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Comparison of Aged and fresh Automotive Three-Way Catalyst in Driving Cycle

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ABSTRACT

Recently, environmental concern and demand for a catalyst's high performance have increased and many research activities focused on the operation of a three-way catalyst (TWC) at the end of its lifetime. Catalyst aging is the loss of catalytic activity over time that has crucial importance in the emission of the three-way catalyst.

The aim of this paper is, investigating experimentally the performance of a fresh and aged three-way catalytic converter (TWC) in the legislative driving cycle. For this, vehicle emission test with fresh and aged catalyst was carried out.

In this study, a commercial catalyst was used and was aged in a motor-rig, with SBC cycle (Standard Bench Cycle). The total conversions of HC, CO and NO_x were decreased over the lean-rich cycles in transient conditions. In the real driving condition, almost in the all-time, the engine has a transient condition and in this condition, the non-aged catalyst achieves higher conversion for times with lambda variations.

1) Introduction

Recently, environmental concern and demand for a catalyst's high performance have increased the research activity focused on the operation of a three-way catalyst (TWC) at the end of its lifetime. Currently-used three-way catalysts are exposed to high operating temperatures due to the use of closed coupled catalysts near the engine.

According to the European Union Standards, known as EURO V, automotive catalysts have a lifetime of at least 160,000 km.

Catalytic materials used in TWC applications have also changed, and the new materials have to be thermally stable under the fluctuating exhaust gas conditions.

Further demands are being placed on discovering other techniques to minimize emissions during the cold start to obtain a fast light-off of a catalyst. [1]

The current three-way catalyst, shown schematically in Figure 1, is generally a multicomponent material, containing the precious metals rhodium, platinum and (to a lesser extent) palladium, ceria (CeO_2), γ-alumina (Al_2O_3), and other metal oxides. It typically consists of a ceramic monolith of cordierite ($2Mg.2Al_2O_3$. $5SiO_2$) with strong porous walls enclosing an array of parallel channels.

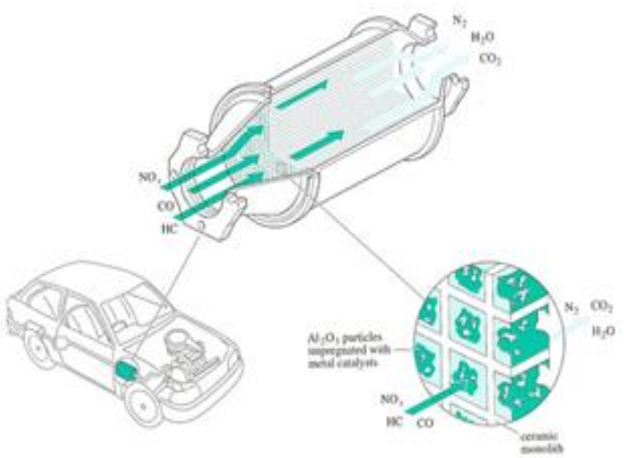

Figure 1: Schematic diagram of the three-way catalytic converter.

To achieve a large surface area for catalysis, the internal surfaces of the monolith are covered with a thin coating (30–50 μm) of a highly porous material, known as the wash coat.

The wash coat generally consists of alumina (70-85%) with a large surface area, with oxides, such as BaO, added as structural promoters (stabilizers to maintain surface area) and others, for example, CeO_2, as chemical promoters. This system becomes the support for the precious metal components (Pt, Pd, and Rh) [3].

Catalyst Aging

Catalyst aging is the loss of catalytic activity over time that has crucial importance in the emission of the three-way catalyst. Catalyst deactivation is defined as a phenomenon in which the structure and state of the catalyst change, leading to the loss of active sites on the catalyst's surface and thus causing a decrease in the catalyst's performance.

The causes of deactivation are classically divided into three categories: chemical, thermal and mechanical. [2]

Although large progress has been made in reducing legislative drive-cycle vehicle emission levels by the employment of three-way catalytic (TWC) converters, there has been significantly less improvement in actual real-world driving emission levels.

The determining factors for the levels of the real world emissions can be grouped into three main categories:

The first category engine-out (pre-catalyst) emissions levels for steady-state and transient engine operating conditions (that take place in cold start and warm up condition

The second category consists of the conversion efficiency of the catalytic converter during: steady-state engine operation for fresh and aged three-way catalytic (TWC) converters

The third category consists of the transient engine operation for fresh and aged three-way catalytic (TWC) converters

Published literature shows that the numerical simulation models can simulate well the steady-state and transient performance of catalytic converters for given legislative drive-cycles [6–8]. However, simulation studies have not extended successfully to the real-world transient performance of the TWC.

S.Samuel and other [5] was investigating the real-world performance of a catalytic converter. Their studies show that that the real-world performance of TWC converters is significantly different from the performance established on legislative test cycles.

The aim of this paper is, investigating experimentally the performance of a fresh and aged three-way catalytic (TWC) converter using an experimental vehicle that was certified for Euro-IV legislative limits and used a TWC converter.

2) Materials and methods

The present work used a Euro-IV, 1.7 litre, four stroke, gasoline multi-point port injection, light-duty passenger vehicle of mass 1360 kg. This vehicle was tested at the, Iran Khodro Powertrain Company (IPCO), on a chassis dynamometer using NEDC drive-cycles for two times:

1. Vehicle Emission test for fresh catalytic converter (3000 km driving)
2. Accelerated catalyst aging
3. Vehicle Emission Test for an aged catalytic converter (160,000 km driving)

Deactivation of a three-way catalyst is typically a very slow phenomenon, a reason why a large number of catalyst aging cycles have been developed for the relatively fast testing of catalyst thermal stability. An accelerated aging method was developed to expose the exhaust after-treatment system aging during 160,000 km real driving within 200 h runtime of the engine test bench.

Several non-vehicle test methods have been developed to achieve the accelerated catalyst aging under laboratory-controlled conditions. These aging methods typically involve the use of test engines; atmosphere controlled aging furnaces and pulse-flame reactors. The aging procedures can be divided into the following three categories: vehicle aging cycles, engine bench aging, and laboratory aging in the furnace. These aging procedures are briefly described in the next paragraphs. [2]

A vehicle aging cycle represents, in the best possible way, the real driving conditions to which a given vehicle could be subjected to during a required catalyst lifetime.

Automotive manufacturers use vehicle aging test procedures to test the stability and durability of catalytic converters under real driving conditions. However, the use of such test procedures is normally limited due to high operation costs.

Engine bench aging aims to test the thermal and chemical stability of a catalyst. An engine bench cycle contains the subjection of the catalyst to thermal loading, high-temperature oxidation and the presence of catalyst poisons. [2]

Catalyst aging test benches with combustion engines are used due to the availability of combustion engines, which have proven their robustness in the field. Also, the idea of providing exhaust gas produced by an engine is generally seen as being the closest to the real aging of a catalyst in a vehicle. Nevertheless, the engine type often used for aging is not the one connected to the after-treatment system. Therefore, not only emission composition but also the flow to the catalyst and the distance of the catalyst from the engine, do not exactly represent the original vehicle conditions. To cope with the high thermal stress and corrosion of the exhaust line, typically the exhaust valves and exhaust system are modified to increase the lifespan of these engines when used for catalyst aging.

The catalytic systems analyzed for this study consisted of two-zone catalysts. The catalyst had a volume of 1 l and a diameter of 118.4 mm and a cylindrical monolith cordierite structure with 600 cpsi. The wash coat consisted of Al_2O_3 and CeO_2–ZrO_2 as support and oxygen storage components and they had a loading mixture of Pd and Rh. The whole system, with both catalysts, was aged according to the SBC (Standard Bench Cycle). Since the objective of this study was to compare and investigate new and real aged catalysts, the vehicle has been used for aging.

The motor-rigs used consisted of a standalone motor, suspended on a metal rack. The driveshaft was connected to a brake with variable resistance, making it possible to vary the load on the engine. The exhaust after-treatment system was connected directly to the engine making it easy to change when another catalyst system was to be tested, and the exhaust gases were vented out through a ventilation system. Temperature and pressure measurements were done at several places inside the engine as well as along the exhaust after-treatment system, and exhaust gases could be extracted at several places for composition analysis.

The number of measurement points, as well as their position, was chosen specifically for every experiment depending on the type of test and on what information that was of interest. The speed (rpm) of the engine and the resistance of the brake could be controlled and programmed through a computer, making it possible to run tests over a long time without the need for constant supervision. This customizability made it possible to test many different characteristics of the catalyst.

The aging of the petrol TWC systems was done in a motor-rig using a cycle based on the SBC (Standard Bench Cycle), figure 2, issued by the United States Environmental Protection Agency [9,10].

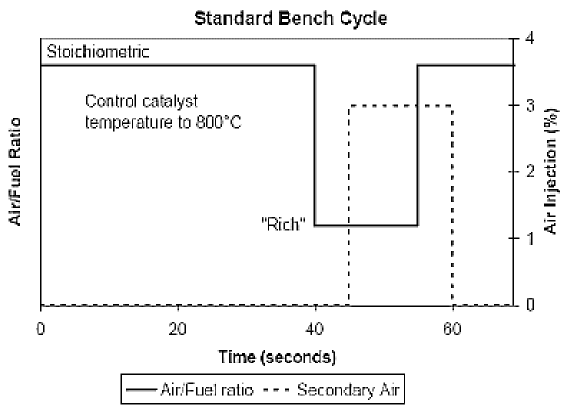

Figure 2: The Standard Bench Cycle used for accelerated aging of the catalyst [9].

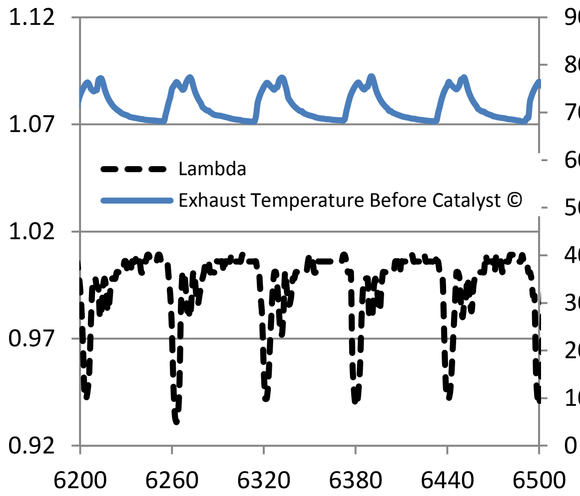

Figure 3: The Standard Bench Cycle used for accelerated aging of the catalyst.

The cycle is designed for the rapid aging of catalytic systems by changing between rich and lean conditions. The cycle consists of four steps which are described in table 1.

The standard aging durability procedure consists of aging a catalyst/oxygen sensor system on an aging bench which follows the standard bench cycle (SBC) described in this section. The SBC requires the use of an aging bench with an engine as the source of feed gas for the catalyst. The SBC is a 60-second cycle which is repeated as necessary on the aging bench to conduct aging for the required period. The SBC is defined based on the catalyst temperature, engine air/fuel (A/F) ratio, and the amount of secondary air injection which is added in front of the first catalyst.

Table 1: The four steps of the SBC in figure 1.

Time (seconds)	Engine Air/Fuel Ratio	Secondary Air Injection
1-40	Stoichiometric with load, spark timing and engine speed controlled to achieve a minimum catalyst temperature of 800° C	None
41-45	"Rich" (A/F ratio selected to achieve a maximum catalyst temperature over the entire cycle of 890° C or 90° C higher than lower control temperature)	None
46-55	"Rich" (A/F ratio selected to achieve a maximum catalyst temperature over the entire cycle of 890° C or 90° C higher than lower control temperature)	3% (±1%)
56-60	Stoichiometric with load, spark timing and engine speed controlled to achieve a minimum catalyst temperature of 800° C	3% (±1%)

Aging on the bench shall be conducted by following the standard bench cycle (SBC) for the period calculated from the bench aging time (BAT) equation. Bench aging time shall be calculated using the bench aging time (BAT) equation as follows:

$$BAT = A.\sum_{min}^{max} \Delta t \left(e^{\frac{R}{Tr} - \frac{R}{Tv}} \right) \quad (1)$$

The BAT equation requires, as input, catalyst time-at-temperature data measured on the Standard Road Cycle (SRC), described in figure 4. Bench aging time according to equation 1 is equal to 300 hours for 160,000 kilometer aging. The standard road cycle (SRC) is a kilometer accumulation cycle. The vehicle may be run on a test track or a kilometer accumulation dynamometer. The cycle consists of 7 laps of a 6 km course.

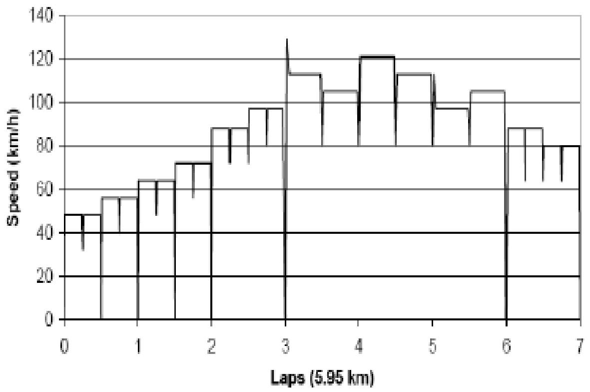

Figure 4: The standard road cycle used for accelerated aging of the catalyst [9].

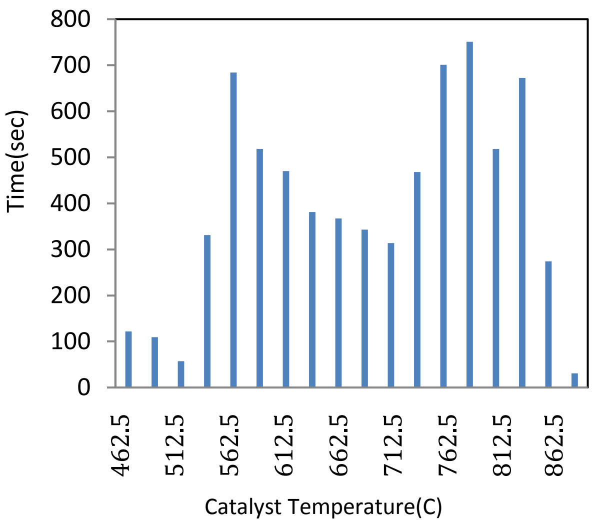

Figure 5: Quality Metric Histograms of vehicle catalyst temperature on SRC cycle.

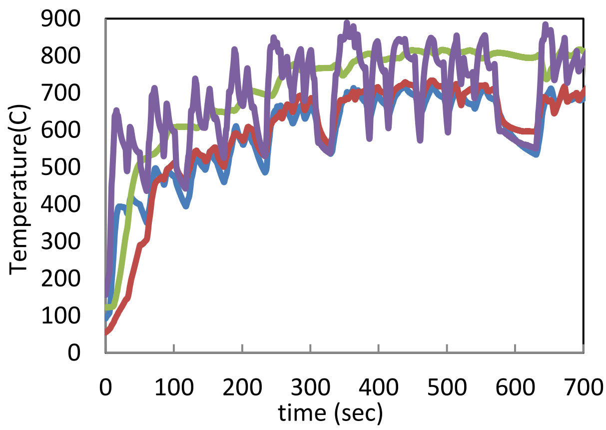

Figure 6: vehicle catalyst temperature on SRC cycle (in different position of catalyst).

3) Results and Discussion

3-1) Car-dynamo experiment

One test was performed in a real car positioned on a dynamo. This test makes it possible to analyze the performance of the catalyst with it mounted in the actual car, without having to drive it on the road. This was tested in a real car using the NEDC cycle.

3-2) Dynamic oxygen storage test

The oxygen storage capacity is regarded as one of the most important parameters of an automotive catalyst; an experiment was conducted analyzing this property during aging cycle.

The dynamic OSC test performed on the catalysts was done by alternating the lambda value at different frequencies while monitoring the lambda value after the catalyst. The dynamic OSC performance was evaluated by comparing the variation of lambda value before and after the catalyst. The exact test conditions are not possible to display because it is classified.

Oxygen storage capacity The OSC test was conducted to compare the oxygen storage capacity of the catalysts since this is one of the most important characteristic and is often greatly affected by the aging.

Figure 7 shows the oxygen storage capacity of the three aged catalysts and the fresh at different temperatures when changing from rich to lean conditions.

It can be seen that the aged catalysts have significantly lower OSC compared to the fresh ones. This indicates that aging has a larger impact on low-temperature performance, something that was also shown in the first stage of the NEDC cycle.

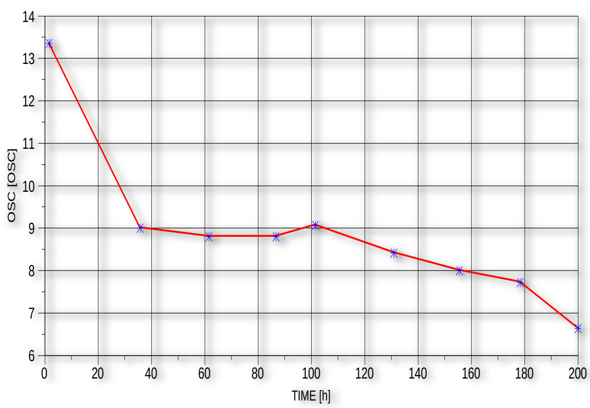

Figure 7: The oxygen storage capacity at different times of the aged catalyst from fresh.

3-3) Emission results

The following section presents and discusses the experimental results and findings obtained through analysis of the vehicle emission.

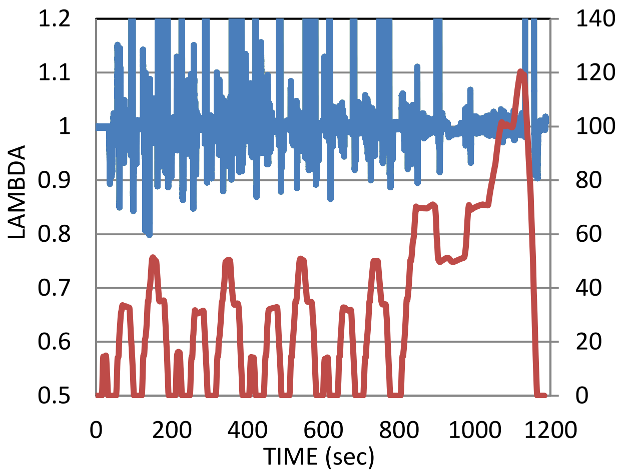

Figure 8: The lambda variation during the NEDC cycle.

Figure 9 shows concentration of CO during first stage of the NEDC cycle. It is shown that the, the non-aged catalyst, achieves higher conversion for almost the entire temperature range compared to the aged systems, except after starting the engine. This is because of the uncertain engine control.

Figure 10 shows the concentration of CO during second stage of the NEDC cycle. It is shown that the, the non-aged catalyst, achieves higher conversion for times with lambda variations. It is shown that the aged catalysts have significantly lower OSC compared to the fresh.

Some tests ended up with a higher engine speed and therefore a higher temperature, directly effecting the temperature of the catalysts and therefore also the conversion results. It is shown that the, the non-aged catalyst, achieves higher conversion for almost the entire temperature range compared to the aged systems.

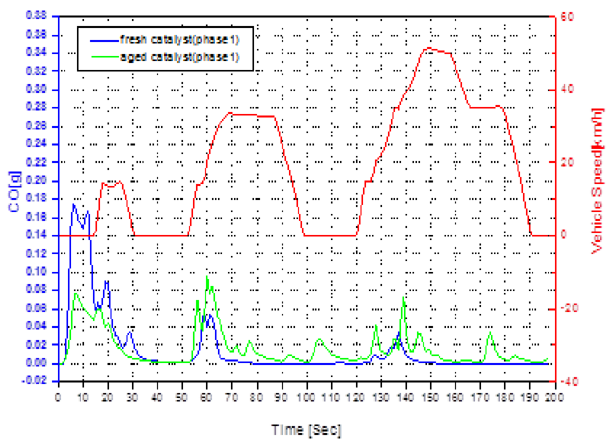

Figure 9: The concentration of CO during the first stage of the NEDC cycle.

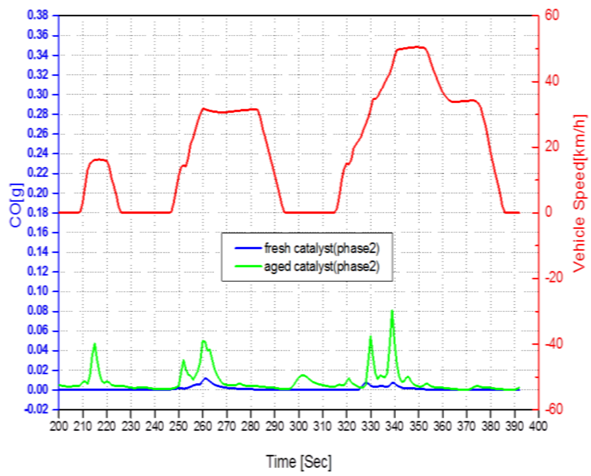

Figure 10: The concentration of CO during second stage of NEDC cycle.

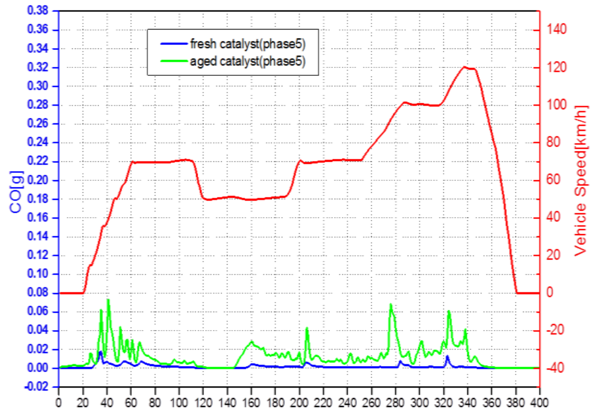

Figure 11: The concentration of CO during last stage of NEDC cycle.

for explanation is that some of the active sites of the aged catalyst was destroyed during aging to CO adsorbs to the catalyst surface, and is shown as a low conversion.

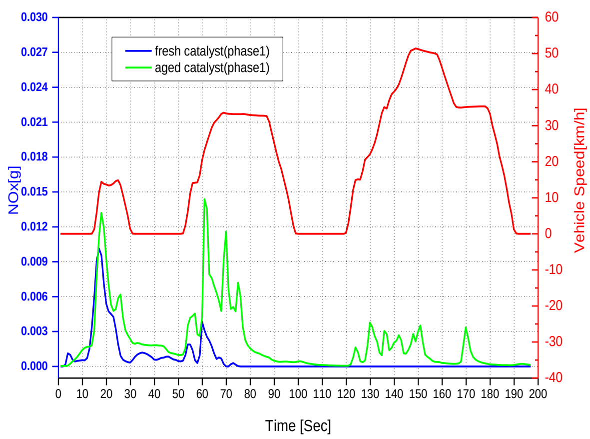

Figure 12: The concentration of NO_x during first stage of NEDC cycle.

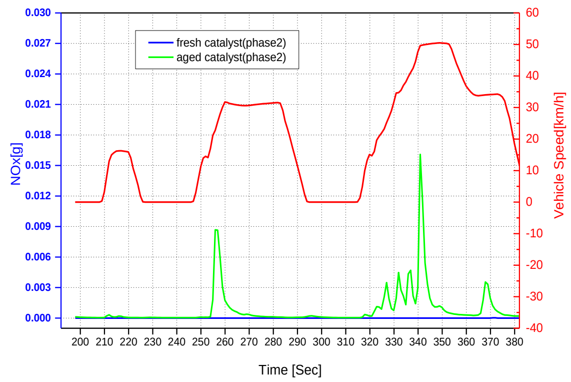

Figure 13: The concentration of NO_x during second stage of NEDC cycle.

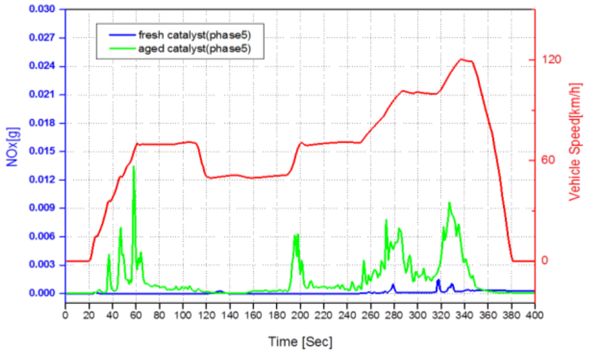

Figure 14: The concentration of NO_x during last stage of NEDC cycle.

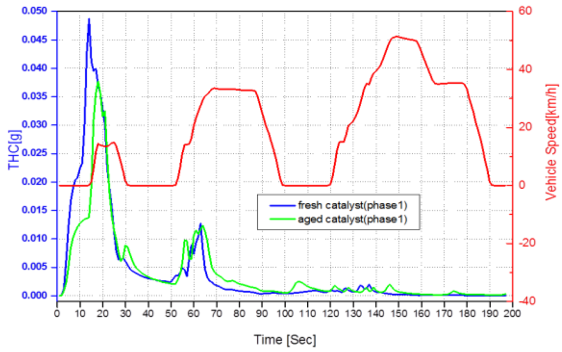

Figure 15: The concentration of THC during first stage of NEDC cycle.

Figure 16: The concentration of THC during second stage of NEDC cycle.

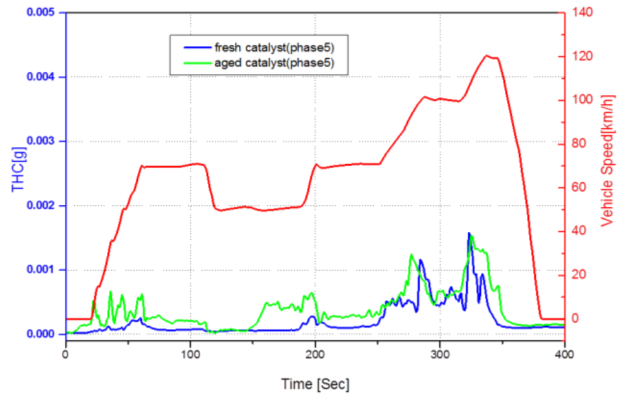

Figure 17: The concentration of THC during last stage of NEDC cycle.

4) Conclusions

The comparison of the fresh and aged catalyst was shown:

1. The total conversions of HC, CO and NO_x were all affected, and the largest decrease was for the conversion of NO_x but the amount of unburned hydrocarbons did not change much. .
2. The light off temperature of catalyst was increased and the catalyst was active later. The post-catalyst emission measurements showed that catalytic converter efficiencies close to zero for the first stage of NEDC driving cycle.
3. The NO_x conversion was also found to be significantly lower over the whole temperature range. The increase of the metal particle size with the aging caused by the agglomeration of metal particles, the presence of metal sintering Explainable by the fact that the activity of the catalyst for NO conversion depends on the size of the Pt particle, being that is worse with larger particle size [12].
4. The total conversions of HC, CO and NO_x were decreased over the lean-rich cycles in transient conditions. In the real driving condition, almost in the all-time, the engine has the transient condition and in this condition, the non-aged catalyst achieves higher conversion for times with lambda variations.
5. The effect of catalyst aging on the catalyst activity and selectivity has been examined by variable temperature and variable-composition experiments. The Pd catalyst is quite effective for the removal of CO and C_3H_6, while the Pt/Rh/Ce catalyst is active for NO reduction. However, the three-way catalytic

activity of both Pd and Pt/Rh/Ce catalysts was decreased as the catalyst mileage increased. For the Pd catalyst, the CO oxidation reaction was mainly affected by catalyst aging. For the Pt/Rh/Ce catalyst, the oxidation reactions of CO and C3H6 were severely deactivated compared to the reduction reaction of NO by CO and C_3H_6. On the other hand, the selectivity of the Pt/Rh/Ce catalyst for NO–CO and NO–H_2 reactions was decreased by catalyst aging, resulting in a decrease of the overall NO removal activity. The results from such partitioning experiments are useful for optimum design and operation of a modern catalytic converter [11].

The mechanisms of the aging of catalytic systems for the automotive industry are still in great need of further investigation. This work showed the different effects of aging effects, but a more extensive analysis is still needed to fully understand the processes behind the aging [10].

Acknowledgment

We thank our colleagues at IPCO (Iran Khodro Powertrain Company) for assisting with vehicle measurements and performing catalyst aging test.

Nomenclature

Symbol	Description
BAT	Bench-Aging Time
A	Deterioration from sources other than thermal aging of the catalyst
$\sum$	Total times
Δt	The time (in hours) measured within the prescribed temperature bin of the vehicle's catalyst temperature histogram
R	Catalyst thermal reactivity =17 500
Tr	The effective fresh temperature (in °K) of the catalyst on the catalyst bench runs on the bench aging cycle
Tv	The mid-point temperature (in °K) of the temperature bin of the vehicle on-road catalyst temperature histogram
THC	Total Hydrocarbon
NO_x	Nitrogen Oxides
CO	Carbon Monoxide
OSC	Oxygen storage capacity
Pd	Palladium
Rh	Rhodium
Ce	Cerium

References

[1] Heck RM & Farrauto RJ (2001) Automobile exhaust catalysts. Applied Catalysis A: General 221:443-457.

[2] O. Samimi Abianeh, S. Abdolmaleki And j. Rudaki "A Review of the Automotive Three-Way Catalyst Aging Technology," 6th International Conference on Internal Combustion Engines, ICICE 2009.

[3]http://www.open.edu/openlearn/science-maths-technology/science/chemistry/the-three-way-catalytic-converter/content-section-0

[4] Ronald M. Heck , Robert J. Farrauto, Suresh T. Gulati," CATALYTIC AIR POLLUTION CONTROL Commercial Technology", Third edition, John Wiley & Sons, Inc., Hoboken, New Jersey ,2009

[5] S Samuel, D Morrey, M Fowkes, D H C Taylor, C P Garner and L Austin, "Real-world performance of catalytic converters", Proceedings of the Institution of Mechanical Engineers, Part D:Journal of Automobile Engineering, 219(7), pp. 881-888,jan 2005

[6] Cornelius, S. J, "Modeling and control of automotive catalysts", PhD thesis, Sydney Sussex College, Cambridge University, UK, 2001.

[7] Eastwood, P, "Critical Topics in Exhaust Gas After treatment", 2000, pp. 7–32, (Research Studies Press Ltd).

[8] Koltsakis, G. C. and Stamatelos, A. M, "Modeling dynamic phenomena in 3-way catalytic converters", Chemical Engineering Sci., 1999, 54, 4567–4578.

[9] STATUS OF UNITED NATIONS REGULATION, ECE 83-06, Rev.1/Add.82/Rev.4/Amend.1 "VEHICLES WITH REGARD TO THE EMISSION OF POLLUTANTS ACCORDING TO ENGINE FUEL REQUIREMENTS', July 7, 2011

[10] SIMON LINDQVIST, "Characterization of Automotive Catalyst Aging", Master of Science thesis, Chalmers University of Technology, Gothenburg, Sweden 2014.

[11] Joon Hyun Baika, Hyuk Jae Kwona, Yong Tak Kwona, In-Sik Nama, and Se H. Ohb, "Effects of catalyst aging on the activity and selectivity of commercial three-way catalysts", Topics in Catalysis Vols. 42–43, May 2007.

[12] Nélida Sofia Tavares Furtado "Aging on commercial automotive catalysts, a structure reactivity study" Master of Science thesis ,Jean Le Rond d'Alembert Institute of Pierre and Marie Curie University, November 2014

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مقایسه واکنشگر شیمیایی سه کاره خودروئی فرسوده و نو درچرخه رانندگی

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چکیده

به تازگی با افزایش نگرانی‌های زیست محیطی تقاضا برای واکنشگرهای شیمیایی خودروئی با عملکرد بهتر افزایش و میزان زیادی از فعالیت‌های پژوهشی محققان بر روی عملکرد و طول عمر واکنشگرهای شمیمیایی سه کاره خودروئی تمرکز یافته است. در این پژوهش یک واکنشگر شیمیایی سه راهه با روش‌های سریع فرسوده‌سازی شده و مقدار آلاینده‌های خروجی خودرو در چرخه رانندگی قبل و بعد از پیرسازی اندازه گیری شده است. در این پژوهش از یک واکنشگر تجاری استفاده شده و فرسوده‌سازی سریع واکنشگر با استفاده از بستر آزمون موتوری و به روش چرخه استاندارد دوام فرسوده سازی واکنشگر انجام شده است. مقایسه نتایج آلایندگی نشان می‌دهد که مقدار هر سه آلایندۀ خروجی افزایش یافته است ولی در شرایط ناپایا این افزایش آلاینده‌های خروجی بسیار بیشتر است و در شرایط واقعی رانندگی که تقریباً موتور همیشه ناپایدار است و نسبت هوا به سوخت در حال نوسان شدید است شرایط بسیار بدتر است و واکنشگرهای فرسوده در شرياط واقعی رانندگی آلاینده‌های بسیار بیشتری تولید خواهند کرد.

اطلاعات مقاله

تاریخچۀ مقاله:
دریافت: ۱۱ اردیبهشت ۱۳۹۸
پذیرش: ۳۰ مرداد ۱۳۹۸

کلیدواژه‌ها:
فعالیت واکنشگر
واکنشگر شیمیایی سه کاره
فرسوده سازی
چرخه رانندگی
غیر فعال شدن