al2O3-CeZrO2) catalyst was aged in two modes. The first mode considers the standard aging regime using an engine bench at a temperature of 1200 °C for 14 h. In the second case, the model engine braking regime was simulated by the fuel cut and rapid cooling from 1200 to 600 °C in air flow for a few minutes. Thus, aged samples of the catalyst were tested for catalytic performance. The light-off parameters and operation window values resulting from these tests are presented in Table 1 and Figure 3. As evident from Table 1, after the model engine braking regime, the catalyst is characterized by the lower temperature values of 50% conversion ($T_{50}$) of hydrocarbons, CO, and NOx. The conversions of THC and NOx at 400 °C are also significantly increased, while the CO conversion remained almost the same. The observed increase in the catalyst’s activity towards hydrocarbons testifies about the higher accessibility of the rhodium surface.

Figure 3. Operation window of the Rh/(Al2O3-CeZrO2) catalyst aged at standard conditions (a) and in the model engine braking regime (b).
As follows from Figure 3, the operation window in the case of the catalyst aged in the model engine braking regime (MEBR) is wider if compared with the standardly aged (StAR) sample. Moreover, due to the higher activity of the MEBR catalyst in the oxidation of hydrocarbons, the corresponding curve for the total hydrocarbons conversion is shifted towards lower values of Lambda. Thereby, the operation window for the StAR sample has a width of 0.00598 units and is limited by the THC curve only (Figure 3a). Oppositely, the MEBR sample shows a wider operation window of 0.00659 units, which is limited by the CO conversion at lower Lambda values and the THC conversion at higher Lambda values (Figure 3b).

The two aged samples were characterized by X-ray diffraction analysis and X-ray photoelectron spectroscopy. The XRD patterns shown in Figure 4a do not reveal any changes in the phase composition of the samples aged in different modes. Both the patterns are mainly represented by the reflections of cordierite, corundum, and cerium-zirconium mixed oxide. The enlarged 20 region of 30–38° presented in Figure 4b indicates that the reflections assigned to Rh$_2$O$_3$ phase [37] are less intensive in the case of MEBR sample, while the intensity of the possible reflection of RhO$_2$ phase [38] slightly increases. It is worth to note that the XRD analysis of low rhodium content in such a complex composition is quite complicated.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** XRD patterns for the Rh/(Al$_2$O$_3$-CeZrO$_2$) catalyst aged at standard conditions (StAR) and in model engine braking regime (MEBR): (a) in a range of 10–80°; (b) in a range of 30–38°.

Additionally, the XPS spectra of Rh3d region presented in Figure 5 discover a significant difference between the two samples under study. The spectrum of the StAR sample contains one duplet peak with the binding energy of 308.3 eV, which can be assigned to rhodium oxide Rh$_2$O$_3$. In the spectrum of the regenerated MEBR sample, an additional doublet with the binding energy of ~310.5 eV attributed to another oxide RhO$_2$ is registered. The ratio of the rhodium oxides (Rh$_2$O$_3$ : RhO$_2$) in this sample was found to be about 1.86:1. It should be emphasized that after the regeneration (aging in the MEBR mode), the atomic ratio [Rh]/[Al] became more noticeable (Table 2). One of the possible reasons for such an increase is the elimination of carbon deposited on the surface of rhodium particles during the last stage of the MEBR aging procedure in an air atmosphere. The deposition of carbon during the catalyst exploitation is a known phenomenon [39]. Thus, deposited carbon is often used as an internal standard for the XPS studies [40,41]. In our case, the assumed oxidation of carbon deposits is testified by the fact that in the regenerated sample, the carbon content is lower if compared with the StAR sample (Table 2). Note that no other impurities, like S, P, Zn, or Ca, were detected in both the samples.
Rhodium ions still diffuse into the bulk of the support, but the formation of corundum phase is prevented by the presence of La\(^{3+}\) ions. Therefore, such rhodium species can be, in principle, regenerated. Oppositely, rhodium more strongly interacts with the ceria-based oxides forming the joint phases during the heating to the temperatures of 1200 °C. This phase can serve as a source of superdispersed Rh particles formed at the stage of the rapid cooling of the catalyst.

Quite recently, the fact of the regeneration was reported for the rhodium catalysts based on the Al\(_2\)O\(_3\) and CeZrO\(_2\) supports [42]. However, the regeneration effect was observed only after the treatment in the reductive atmosphere at 550 °C. Contrary, the oxidative treatment at elevated temperatures is commonly considered as the strongest deactivation factor for the rhodium catalysts [7,31,42]. On the other hand, in the oxidative medium, the mobility of rhodium ions is significantly increased, that leads to its migration within the layers up to tens of microns [43]. In the present study it was found that the action of the oxidative medium at rapid cooling of the catalyst facilitates its regeneration. This is accompanied with an increase in the rhodium surface concentration. Despite there is no evident answer which support, Al\(_2\)O\(_3\) or CeZrO\(_2\), is responsible for the rhodium activation, the preferences can be made towards the ceria-containing support. In the case of alumina, the bulk diffusion of rhodium ions was shown to be irreversible due to the local formation of corundum phase encapsulating the rhodium species [31]. On the other hand, La\(_2\)O\(_3\)-doped alumina was used in the present work. For this support, its interactions with rhodium species are not so dramatic [32,33]. Rhodium ions still diffuse into the bulk of the support, but the formation of corundum phase is prevented by the presence of La\(^{3+}\) ions. Therefore, such rhodium species can be, in principle, regenerated. Oppositely, rhodium more strongly interacts with the ceria-based oxides forming the joint phases during the heating to the temperatures of 1200 °C. This phase can serve as a source of superdispersed Rh particles formed at the stage of the rapid cooling of the catalyst.

In order to check the made assumption, the reference Rh/Al\(_2\)O\(_3\) and Rh/CeZrO\(_2\) catalysts were prepared, aged in two modes, and tested for catalytic performance. Table 3 summarizes the results of the light-off tests. As evidently seen from the presented data, in the case of individual alumina support, the aging in the model engine braking regime leads to a significant worsening of the activity. The values of T\(_{50}\) increased on 40–70 °C, while the conversions of THC and CO decreased. This evidently testifies that no reactivation of the Rh/Al\(_2\)O\(_3\) component takes place under the MEBR condition. Oppositely, for

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**Figure 5.** XPS spectra (Rh3d region) for the Rh/(Al\(_2\)O\(_3\)-CeZrO\(_2\)) catalyst aged at standard conditions (1) and in the model engine braking regime (2).

**Table 2.** XPS data for the aged samples of Rh/(Al\(_2\)O\(_3\)-CeZrO\(_2\)) catalyst.

| Aging Conditions                  | Rh3d5/2 | [Rh]/[Al] | [C]/[Al] |
|----------------------------------|---------|-----------|----------|
| Model engine braking regime (MEBR) | 308.4   | 310.5     | 0.0072   | 0.742    |
| Standard aging regime (STAR)     | 308.3   | -         | 0.0050   | 0.927    |

Hereby, it can be concluded that the rapid cooling of the rhodium-containing three-way catalyst in air results in an increase of the atomic rhodium concentration in 1.5 times and an appearance of additional rhodium state with higher binding energy. The latter can be interpreted by a change in as rhodium oxidation state as its dispersion.
the Rh/CeZrO₂ sample, the same aging procedure improves the catalytic activity. The T₅₀ values for the THC, CO, and NOₓ conversions lowered on 51, 38, and 28 °C, correspondingly. The THC conversion at 400 °C increased by 12% that leads to a decrease in CO conversion due to the formation of odd CO from hydrocarbons via their reaction with NOₓ. As already mentioned, the main function of rhodium in the composition of three-way catalysts is not CO oxidation but NOₓ conversion, including their reduction by hydrocarbons [3]. The high value of NOₓ conversion along with the increased value of THC conversion indicates the reactivation effect. Therefore, the performed experiments evidently confirmed the main contribution of the ceria-containing component in the self-regeneration process of the three-way catalytic system.

Table 3. Light-off parameters for the aged reference catalysts.

| Sample            | Aging Conditions | T₅₀, °C | Conversion at 400 °C, % |
|-------------------|------------------|--------|-------------------------|
|                   |                  | THC    | CO          | NOₓ     | THC    | CO          | NOₓ     |
| Rh/Al₂O₃         | StAR         | 291    | 280         | 272     | 89     | 95          | 88      |
| Rh/Al₂O₃         | MEBR         | 361    | 326         | 312     | 69     | 93          | 90      |
| Rh/CeZrO₂        | StAR         | 356    | 326         | 306     | 68     | 90          | 96      |
| Rh/CeZrO₂        | MEBR         | 305    | 288         | 278     | 80     | 80          | 97      |

It should be emphasized that the present research was focused on monometallic Rh-only catalysts to elucidate the effect of rhodium reactivation. In the case of complete composition of three-way catalyst, when palladium is also present, the performance in oxidation processes can be noticeably different. For instance, as recently reported for bimetallic Pd-Rh/Al₂O₃ catalysts [44], the T₅₀ values for CO and THC are as low as 244 and 260 °C, accordingly, and the corresponding conversions at 400 °C are 97% and 99%. The presence of palladium species provides the complete oxidation of hydrocarbons and the effective utilization of CO. Such an enhanced functioning of the bimetallic three-way catalyst gives the operation window values of 0.0089–0.0114 units, which are 1.5–2 times wider than obtained in the present research (Figure 3).

3. Materials and Methods

3.1. Preparation of the Catalysts

The samples of the catalysts were prepared by an incipient wetness impregnation of the mixed Al₂O₃-CeZrO₂ support with an aqueous solution of rhodium nitrate. The support was composed of commercial La₂O₃-doped γ-Al₂O₃ (TM 100/150 L4, Sasol, Hamburg, Germany) and commercial Ce₀.₅Zr₀.₅O₂ (Optalys-14, Solvay, Brussels, Belgium) in a weight ratio of 70:30. The Rh loading was 1 wt%. After the deposition of rhodium, the catalyst was impregnated with an aqueous solution of barium nitrate (Adelit, Ufa, Russia). The BaO loading was 3.0 wt%. The wet powder was mixed with water and subjected to grinding in a beaded mill (NETZSCH-Feinmahltechnik, Selb, Germany). The average particle size in the final suspension was about 6-7 microns (D90). Suspension contained 30–35 wt% of solids was supported on a honeycomb cordierite monolithic substrate RD 4 × 5" (101.6 mm in diameter and 127.0 mm in length, 63 cells per square cm) (Corning, Kaiserslautern-Wiesbaden, Germany) by an aspiration procedure. The loading of the active components in the monolith sample was 150 g/L. The monolith was dried at 120 °C and calcined at 550 °C for 1 h. The total loading of rhodium in the monolith-supported catalysts was 1.413 g/dm³.

The reference samples Rh/Al₂O₃ and Rh/CeZrO₂ containing 1 wt% of rhodium were prepared by the same procedures using the individual alumina and ceria-zirconia supports.

3.2. Characterization of the Catalysts

X-ray diffraction (XRD) analysis was carried out on a Rigaku ULTIMA IV diffractometer (Rigaku Corporation, Tokyo, Japan) (CuKα radiation) using a scintillation counter with a monochromator.
crystal placed in the diffracted beam ($2\theta = 0.05^\circ$ steps, counting time of 5 s per data point). The crystallite size was calculated by the Williamson-Hall method using the Scherrer formula.

X-ray photoelectron spectroscopy (XPS) studies were carried out using a SPECS spectrometer (SPECS GmbH, Berlin, Germany) with MgK$\alpha$ radiation ($hv = 1253.6$ eV). Firstly, the survey spectra of the samples were recorded in a range of binding energies (BE) from 0 to 1000 eV. The precise analysis of each spectrum was done for the regions assigned to the elements found on the surface. The BE values were defined according to the Al2p line in alumina (BE = 74.5 eV [45]). The rhodium atomic concentration was calculated with regard to the aluminum concentration taking into account the atomic sensitivity factors reported elsewhere [46].

In order to characterize the catalysts by XRD and XPS methods, the catalytic layer (washcoat) was delaminated from the cordierite monolith. Thus, obtained flakes were placed in a sealed container to prevent their contact with air until the characterization procedures.

3.3. Testing and Aging of the Catalysts

The operation window of the monolith samples was measured using a Horiba CTSJ-2003.12 analytical setup (Horiba, Kyoto, Japan) by scanning Lambda from 0.97 to 1.01 at a temperature of 500 °C. The following reaction mixture was passed through the monolith catalyst: O$_2$ in a range from 0.196 to 1.058 vol. % for $\lambda = 1$; CO—1.60 vol. %; NO$_x$—1000 ppm; C$_3$H$_6$—250 ppm; C$_3$H$_8$—250 ppm; H$_2$—0.4 vol. %; CO$_2$—9.35 vol. %; H$_2$O—10 vol. %; N$_2$ as a balance. The gas hourly space velocity (GHSV) was 70,000 h$^{-1}$. The borders of the operation window were limited by 80% conversion of at least one of three types of contaminants: CO, total hydrocarbons (THC), and NO$_x$.

Light-off performance (temperature of 50% conversion of CO, THC, and NO$_x$) and maximum conversion in a pulse regime at 400 °C for the monolith samples were studied using a Horiba CTSJ-2003.12 analytical setup (Horiba, Kyoto, Japan) under the same reaction conditions. The sample was heated up in a range of 80–400 °C with a ramping rate of 20 °C/min, and then was kept at 400 °C for 3 min.

The examination of the onboard diagnostic (OBD) catalyst was carried out on a Lada Vesta 1.6 automobile (16 valves) using a dynamometric setup VULCAN II EMS-CD 48 L 2WD (Horiba Europe Gmbh, Darmstadt, Germany). The New European Driving Cycle (NEDC) was used in accordance with Regulation No 83 (type I test) of the Economic Commission for Europe of the United Nations (UN/ECE). The OBD catalyst contained 1.236 g/dm$^3$ of precious metals with a Pd:Rh ratio of 5:1 and was aged equivalently to 160,000 km of travelling.

The high-temperature aging of the ceramic blocks RD 4 × 5” with deposited catalyst layer was performed using an engine bench DYNAS$_2$ Li-145 181441, (Horiba Europe Gmbh, Darmstadt, Germany) based on the VAZ 21126 (1.6 L) engine (JST AvtoVAZ, Tolyatti, Russia) shown in Figure 6. The exhaust gases were passed through the catalyst under the following conditions: $T = 1200$ °C; $t = 14$ h; Lambda = 1. Cycling of the temperature or gas phase composition was not applied. This procedure was named as a standard aging regime (StAR). Additionally, for some of the samples, a regime of the engine braking was imitated. In this case, after the same StAR procedures, the fuel cut and the rapid cooling from 1200 to 600 °C in air flow for a few minutes were applied. This procedure was named as a model engine braking regime (MEBR).
4. Conclusions

Various aging procedures are used in world practice to estimate the exploitation resource of the developed three-way catalysts. In the cases when the processes of the deactivation of the catalysts are reversible, the search for the regeneration approaches or conditions is highly demanded. Most commonly, the high-temperature oxidative treatment is considered as the main factor resulting in the significant loss of activity, while the regeneration procedures require the reductive atmosphere. In the present research, numerous driving cycle (roll) tests revealed that the preliminary aged rhodium-containing three-way catalysts undergo the self-regeneration during the examination. The most crucial stage of the driving cycle was supposed the rapid cooling of the catalyst during the braking from 120 km/h. The model engine braking regime was proposed and applied in the present work. This regime considers the rapid cooling of the catalyst from 1200 to 600 °C in air flow for 1–2 min. Such treatment results in an increase of the activity of the catalysts towards the hydrocarbons conversion and NOx reduction. Comparative characterization of the samples aged under the standard conditions and in the model engine braking regime evidently showed that the main contribution to the self-regeneration process is made by an increased accessible surface of the rhodium species and a change in a rhodium oxidation state. According to the results of XRD and XPS characterization, RhO2 species appeared after the model engine braking regime in addition to Rh2O3 species presented after the standard aging regime. This observation of the rhodium-ceria component’s self-reactivation within the composition of three-way catalysts under oxidative conditions opens new horizons for further development of the on-board regeneration concept.

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