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Laboratory scale simulation of three-way catalyst engine ageing

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Abstract

In this work, a laboratory ageing cycle simulating the real engine ageing for three-way catalysts was developed. The laboratory cycle was created based on the rapid ageing hot (RAH) cycle used in the engine bench ageings. The simultaneous gas concentration and temperature changes were achieved by adjusting the IR-furnace and the gas flow parameters. The laboratory ageing cycle was verified by testing different samples after different ageings with the laboratory and the engine tests. In addition, some characterization methods: specific surface area (BET-method), dispersion (CO-chemisorption), particle size (CO-chemisorption) and oxygen storage capacity (with CO–O_2 exchange experiments), were used to compare the effect of the different ageings on the catalyst samples.

Keywords: Ageing; Three-way catalyst; Simulation

1. Introduction

The requirements of the better efficiency and economy of cars have led to the development of different operational strategies by the manufacturers. Nowadays, in order to achieve tight emission legislations, besides the more efficient engines, also the exhaust after-treatment systems have to be optimized towards cold start performance and the transient driving conditions [1]. Therefore, the conversion of the emissions should begin nearly immediately after the engine start up and so the catalyst should be mounted next to the engine just after the manifold. This accelerates the temperature increase during the start up region, but it also means that during the driving cycle the catalyst is subjected to high temperatures which have a strong ageing effect on the catalyst and the washcoat [2]. In addition, the fuel economy targets have led to the changes of the driving strategies which means that fuel injection is shut down during deceleration [3]. Then, the catalyst is subjected to oxidative atmosphere at high temperatures leading to the deactivation of the active components in the washcoat. However, some of these deactivation processes can be reversible. So, the performance of the catalyst could be restored during driving, when the catalyst is exposed to the conditions where the regeneration processes can exist, i.e. reducing conditions in rich λ-values. In the literature the deactivation and regeneration processes of the catalysts are widely examined [4–10]. In the engine ageing cycles, the catalyst is exposed to varying conditions: stoichiometric, strongly oxidising and reducing with simultaneous rapid temperature variations. In engine dynamometers, this can be carried out by repeated cycles which consist of different steps with varying engine speed and load, the air/fuel ratio changes or injection of air or reducing gas into the exhaust stream. These effects cause different temperatures in the washcoat because of the exothermal reactions in the washcoat or due to the cooling effect of the injected gas and minor reactions on the surface of the washcoat. On the laboratory scale, an oven ageing under air or in hydrothermal conditions has been normally used as an ageing method for the three-way exhaust catalysts. However, the conditions in which the three-way catalysts are exposed during the real driving or engine ageing conditions are more or less transient. Thus, the correlation of the oven ageing to the engine ageing has not been very good due to the high ageing effect of air at high temperatures. Therefore, the development of the laboratory ageing method, which correlates

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better to the real engine conditions is necessary. In this work, a laboratory method for simulating the engine ageing of a three-way catalyst has been developed.

2. Experimental

2.1. Samples

Catalytic samples (S1–S6) for the laboratory measurements were made by coating a thin Fe–Cr–Al metal foil with a washcoat slurry containing γ-alumina, $Ce_xZr_{1-x}O_2$ mixed oxides and Ce-, La- and/or Ba-oxides as additives. Active materials were added by impregnations onto the porous washcoat or mixed into the washcoat to the relevant precious metal loadings. Catalysts contained 45 g/m^2 support material and the active metal content was 0.72 wt.% in washcoat. In Table 1 the content of the samples are described. The catalyst samples are dried at 100–150 °C and then calcined at 300–550 °C. The dried and calcined samples are referred as ''fresh''. The prototype samples for the engine ageing and testing were made by dipping method to the ready substrate, washcoat slurry being made with the same procedure as the laboratory samples.

2.2. Ageing and testing

Engine ageing for the prototype samples was made with a Chevrolet V-8 5.0 dm^3 engine using rapid ageing hot (RAH) test schedule [11–13]. The ageing procedure consists of both rich, stoichiometric and lean air/fuel ratio modes which is repeated once in a minute. The ageing time has been 40 h. Prototype samples were tested with a Fiat Seicento 1.1 dm^3 engine using the MVEG-B test (motor vehicle emission group) [11], European stage four drive cycle, which consists of four similar cycle simulating the driving in city area and one cycle simulating the driving in motor way, the test is also called as CVS-test (constant volume sampling). Ageing simulations in laboratory were made in an IR-furnace which enables rapid temperature changes. In the laboratory ageing system a quartz tube reactor installed inside a tube furnace was used. The oven ageing was made in static air in a muffle furnace at 1050 °C for 3 h. Similar kinds of reactors as in the ageing procedure were used in the laboratory activity measurements which were done in ceramic tube ovens. Activity measurements were carried out at normal pressure by using laboratory scale cylindrical catalysts with dimensions of diameter 14 mm and length 75 mm. Inlet gas mixtures were mixed with mass flow meters and valves controlled by a computer. The gas compositions were analyzed by a Gasmet FTIR analyzer or with single analyzers (IR for CO/CO_2, FID for HC, chemiluminescence for NO_x and paramagnetic for O_2). The activity of the samples was measured with light-off tests, where the constant heating rate 10 °C/min from 110 to 400 °C was used. During the test O_2 oscillation with $\lambda = \pm 0.014$ and a constant flow rate with the space velocity 50,000 1/h were used. The light-off was determined as the temperature of 50% conversion of each component CO, THC and NO_x.

Table 1
The composition of the used samples: A, B, C three different $Ce_xZr_{1-x}O_2$ oxides

Sample	Washcoat composition	Precious metal
S1	γ-alumina, $Ce_tZr_{1-x}O_2$–A, Ce/La-oxide	Pd impregnated, Rh in washcoat
S2	γ-alumina, $Ce_xZr_{1-x}O_2$–A, Ce/La-oxide	Pd and Rh in washcoat
S3	γ-alumina, $Ce_xZr_{1-x}O_2$–B, Ce/La-oxide	Pd impregnated, Rh in washcoat
S4	γ-alumina, $Ce_xZr_{1-x}O_2$–A*, Ce/La-oxide	Pd impregnated, Rh in washcoat
S5	γ-alumina, $Ce_xZr_{1-x}O_2$–C, Ce/La-oxide	Pd impregnated, Rh in washcoat
S6	γ-alumina, $Ce_xZr_{1-x}O_2$–B, Ce/La-oxide, Ba	Pd and Rh in washcoat

A* sample contains different amount of $Ce_xZr_{1-x}O_2$ oxide than other samples.

2.3. Characterization methods

The characterization of the fresh and differently aged catalyst samples are based on the specific surface analysis (by BET-method), dispersion, particle size and oxygen storage capacity (OSC) measurements. The specific surface areas (SSA) for fresh and aged catalysts were determined from the nitrogen adsorption isotherms at −196 °C with the standard BET-method using a Sorptomatic 1990 equipment. The same equipment was used to determine the dispersions and the particle size of the precious metals by the chemisorption method at room temperature using CO as a probe gas. Active metal particle sizes and dispersions were calculated by assuming the stoichiometric factor between chemisorbed gas molecule and metal atoms being 1:1. Precious metal particle sizes were calculated from the dispersion measurement results. Pretreatment for the SSA measurement consisted of holding the sample in vacuum at 350 °C for 16 h. For the dispersion measurement the pretreatment was done with hydrogen at 300 °C for 30 min after which the sample was held in vacuum at 350 °C for 30 min. Total oxygen storage capacity (OSC) was measured with the laboratory equipment using a quartz reactor and a ceramic furnace [11]. The storage capacity (ml), oxygen in washcoat (g) was calculated/measured from the difference between totally CO-adsorbed and O_2-adsorbed catalyst surface. The gases were analyzed using OmniStar mass spectrometer.

3. Results

3.1. Engine and laboratory ageing

The rapid engine ageing in real exhaust gas stream was carried out in a Chevrolet V-8 5.0 dm^3 engine using RAH

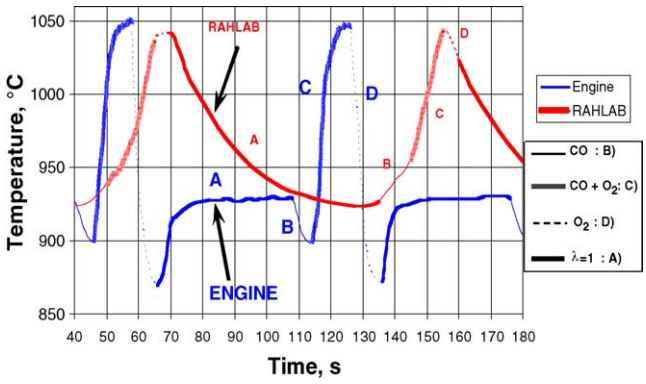

Fig. 1. Temperatures of the cell during the engine and the laboratory ageing cycles: (A) stoichiometric phase, dark thick line; (B) enrichment phase, dark thin line; (C) additional air and CO phase, thick cracked line; (D) oxidizing phase, thin dash line.

test schedule. During the first stage (40 s) of the ageing cycle, the gas mixture is stoichiometric and the temperature of the exhaust gas is about 900 °C and the temperature inside the cell is about 930 °C. Then, the enrichment with 4% CO is made and as seen from the temperature curve the temperature is decreased about 20–30 °C. Then, after 46 s the additional air (4% O_2) is introduced into the exhaust gas stream in order to increase the temperature of the catalyst. During this phase the exhaust temperature is increased up to 1050 °C. Then, the enrichment with CO is closed after 56 s, additional air still on, and the temperature is rapidly decreased about 150 °C during few seconds. After 60 s the additional air is also enclosed and the cycle is began again from the beginning. The temperature diagram can be seen in the Fig. 1.

In order to simulate both the rapid temperature and atmosphere changes in the laboratory equipment the IR-furnace with mass flow meters and valves was used. The laboratory ageing method (RAHLAB, Rapid Ageing Hot in Laboratory) was developed by adjusting the furnace values together with the changes of the gas flows correlating to the engine ageing. Synthetic gases were used and the gas atmosphere used during the ageing simulation was based on the exhaust gas composition in the real exhaust gas in the exhaust pipe of the above described ageing engine. In addition, the oxidising and the reducing atmospheres were calculated by using the same procedure as used in the engine ageing. The gas compositions during the laboratory ageing cycle are introduced in Table 2. The temperature changes were created by adjusting the furnace and the gas flow parameters. The laboratory ageing cycle consists of the following phases and temperatures: stoichiometric phase at 930 °C for 60 s, CO enrichment phase for 15 s during of which the temperature of the furnace was raised from 930 to 1020 °C, additional air + CO phase at 1020 °C for 7 and 3 s during which the furnace temperature was reduced from 1020 to 930 °C and finally the oxidising phase for 1 s at 930 °C. So, these temperatures are the temperatures of the

Table 2
Gas compositions used during the laboratory ageing cycle in different ageing phases

	O_2 (%)	NO (ppm)	H_2O (%)	CO_2 (%)	CO (ppm)	C_3H_6 (ppm)	C_3H_8 (ppm)
Stoichiometric phase	0.06	600	13	15	1400	30	13
CO enrichment	0.06	400	13	13	40000	750	250
Additional air + CO	3.5	400	13	13	40000	750	250
Oxidising phase	3.5	600	13	13	1400	30	13

IR-furnace (or incoming gases) and the temperatures inside the sample cell during the different phases can be seen from Fig. 1. In addition, Fig. 1 shows the temperature curve of the engine ageing as comparison. The temperature of the IR-furnace was controlled with thermocouples. The one which controls the temperatures of the incoming gases was placed about 2 cm before the sample catalyst and the other which measures the temperatures of the catalyst was placed into the rear side of the sample catalyst about 1 cm deep from the rear face inside the catalyst. The control of the PID values of the IR-furnace was based on the temperatures of the incoming gases. During the enrichment with excess of CO + additional air in laboratory cycle the catalyst temperature could be increased quite rapidly up to 1050 °C as also in the real ageing engine, but the rapid temperature decrease, that is observed in the engine ageing during the excess of air was not achieved with the laboratory equipment. Because the temperature fluctuation of the sample is created by heating with oven, it is difficult to generate as rapid temperature changes as with the exhaust gas enrichment and excess of air in real engine. Due to the slower cooling the one single laboratory cycle is longer (87 s) than the engine ageing cycle (60 s). Nevertheless, with the simulation cycle in laboratory equipment it is possible to follow quite well the temperature changes in the real engine ageing.

3.2. The performance of the engine and laboratory aged samples

In order to examine the influence of the different ageings (engine, oven and laboratory simulation ageing) to the light-off temperatures, two samples (S1 and S2) were tested in laboratory with the light-off performance tests. One starting point in the development of the laboratory simulation ageing was that the laboratory cycle should age the sample but not very much further after the real engine ageing. From Fig. 2 it can be seen that the engine aged sample S2 has the light-off values 271, 262 and 266 °C for THC, CO and NO_x, respectively, in the laboratory tests. The same sample after the 1 h additional ageing with the RAHLAB cycle has the light-off values 275, 265 and 267 °C for THC, CO and NO_x, respectively, very close to those achieved after the real engine ageing showing the suitability of the used laboratory

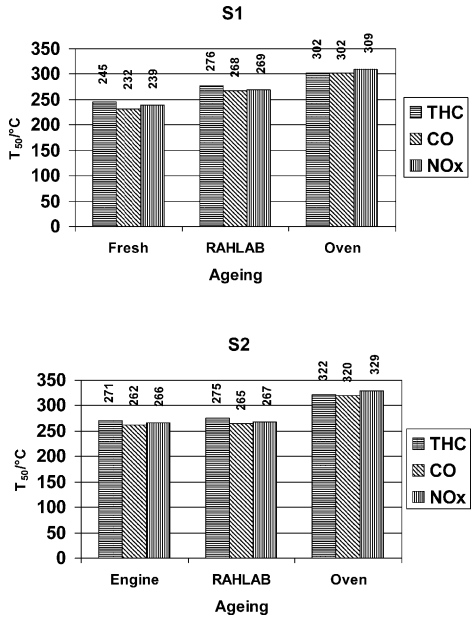

Fig. 2. Laboratory light-off temperatures (T_{50}) for fresh, engine, RAHLAB and oven aged samples S1 (above) and S2 (below).

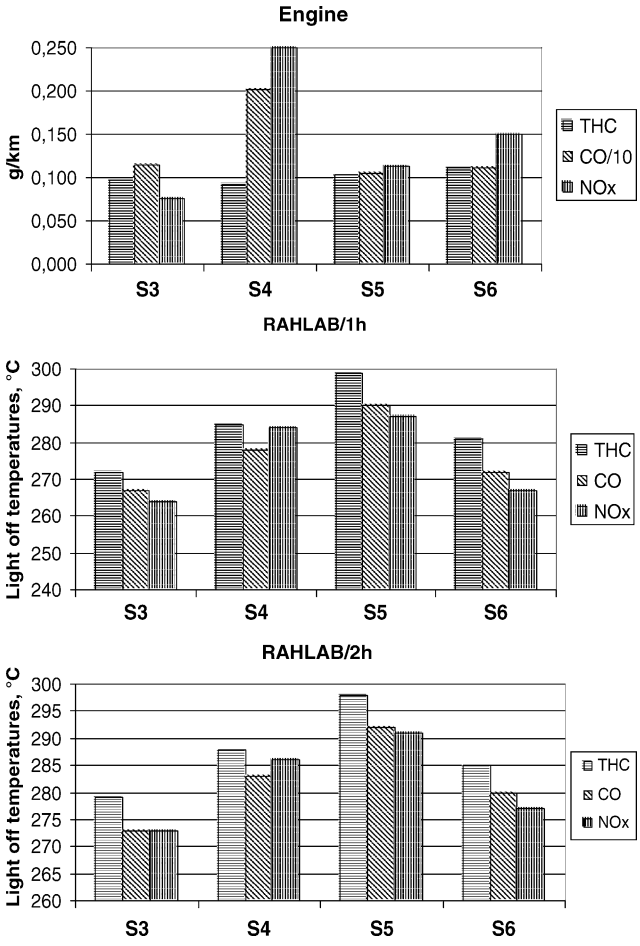

Fig. 3. Emission results from the engine tests (above) and the light-off temperatures (T_{50}) from the laboratory performance tests for the samples S3–S6; after 1-h ageing (in the middle) and after 2-h ageing (below).

ageing cycle. The corresponding light-off values after the oven ageing (at 1050 °C/3 h in static air atmosphere) for the sample S2 (already aged in engine) were 322, 320 and 329 °C for THC, CO and NO_x, respectively. These light-off values show that the oven ageing at 1050 °C under air atmosphere continues the ageing of the engine aged sample and therefore has too severe ageing effect. The ageing effect of the laboratory ageing cycle, RAHLAB, was tested with the fresh sample S1. The light-off values in the laboratory performance tests for the fresh sample S1 were 245, 232 and 239 °C for THC, CO and NO_x, respectively, and the corresponding light-off values for the RAHLAB aged S1 were 276, 268 and 269 °C for THC, CO and NO_x, respectively. These results indicate that on one hand, the simulation ageing cycle, RAHLAB, has a real ageing effect on the catalyst sample, but on the other hand, has not as severe ageing effect as the oven ageing at 1050 °C, because the corresponding light-off values for the oven aged sample S1 were 302, 302 and 309 °C for THC, CO and NO_x, respectively. The comparison of the light-off values (T_{50} °C) in the laboratory performance tests to the emission test results in the engine (g/km) with Fiat Seicento 1.1 engine were done for four different samples, S3–S6. One- and 2-h laboratory ageings were done in order to examine the effect of the ageing time on the light-off values of the samples in laboratory light-off tests. The results of the performance tests are introduced in Fig. 3. The order of the samples arranged by the light-off values were S3, S6, S4 and S5, S3 and S5 having the best and worst light-off values, respectively. This order was the same also after the 2-h ageing. As seen from the Fig. 3 all the samples are ageing little further during the 2-h ageing when compared to the light-off values achieved after the 1-h ageing. After engine ageing the order of the samples ranked by the emission values (g/km) were S3, S5, S6 and S4. So, the same sample (S3) was found to be the best one after both the ageings, engine and laboratory, but the difference of the samples S4 and S5 was the opposite between the ageings. In engine tests the emission values for the S4 sample was found to be quite bad showing the strong ageing effect of the engine ageing to the S4 catalyst. Also the light-off values in the laboratory tests were poorer for the sample S4 than for the best samples, S3 and S6. The long engine ageing has induced a collapse of the S4 performance in the engine test. Same kind of collapse was not found after the 1- or 2-h laboratory ageing in laboratory light-off tests. The conversions (%) at 400 °C after the RAHLAB 1-h ageing in laboratory tests for CO, THC and NO_x have been 93, 93, 88; 94, 93, 84; 86, 86, 83 and 89, 89, 86 for the S3, S4, S5 and S6, respectively. The conversions (%) at 400 °C after the RAHLAB 2-h ageing in laboratory tests for CO, THC and NO_x have been 94, 93, 90; 94, 93, 90; 90, 91, 90 and 89, 89, 89 for the S3, S4, S5 and S6, respectively. After the 1-h ageing the best values were found for S3 and the worst for S5, whereas after the 2-h ageing the best values were found for S3 and the worst for S6.

Table 3
The surface analysis results of the samples S3 and S6

Ageing	S3				S6			
	Fresh	Laboratory	Oven	Engine	Fresh	Laboratory	Oven	Engine
SSA (m^2/g)	88	35	39	29	96	72	44	32
Dispersion (%)	33	<2	<2	<2	48	<2	<2	<2
Particle size by chemisorption (nm)	3	79	112	93	2	133	111	145
Total OSC at 600 °C (ml O_2/g)	2.7	1.8	2.0	1.5	2.3	2.7	2.3	1.9

3.3. The characterization results

Two samples, S3 and S6, were characterized by the surface analysis after different ageings. Specific surface area, dispersion, particle size and the oxygen storage capacity results are presented in Table 3. The specific surface areas for the fresh samples (S3 and S6) were 88 and 96 m^2/g, for laboratory aged samples 35 and 72 m^2/g, for oven aged samples 39 and 44 m^2/g and for engine aged samples 29 and 32 m^2/g, respectively. Dispersions of the active metal was found to be 33% and 48% for the samples S3 and S6, respectively, as fresh and as aged the dispersion values were less than 2% after all ageings for both samples. Particle sizes calculated by the chemisorption method were 3, 79, 112 and 93 nm for fresh, laboratory aged, oven aged and engine aged sample S3, respectively. The same values were 2, 133, 111 and 145 nm for fresh, laboratory aged, oven aged and engine aged sample S6, respectively. For both samples the particle size value after the engine ageing was found to be near the corresponding value after the laboratory ageing. However, the oven ageing has induced smaller particle size for S6 than the engine or laboratory ageing. With both samples the specific surface value decreases when going from the fresh samples to the aged samples, the smallest values found after the engine ageing. The specific surface area of the engine aged sample is near to the value of the laboratory aged sample for the S3 sample, but for the S6 sample the value of the engine aged sample is near to the oven aged sample. The oxygen storage capacity values were 2.7, 1.8, 2.0 and 1.5 ml O_2/g washcoat for fresh, laboratory aged, oven aged and engine aged sample S3, respectively. The corresponding values for S6 were 2.5, 2.7, 2.3 and 1.9 ml O_2/g washcoat for fresh, laboratory aged, oven aged and engine aged sample, respectively. For the sample S3 the OSC-values after engine ageing correlate to the values achieved after laboratory ageing, but with the sample S6 such a correlation has not been found.

4. Discussion and conclusions

The ageing in which the catalysts are exposed in the real engine, consists of the thermal effect combined with the simultaneous effect of the catalyst poisons during the road or engine bench ageings of the three-way catalysts. Traditionally, the ageing is classified to three differently affecting categories: chemical, mechanical and thermal [5]. In this work, only the thermal ageing effect with simultaneous changes in atmosphere on the catalyst during the laboratory ageing was examined. Synthetic gases were used to make a model exhaust gas mixture simulating the real exhaust gas of the gasoline engine. Normally, the fuel burned in an engine contains some impurities such as sulphur and on the other hand the catalyst poisons are originated also from the lubricating oil burned in the engine. These catalytic poisons (e.g. S, P, Ca, Zn) have their own effect on the ageing of the catalyst, especially to the light-off temperatures of the catalyst [4]. The laboratory ageing cycle developed in this work can follow quite well the temperature increase of the real RAH ageing cycle in engine, but as deep temperature decrease curve was not achieved. These simultaneous concentration changes of the exhaust gas and the temperature changes together are, nevertheless, the driving forces in the ageing of the catalyst. The most damaging effect on the catalyst performance is originated from the oxidising atmosphere at high temperatures [14,15]. In real driving conditions, such conditions can be found before the deceleration from the high or moderate speed during the s.c. fuel-cut and due to this the temperature of the catalyst is high in oxidising atmosphere for a short time before cooling under excess of air. When exposed to the reducing conditions during the accelerating stage or at moderate or high load stage the catalyst can go through some regeneration processes which delay the ageing of the catalyst. These thermal effects under oxidising, stoichiometric and reducing conditions are quite well simulated with the engine RAH ageing type cycles. The same kinds of phenomena are more difficult to build in the laboratory when using synthetic gases and outer heating, which can not follow the rapid temperature changes. After our laboratory ageing cycle the order of the sample catalysts was found to remain the same in the light-off tests after 2-h ageing compared to the order after 1-h ageing and the catalysts did not age much further during the 2-h ageing. However, the oven ageing (made for the samples S1 and S2) aged the samples further. From the emission results, it could be seen that the engine ageing has aged the sample S4 more severely than the other samples, despite the same kind of ageing effect after the laboratory ageing was not found. This could be due to the insufficient ageing time in the laboratory, because in engine ageing the same ageing cycle (1-min interval) is repeated tens of hours, but in the laboratory we have used only 1- or 2-h ageing. Because of practical reasons the laboratory cycle could not be very long, but the similar

ageing effect should be achieved in shorter time than in the engine. On the other hand, the comparison between the laboratory light-off tests and the emission results (g/km) of the engine tests is not necessarily the best way to do the evaluations between the performance results after the different ageings. In addition, the light-off tests in engine, performance during the engine test cycle and the lambda performance (both in engine and laboratory) should be considered.

The performance of the catalyst is dependent on the several elements, for example the character and the composition of the washcoat, the role and the state of the active metals and durability against the ageing. The ageing has an effect for example on the sintering of the active metals and therefore causes a loss of the metal dispersion and changes to the interaction between the active metals and the washcoat. This together with the changes in the washcoat, such as reduction of the specific surface area, results in the reduced activity of the catalyst [5–10]. The aim of this work has not been the exact characterization of the catalysts after the different ageings, but the characterization methods were used as a support for the observations found from the performance and the ageing tests. The SSA of the sample S3 was decreased to 30–40 m^2/g (from 88 m^2 as fresh) after all ageings, but the SSA of the S6 was observed to be quite high level (72 m^2/g) after the laboratory ageing. This seemed not to have any improvement in the catalyst performance, because the S6 had worse light-off values in the laboratory light-off tests after both 1- and 2-h ageing. Similarly, even though the both samples S3 and S6 have the similar SSA values after the engine ageing the S3 has better performance in the engine tests. After all the ageings the dispersion values were less than 2% for both samples and therefore any reliable conclusions could not be done. The particle size seemed to correlate to the performance of the catalysts S3 and S6. After the laboratory and engine ageing S3 has smaller particle size and it has better performance in both the laboratory light-off and the engine emission tests. Because of the heterogeneity of the changes induced into the catalyst during the ageing, the performance of the catalyst can not be predicted based on the single character of the washcoat.

Even though temperature changes as fast as in the engine ageing were not achieved, a useful laboratory cycle was developed. The rapid temperature changes together with the concentration changes have a different ageing effect than the simple oven ageing under air. The results showed that the simulation in laboratory has some correlation to the real engine ageing, although the ageing time in laboratory was significantly shorter than in the engine ageing procedure. The change of concentration and temperature gradients in situ enables to reach a correlation between the real engine conditions and the laboratory conditions. Because the ageing is strongly dependent on the washcoat chemistry and also on the ageing time, further tests are needed to optimize the ageing time in laboratory. In addition, further tests to find out the correlation to the characteristics of the washcoat after different ageings are needed. In this work, the effect of the catalyst poisons during the laboratory ageing was omitted, but if a more realistic ageing effect in laboratory is wanted the poisoning should be considered, as well.

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