

Development of LEV-II Compliant Low Precious Metal Perovskite Catalytic System

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ABSTRACT

A LEV-II compliant catalytic system employing a low precious metal perovskite catalyst has been developed as part of research efforts to contribute to the preservation of the global environment and the conservation of natural resources. Conventional catalyst systems are effective in purifying exhaust gases, but the reduction of the large amounts of precious metals they employ (Pt, Rh, Pd, etc.) is desirable in order to conserve resources.

However, perovskite catalysts containing no precious metals have lower durability and purify exhaust emissions less effectively during warm-up than catalysts with high precious metal content.

The research described in this paper combined a perovskite catalyst with Honda's original high-accuracy A/F control and quick warm-up systems, enabling the LEV-II regulations to be cleared and achieving a level of performance with 2 g of precious metal catalyst equivalent to that previously requiring 4 g or more.

1. Introduction

Exhaust gas regulations are becoming increasingly stringent around the world. In California, the LEV-I (Low Emission Vehicle Phase I) regulations will be replaced by the LEV-II (Phase II) regulations in 2004. In addition, Tier II regulations have already been decided on for the entire US. These regulations require that NO_x emissions be reduced to approximately one-quarter of currently stipulated levels, and extend the useful life to 120 kmiles. Figure 1 shows an outline of the emissions levels stipulated by these regulations.

Catalytic systems are the major after treatment systems for exhaust gas. The increased amounts of precious metals that must be used in these systems to meet the requirements of these enhanced regulations has sparked concerns over the worldwide exhaustion of these resources. The development of high-performance, low precious metal exhaust gas after

treatment systems is therefore an urgent research agenda. However, if the precious metal content of conventional catalysts is reduced, their after treatment performance during warm-up and after long-term aging declines. Perovskite-type mixed metal oxides are widely used in semi-conductors, etc., but their use in catalytic systems produces the same set of issues generated by reducing the amount of precious metals, and they have therefore to date received little use as a catalyst material.

In the research discussed in this paper, a new low precious metal catalyst employing a perovskite mixed metal oxide⁽¹⁾ jointly developed with Catalyst Solution Inc. is combined with Honda's original high-accuracy A/F control and quick warm-up systems. This combination enabled the standard of the LEV-II regulations to be met, including the newly extended useful life, and has reduced the formerly required 4 g or more of precious metals per unit to 2 g.

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2. Test Conditions

2.1. Test Vehicle

This project used the '01 Accord EX 2.3L in-line four-cylinder VTEC SULEV as the base test vehicle. Tests are conducted without alteration of the under-floor catalytic

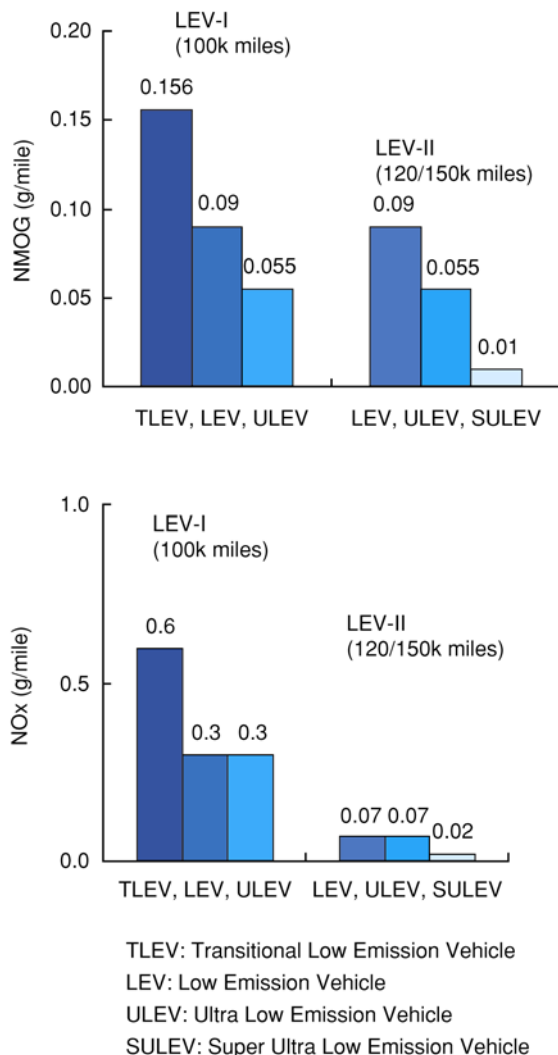


Fig. 1 Relationship between LEV-II and LEV-II regulations

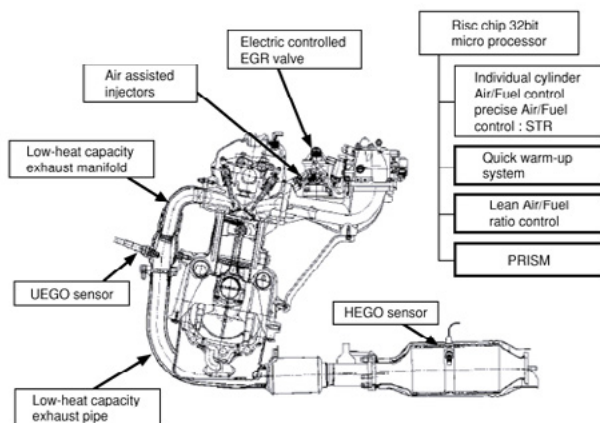


Fig. 2 Overview of test vehicle system

system or exhaust system layout. The volume of catalyst used remained the same at 1.7 L, and the control system was also unchanged. Figure 2 shows an outline of the test system.

2.2. Control System

The control system employed in the test vehicle is high-accuracy A/F control, PRISM (Prediction and Identification Sliding Mode control^{(2),(3)}). The PRISM system is employed to provide rapid activation of the catalyst at start-up, reduce feed gases by the use of lean burn after start-up, and reduce exhaust gases after activation of the catalyst.

2.3. Rapid Catalyst Warm-up System

Engine exhaust energy increases the temperature of three-way catalysts, raising their level of activation. To maximize this effect, a Quick Warm-up System (QWS⁽⁴⁾) was developed which uses a rotary air control valve (RACV) to control the volume of intake air at a cold start (before activation of the three-way catalyst), and simultaneously controls ignition timing.

The concept behind the control used in QWS is illustrated in Fig. 3. From top to bottom, the graphs show changes over time in the degree of opening of the RACV, the engine speed, and ignition timing. QWS uses feed forward control when the engine is idling after start-up to provide a high volume of intake air. Proportional and integral (PI) feedback control is used to control the ignition timing in order to maintain the target engine speed.

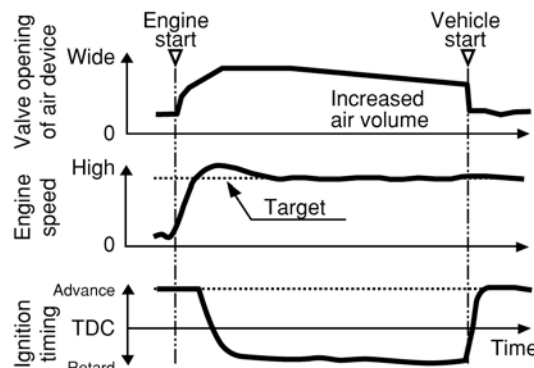


Fig. 3 Ignition feedback control for QWS

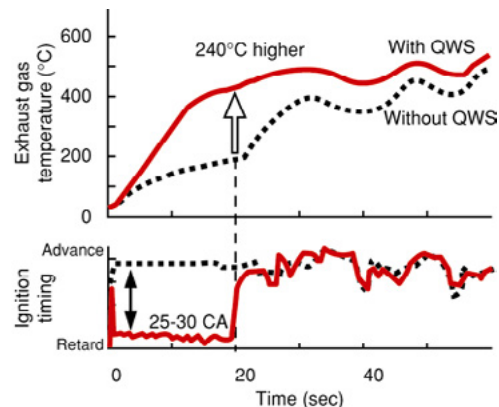


Fig. 4 Effect of QWS at start-up period of FTP

Figure 4 shows the ignition timing control provided by QWS and its effect in increasing exhaust gas temperature at start-up. The use of QWS increases the temperature of the exhaust gas by 240 °C in 20 seconds after start-up against a conventional control system. This enables rapid activation of the catalyst.

2.4. Reduction of Exhaust Gas after Activation of Catalyst

Figure 5 shows a conceptual diagram of the feedback-system. The aim of this system is to precisely control the exhaust gas A/F ratio to a value suitable for the catalyst. There is an extended period of time in which no effect is produced until the fuel from the injector is detected by the post-catalyst Heated Exhaust Gas Oxygen sensor (HEGO), and the control application takes this period into consideration. It is also now possible to obtain an understanding of how the properties of the catalyst change with the vehicle mileage. The section in which calculations are performed is made up of three modules, the real-time identifier, the predictor and the sliding mode controller.

The real-time identifier contains a model of the catalyst, and identifies the dynamic characteristics of the model in real time on the basis of output from the pre- and post-catalyst sensor.

The predictor uses $\theta(a_1, a_2, b_1)$, the parameters of the catalyst model calculated by the real time identifier, and output from the pre- and post-catalyst HEGO sensors to make a predictive calculation of the future value of the output of the post-catalyst HEGO sensor.

The controller is highly robust, and employs adaptive sliding mode control⁽⁵⁾.

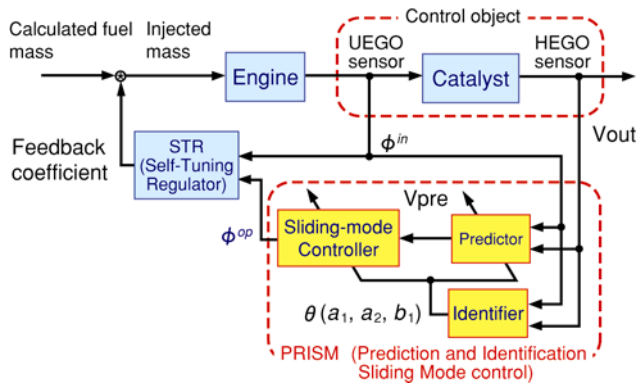


Fig. 5 Overview of feedback-system

Figure 6 shows the dynamic principle of sliding mode. The sliding mode controller in PRISM functions to restrict the output, VO_2 , from the HEGO sensor to the switching line in a phase plane with axis representing the deviation from target values for sensor output and allows VO_2 to slide back to the zero point. To determine the target value for VO_2 , the controller calculates the target A/F ratio for the self-tuning regulator (STR)⁽⁶⁾, which feeds back the pre-catalyst A/F ratio.

Figure 7 shows the effect of PRISM control during an FTP cycle. The post-catalyst HEGO sensor output is

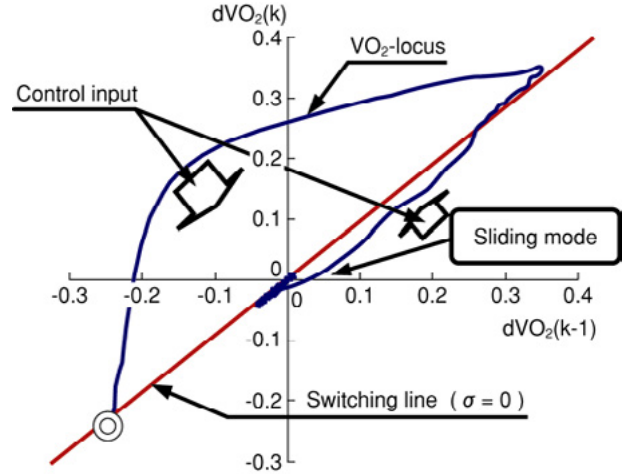


Fig. 6 VO_2 locus in phase plane

accurately controlled to the target value with no bias towards either 0 V (lean environment) or 1 V (rich environment). This indicates that the environment in the three-way catalyst is always close to the theoretical A/F ratio, and verifies the fact that PRISM provides high-accuracy control to produce the optimum A/F ratio for a three-way catalyst.

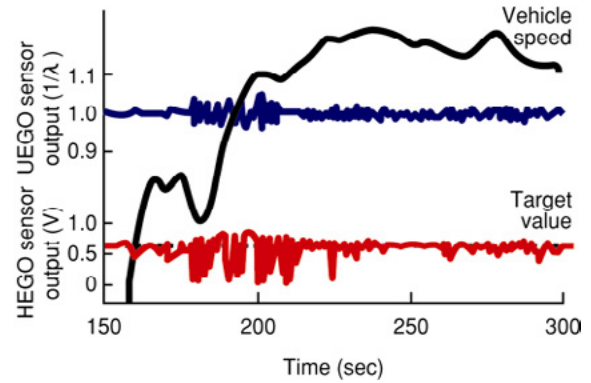


Fig. 7 Improved controllability of secondary HEGO sensor output

2.5. Catalyst

The catalyst substrate is a 600 cell per square inch model with a wall thickness of 4.3 mil manufactured by NGK Co., Ltd., and is made up of two ceramic beds of 0.7 and 1.0 L. For the tests, two types of catalyst coatings, perovskite-type mixed metal oxides and precious metals, were prepared. One was termed catalyst A, and is presently used in vehicles for the Japanese market, and the other was catalyst B, newly developed in this project to comply with the US LEV-II regulations. The amount of precious metals employed in both A and B was 33 g/ft³ (Pt:Pd:Rh = 4:25:4). These catalysts were tested in the vehicle after aging to the equivalent of 120 kmiles.

2.6. A/F Sweep Test

The A/F sweep test was conducted using a 2.3 L in-line

four-cylinder engine on an engine dynamo. The engine runs at 2 000 rpm and manifold vacuum is maintained at -350 mmHg. A/F ratio is controlled with an external control unit. The pre- and post-catalyst exhaust gas concentrations are measured, and the catalyst reduction ratio is measured within a fixed range of A/F ratios. The value at which the CO and NOx reduction ratios are the same is used for the catalyst reduction ratio.

2.7. Light-off Temperature Test

The light-off temperature test is conducted using the same equipment as the A/F sweep test. The catalyst temperature is kept constant using a heat exchanger. The pre- and post-catalyst exhaust gas concentration is measured and the catalyst reduction ratio is measured within a fixed range of catalyst temperatures and evaluated. As in the A/F sweep test, a value at which the reduction ratio of CO and NOx is the same is used as the catalyst reduction rate.

3. Test Results

3.1. Light-off Temperature Test

Figure 8 shows results obtained for catalysts A and B. Catalyst C is also included for the purpose of comparison. Catalyst C is utilized in the '98M Accord ULEV, which is fitted with an in-line four-cylinder 2.3 L engine. In the light-off temperature tests, catalyst A achieved a 99% reduction ratio at 430 °C, and catalyst B at 380 °C. In other words, catalyst B demonstrated a 50 °C improvement in light-off temperature against catalyst A. Catalyst C achieved a 99% reduction ratio at 340 °C.

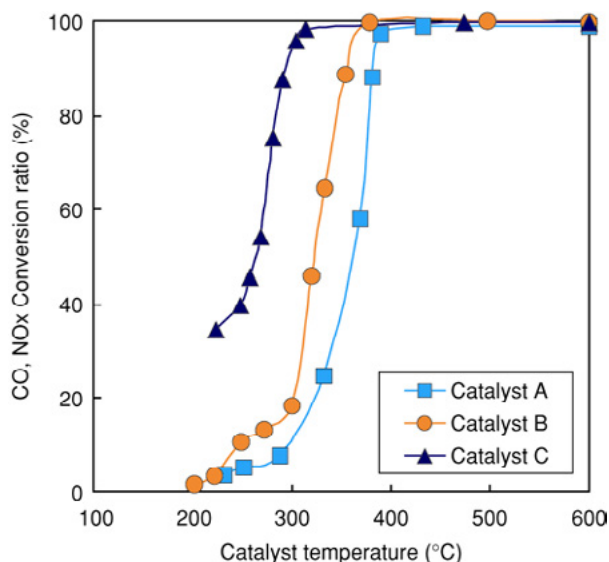


Fig. 8 Reduction ratios vs. catalyst temperature

3.2. A/F Sweep Test

Figures 9 and 10 show results for catalysts B and C in A/F sweep tests. Catalysts B and C display very similar reduction ratio characteristics in the 43 000/hr area of space

velocity (SV), but there are clear differences in the SV = 72 900/hr area. Here, catalyst B shows a narrower range of A/F ratio in which a target or higher reduction ratio can be obtained compared to catalyst C.

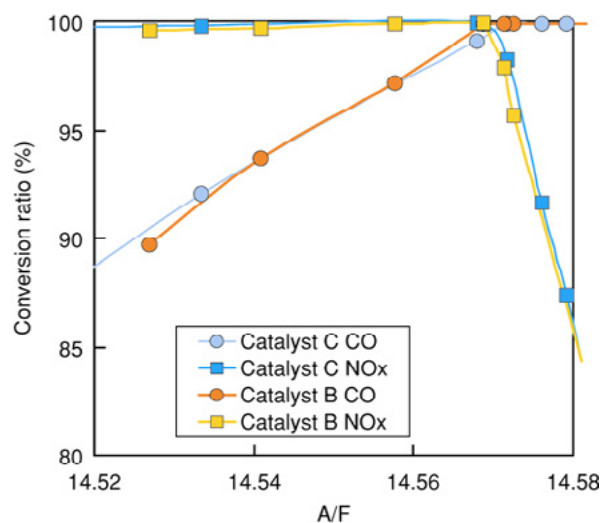


Fig. 9 Reduction ratio properties vs. air fuel ratio (SV = 43 000/hr)

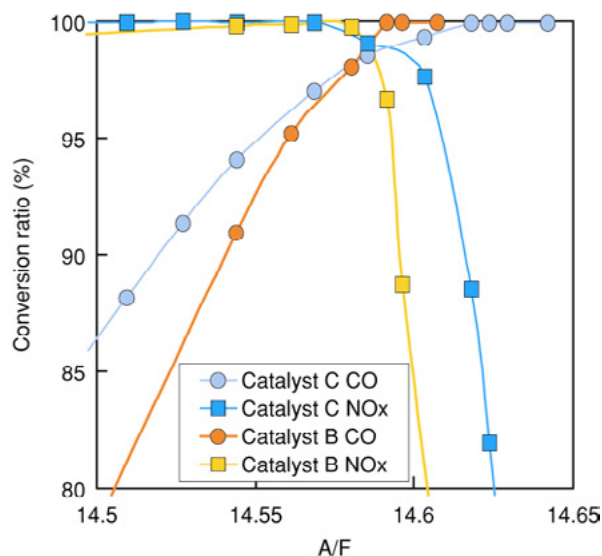


Fig. 10 Reduction ratio properties vs. air fuel ratio (SV = 72 900/hr)

3.3. Effect of QWS

Figures 11 and 12 show the effect of QWS in increasing catalyst temperature and reducing exhaust gases during an FTP cycle. As Fig. 11 shows, when QWS is not employed, the catalyst temperature only reaches 250 °C 20 seconds after start-up. However, when QWS is employed, the temperature reaches 400 °C. This indicates that the reduction ratio 20 seconds after start-up increases from 10% to 99%. As Fig. 12 shows, this enables a significant reduction in exhaust gases at start-up in an FTP cycle.

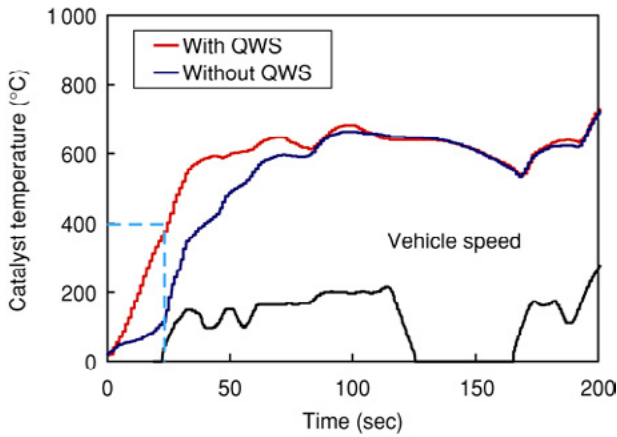


Fig. 11 Catalyst temperature during the start of FTP

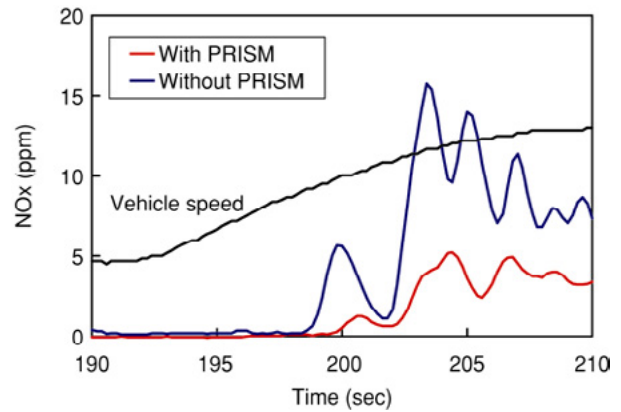


Fig. 14 NOx emission during FTP (with PRISM)

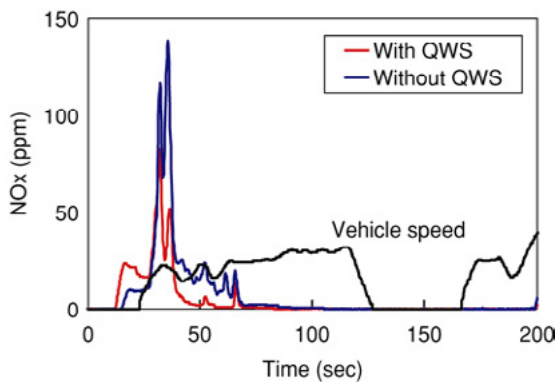


Fig. 12 NOx emission during the start of FTP

3.4. Effect of High-accuracy A/F Control

Figures 13 and 14 show exhaust gas emissions and the behavior of the post-catalyst HEGO sensor output in an FTP cycle when the PRISM high-accuracy A/F control system is employed. When PRISM control is not utilized, the output of the post-catalyst HEGO sensor diverges significantly from the target values. Employment of PRISM control increases the level of convergence with target values, and makes the sensor output more stable. As the results shown in Fig. 14 demonstrate, this leads to a significant reduction of exhaust gas emissions in the high-SV area of the FTP cycle.

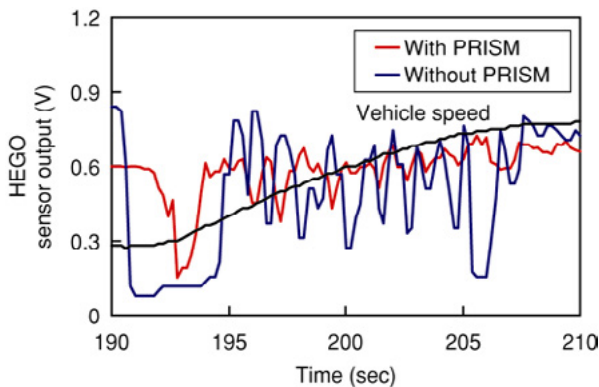


Fig. 13 Post-catalyst HEGO sensor output during FTP

3.5. Effect of Extended Mileage

Figure 15 shows results for exhaust gas emissions obtained from vehicles fitted with rapid aging catalysts A and B and run in an FTP cycle. No significant differences in performance between catalysts A and B with respect to CO and HC components were observed during aging to 120 kmiles. With respect to NOx components, despite the fact that no major difference is observable in aging up to 50 kmiles, there is a significant difference in performance at 120 kmiles, with catalyst B reducing emissions to 1/4 the level of catalyst A. These results demonstrate that catalyst B is superior to conventional catalyst A in exhaust gas reduction performance even after extended mileage.

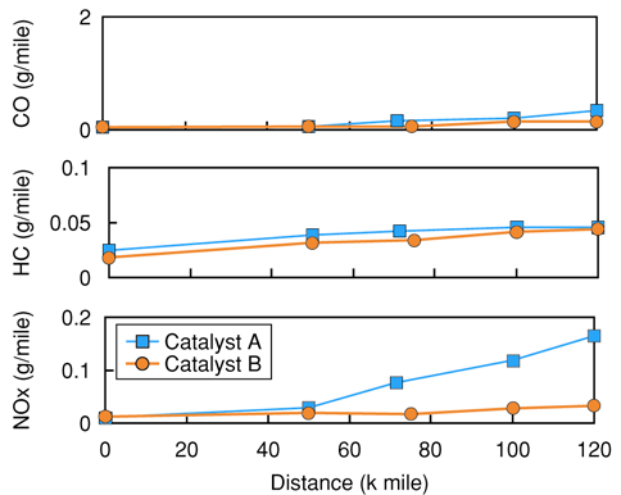


Fig. 15 FTP emission shift at extended mileage

3.6. Results of Exhaust Gas Measurements in FTP Mode

Figure 16 shows the results of measurements of exhaust gas emissions in FTP mode using newly developed catalyst B. A catalyst aged to the equivalent of 120 kmiles is used for measurements. The results show that the new catalyst meets the LEV-II standard for CO, HC and NOx.

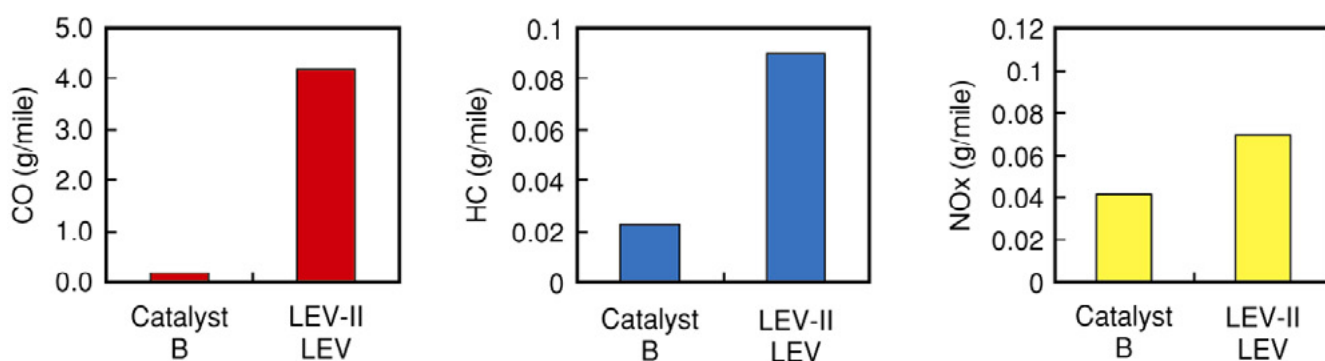


Fig.16 FTP emission results for development catalyst after being aged to the equivalent of 120 kmiles

4. Conclusion

A perovskite catalyst was developed which possesses superior light-off performance and durability to conventional perovskite catalysts. However, while the new catalyst shows equivalent performance to that of catalysts with a high precious metal content at low SV in the A/F sweep test, it cannot match the performance at high SV or in the light-off test.

Combining the new catalyst with Honda's original PRISM (high-accuracy A/F control) and QWS (quick catalyst warm-up system) supplemented its light-off performance and reduced A/F window width at high SV, and enabled the achievement of an equivalent level of exhaust gas reduction performance to conventional high precious metal catalysts.

The adoption of this catalyst technology for use in a 2.3 L in-line four-cylinder engine enabled conformity to the requirements of the LEV-II regulations.

In addition, it is possible to reduce the conventionally required 4 g or more of precious metals by more than 50% to 2 g. The future broader application of this system will be very effective in preserving the world's limited reserves of precious metals, and represents one of Honda's solutions to the issue of the potential exhaustion of these resources.

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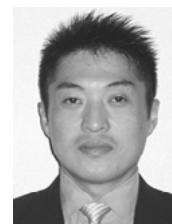
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