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Zeolite-supported precious metal catalysts for NOx reduction in lean burn engine exhaust

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Abstract

The effects of the zeolite-supported precious metal catalysts on NOx reduction in oxygen-rich exhaust have been investigated. It became clear that NOx conversion related the number of NO adsorption sites of precious metal and the number of HC (C_3H_6) adsorption of support (zeolite). Pt–Ir–Rh/MFI zeolite catalyst showed higher performance and durability than the current Pt–Rh supported on alumina and ceria catalyst.

Keywords: Lean burn engine; Zeolite; Precious metal; Lean NO_x catalyst

1. Introduction

Lean combustion is one of the known methods to improve the thermal efficiency of a spark ignition engine, but the lean operation area has been limited due to the NOx emission. Recently, several studies of lean NOx catalysts which reduce NOx under the lean conditions, for example, the copper ion-exchanged zeolite, the Pt loaded zeolite and so on, have been conducted at many research institutes [1–3].

The requirements of lean NOx catalyst are high NOx conversion under the oxygen-rich exhaust and durability performance. For example, the catalyst temperature of vehicle reaches over than 800°C in practical use. Such studies confirmed that the copper ion-exchanged zeolite did not have durability. Then, precious metals were chosen as active metals for heat-resistance. The objectives of this study are: (1) characterization into precious metals and supports on NOx reduction in oxygen-rich exhaust; and (2) performance and durability of precious metal catalyst.

This paper presents the study of zeolite-supported precious metal catalysts for lean NOx reduction through developing a new lean burn catalyst which has been mass-produced for Mazda 323 lean burn vehicles for the Japanese domestic market [4,5].

2. Experimental

2.1. Catalyst sample

Specifications of test catalyst powders which were prepared for this study were Pt, Ir, Rh as precious metal and H–MFI (SiO_2/Al_2O_3 = 30–200), H–FAU (SiO_2/Al_2O_3 = 30), H–MOR (SiO_2/Al_2O_3 = 15) and H–L (LTL,

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$SiO_2/Al_2O_3 = 6$) type zeolite as supports. Each zeolite was made at the laboratory. Test catalyst samples were prepared as follows: the support zeolite was added to aqueous precious metal solutions, mixed, dried by a heat-blower, and calcined at 200°C in the electric furnace. Catalyst powders were coated on cordierite honeycomb (62 cells/cm^2). Current three-way catalyst, Pt and Rh (Pt/Rh = 5/1, 0.9 wt%) supported on γ-alumina and ceria, was prepared.

2.2. Analysis of catalyst sample

Specific surface area of catalyst samples was measured by the BET method using nitrogen gas. Dispersion of active metals was measured by a transmission electron microscope (TEM). Active metal was confirmed by an energy diffraction X-ray (XRD), and the amount of NO and HC adsorption on each catalyst sample were investigated by the temperature-programmed desorption (TPD) with the quadruple mass spectrometer (Q-Mass). The procedure of NO and HC desorption analysis is shown in Fig. 1.

2.3. Aging treatment

The thermal aging was conducted in the electric furnace under 800°C × 6 h in air atmosphere with steam. For engine aging, the full-size brick catalyst was aged with a lean burn engine. The aging treatment consisted of about 1100 cycles, which correlated with 100 000 km of practical driving distance. Catalyst bed temperature was about 480–620°C and the aging time was 200 h.

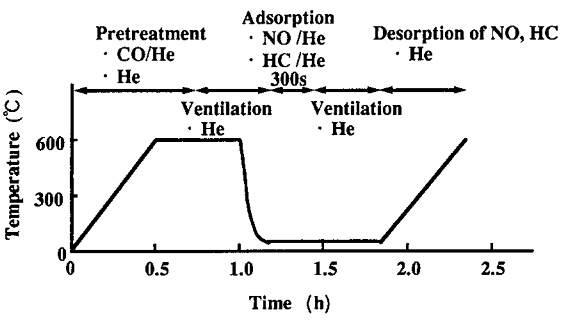

Fig. 1. Procedure of NO and HC desorption analysis.

2.4. Laboratory evaluation

Conversion performances were evaluated by placing the honeycomb core form of catalyst sample (25 mm^3) in the center of a tube furnace. The synthetic gas composition includes 7% oxygen, 4000 ppm C (C_3H_6), 250 ppm NO and 10% H_2O, the same as for the normal driving conditions, and the gas was passed through the heat exchanger and the catalyst sample at SV = 55 000/h. The range of the reaction temperature was from 100 to 400°C, because the temperature range of the lean burn system under normal driving conditions was between 200 and 400°C, and, except for one particular case, the catalyst reaction temperature was 300°C. The NOx conversion was measured with a chemiluminescent analyzer (Horiba MEXA-8000).

2.5. Emission test

Catalysts were evaluated in the Japanese 10–15 emission test mode with the lean burn vehicle (1.5 L, DOHC). The engine's lean-limit was about A/F = 27, which was improved by tumble and swirl multiplex. The weight of the lean burn vehicle was 1250 kg.

3. Results and discussion

3.1. The effect of precious metal

3.1.1. The effect of precious metal on lean NOx conversion

At first, Pt, Ir and Rh were chosen as active metals. Pd showed high HC conversion, but it had low NOx conversion in oxygen-rich exhaust, so, Pt, Ir and Rh were investigated in detail. In order to investigate the effect of precious metal, lean NOx conversions of each catalysts were measured. Several catalysts, which were loaded with various combinations: single, binary and triple of Pt, Ir and Rh, were prepared. The result of evaluation tests after aging is shown in Fig. 2: Pt–Ir–Rh/MFI catalyst showed the best lean NOx conversion. All catalysts which included Pt/MFI showed high lean NOx conversion. Ir/MFI catalyst showed the lowest NOx conversion, but Pt–Ir binary type MFI catalysts had higher NOx conversion than other binary type MFI catalysts. Rh only and Rh binary type MFI catalysts did not show the better NOx conversion. We suppose that Ir makes the lean NOx conversion of other Pt-type MFI catalysts improve.

3.1.2. Influence of precious metals on the characteristics of NO desorption of the catalysts

To understand the effect of the precious metals on lean NOx conversion, NO desorption from the catalyst was analyzed by the TPD. Each sample, except the Rh and Rh binary type MFI catalysts for NO desorption is shown in Fig. 3. The reason was that Rh only and Rh binary type MFI catalysts showed the lower NOx conversion than the others. The aged samples were deoxize-treated by CO gas, so the characteristics of NO adsorption were clearly observed. Exactly, when there was no oxygen on the surface of a precious metal, NO could be adsorbed on it smoothly. As a result of this test, we observed that the order of the amount of NO adsorption on catalysts was Pt–Ir–Rh > Pt–Ir > Pt > Ir. The order coincided with that of NOx conversion efficiency, as shown in Fig. 2.

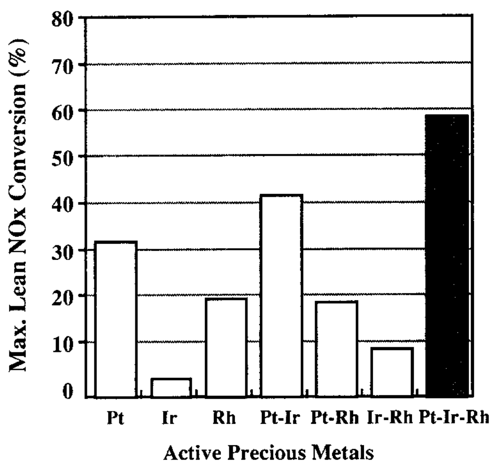

Fig. 2. Lean NOx conversion of catalysts. Catalyst temperature, 300°C; Support, MFI zeolite; total precious metals, 3.7 wt%.

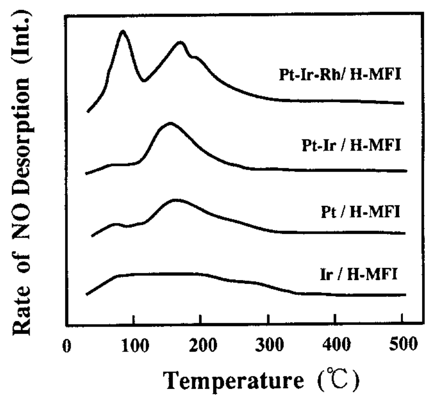

Fig. 3. TPD profiles of NO desorption.

So, we considered that the amount of NOx decomposition may be affected by the number of NO adsorption sites. Pt–Ir–Rh/MFI zeolite showed a wider temperature range of NO adsorption than that of mono-metal loaded zeolites.

3.1.3. Changes of NOx conversion of precious metal after thermal aging

To investigate the durability of precious metal catalysts, Pt/MFI and Pt–Ir–Rh/MFI, which were treated under various thermal aging conditions, were evaluated. Fig. 4 shows the changes of NOx conversion after thermal aging. Both Pt/MFI and Pt–Ir–Rh/MFI did not deteriorate remarkably. It became clear that such precious metal catalysts had durability. Particularly, the deterioration rate of NOx conversion of Pt–Ir–Rh/MFI was quite small.

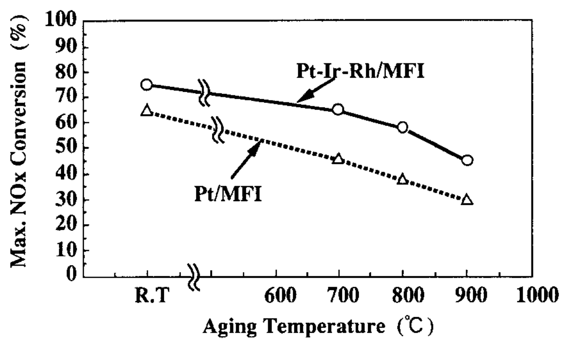

Fig. 4. Changes of NOx conversion of Pt catalyst and Pt–Ir–Rh catalyst after thermal aging. Aging time, 6 h in air; SiO_2/Al_2O_3 = 80; precious metal, 3.7 wt%.

To analyze the behavior of precious metals on support, the catalyst was oberved by TEM. The changes of average diameter of precious metal after thermal aging are shown in Fig. 5. Fresh, precious metal particles of Pt–Ir–Rh/MFI were smaller than that of Pt/MFI. After aging, precious metal particles of Pt/MFI grew considerably, while the growth of Pt–Ir–Rh/MFI was little. As the result of this analysis, we considered that the composite of Pt, Ir and Rh makes the particle size of active metals small and suppresses the growth of the particle size after thermal aging.

3.2. *The effect of support on lean NOx catalyst*

Our studies about precious metals showed that the precious metal did not enter into the reaction with support. So, the investigation into the effect of support on lean NOx conversion was conducted.

3.2.1. *Heat resistance of support*

In order to suppress deterioration of catalytic performance after aging, high heat resistance was required for both active metals and supports. The heat resistance of various supports was evaluated by the change in BET specific surface area. The test results, shown in Fig. 6, indicates that the BET specific surface area of MOR-, FAU- and L-type zeolites were much decreased after aging, but, the change of MFI

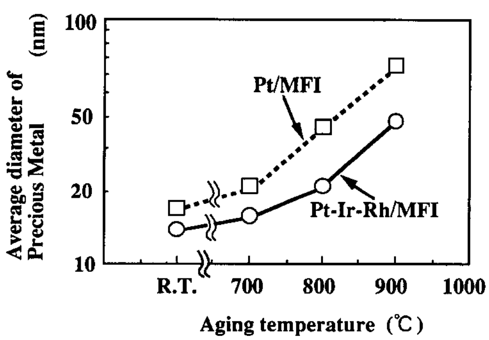

Fig. 5. Changes of average diameter of precious metal after thermal aging. Aging time, 6 h in air; $SiO_2/Al_2O_3 = 80$; precious metal, 3.7 wt%.

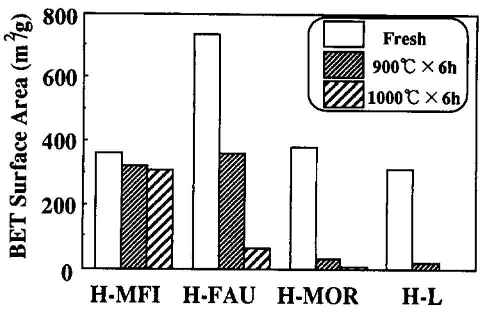

Fig. 6. Heat resistance of various zeolite supports. Treatment condition, 10% H_2O/N_2.

zeolite's BET specific surface area was small compared with that of others. As the stability of zeolite relates to the specific surface area almost linearly, so MFI zeolite was determined to be the support with the highest heat resistance.

3.2.2. *Influence of precious metals on the characteristics of HC desorption of the catalysts*

Generally, zeolite is famous as an HC trapper. Fig. 7 shows this effect of HC concentration on lean NOx conversion. It became clear that precious metal catalyst needed HC to reduce NOx in oxygen-rich exhaust and that lean NOx conversion increases in proportion to HC concentration. So, it was plausible that the HC and the adsorbed NOx play a key role in NOx reduction under lean conditions. We looked up to the point of HC adsorption performance of

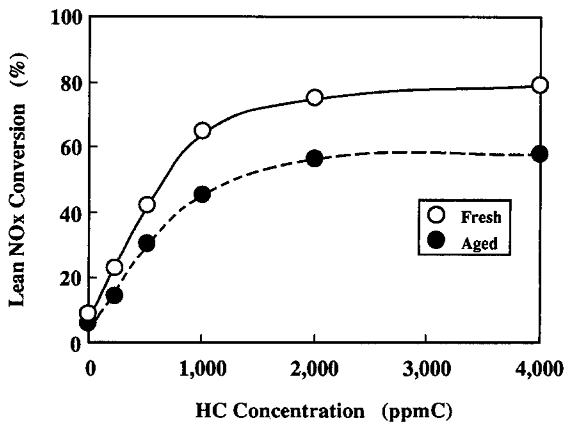

Fig. 7. HC concentration vs. NOx conversion. Catalyst, Pt–Ir–Rh/MFI; HC, C_3H_6; aging condition, 800°C × 6 h in Air.

support to investigate the effect of support on lean NOx conversion.

To understand the effect of support on NOx conversion, HC (C_3H_6) desorption of zeolite was analyzed by the TPD. The results of our tests are shown in Fig. 8.

It was observed that SiO_2/Al_2O_3 ratio of 30 and 200 of zeolite could not keep the most part of HC adsorption before the temperature was getting to the degree of NO desorption.

SiO_2/Al_2O_3 ratio of 80 of zeolite maintained HC at that temperature of NO desorption. That is, in the case that support has a SiO_2/Al_2O_3 ratio of 80, precious metal catalyst shows high NOx conversion, because there is much HC and NOx on the surface of the catalyst at that time. It is supposed that a support which has good HC adsorption performance shows high NOx conversion.

3.2.3. *Effect of the amount of HC adsorption of MFI support on lean NOx conversion*

Lean NOx conversion of various SiO_2/Al_2O_3 ratios of MFI zeolite was evaluated. The results of tests are shown in Fig. 9. In general, the larger the SiO_2/Al_2O_3 ratio of MFI zeolite is, the higher the heat resistance of zeolite is. However, this result indicated that the best SiO_2/Al_2O_3 ratio was 80 to reduce NOx. The amount of HC adsorption on various SiO_2/Al_2O_3 ratios of zeolite is shown in Fig. 9. The amount of HC adsorption was calculated by the rate of HC desorption which was measured by TPD. As shown in Fig. 9, the SiO_2/Al_2O_3 ratio of 80 gave the highest HC adsorption, the same as the results of NOx conversion. It is supposed that the reason for this is that the zeolite support with the SiO_2/Al_2O_3 ratio of 80 maintained many acid sites for the HC adsorption after aging. According to the amount of HC adsorption in a fresh sample, the smaller the SiO_2/Al_2O_3 ratio, the larger is the amount of HC adsorption. However, the amount of HC adsorption on the zeolite with the SiO_2/Al_2O_3 ratio of 30 deteriorated remarkably after aging in relation to the decrease in the number of acid sites. There was no difference in the amount of HC adsorption between the zeolite support and the supported precious metal. It is confirmed that the amount of HC adsorption of support has influence on lean NOx conversion.

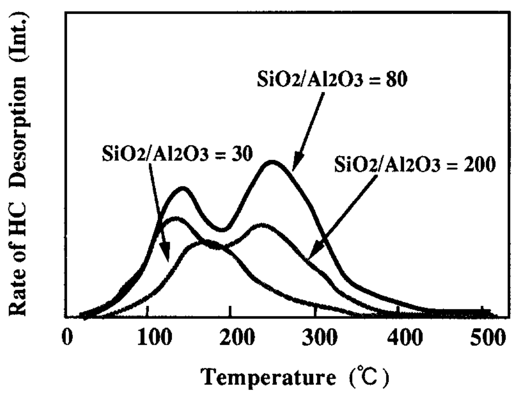

Fig. 8. TPD profile of HC desorption.

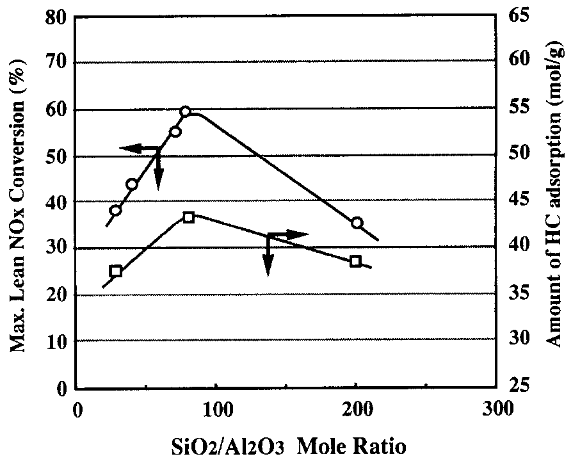

Fig. 9. Effect of SiO_2/Al_2O_3 ratio of MFI zeolite on lean NOx conversion and the amount of HC adsorption. Precious metal, Pt-Ir-Rh; HC, C_3H_6; aging condition, 800°C×6 h in air.

4. Specification of best precious metal catalyst

The best component of catalyst, according to the results obtained by laboratory tests, is shown in Table 1. Regarding the effect of additives,

Table 1
Specification of catalyst for lean burn engine test

Active metals	Pt/Ir/Rh	
Support	H^+ exchanged zeolite	
	Structure	MFI
	SiO_2/Al_2O_3	80±10
	Contaminations	Na < 0.10 wt%
	Crystalinity	> 90%
	BET surface area	> 300 m^2/g
Additives	Ceria, alumina	

Al_2O_3 and CeO_2 showed positive effects on lean NOx conversion [6].

5. Performance of Pt–Ir–Rh catalyst

A full-size brick catalyst (1.7 L) was prepared for vehicle test and engine aging. Catalysts were evaluated in the Japanese 10–15 mode with the lean burn vehicle.

5.1. The effect of SOx on lean NOx conversion

The exhaust from the vehicle includes SO_2 gas. It is well known that SO_2 is adsorbed on the surface of catalysts and poisons the conversion performance. In order to desorb SO_2 from the catalyst, one has to heat the catalyst to more than 500°C. However, the temperature of exhaust under the city driving was usually less than 500°C. Therefore, for practical use, high sulfur resistance is required. So, the degree of SO_2 poisoning effect was examined. The SO_2 poisoning treatment was conducted as follows. The test condition was with an A/F = 22 with 80 ppm SO_2 and without SO_2 for 0.5 h at 600°C. The result is shown in Fig. 10. This clarified that the conversion efficiency of Pt–Ir–Rh/MFI did not deteriorate with SO_2.

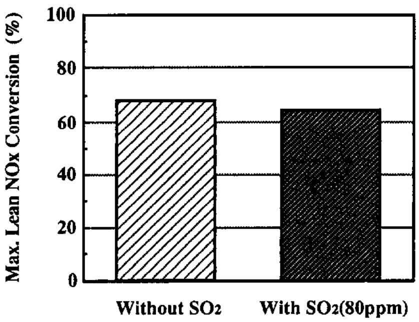

Fig. 10. SO_2 poisoning effect. Catalyst, Pt–Ir–Rh/MFI.

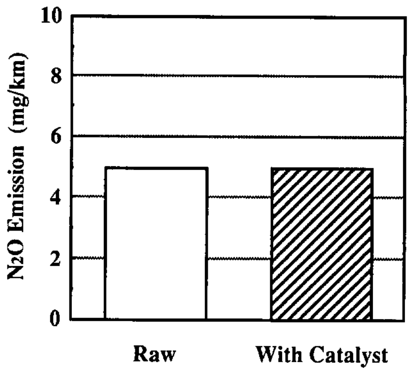

Fig. 11. N_2O formation performance. Catalyst, Pt–Ir–Rh/MFI; test mode, 10–15 mode.

5.2. The influence of Pt–Ir–Rh catalyst on involving N_2O

Recently, due to the problem of global warming, N_2O gas has caused concern. The contribution rate of N_2O is lower than CO_2, but it has a high greenhouse effect potential as compared with that of CO_2.

Then the amount of N_2O emission with this catalyst and without catalyst at 10–15 mode were measured by Q-Mass. The result is shown in Fig. 11. It was confirmed that this catalyst did not increase N_2O emission.

5.3. The conversion of unregulated emissions

In exhaust, there are some unregulated emissions which may be harmful to human health. One must investigate to reduce not only regu-

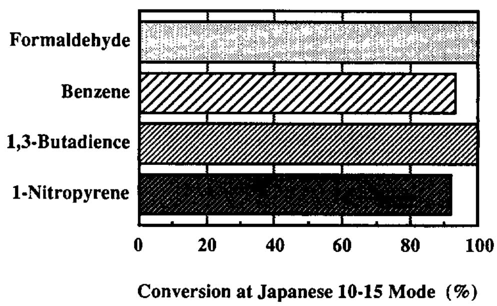

Fig. 12. Conversion of unregulated emissions.

lated emissions, but also unregulated emissions. Fig. 12 shows the conversion of typical unregulated emissions. These conversions were as same as that of the current three-way catalyst, and, NH_3 and HCN were not observed.

5.4. Durability of this catalyst for lean burn engine

Durability of Pt–Ir–Rh/MFI zeolite was evaluated by an endurance test with lean burn engine. Conversion efficiency at 10–15 mode test is shown in Fig. 13. This durability test with lean burn engine relates with a vehicle-driving distance of about 100 000 km. The result of the test shows that this catalyst has high durability with the lean burn engine. Durability performance depends on the effect of the composition of precious metals.

5.5. Fuel economy

Fuel economy of the lean burn vehicle is shown in Fig. 14. This catalyst made it possible to enlarge the lean operating region of the lean burn engine, because it had higher conversion efficiency of NOx than that of current TWC (Pt–Rh/Alumina · Ceria). Lean burn vehicles equipped with this catalyst had about 16% improvement of fuel economy in comparison with the stoichiometric vehicle at 10–15 mode test. Compared with current potential lean burn vehicles which operate in lean condition at steady states, it showed about 8% improvement in fuel economy.

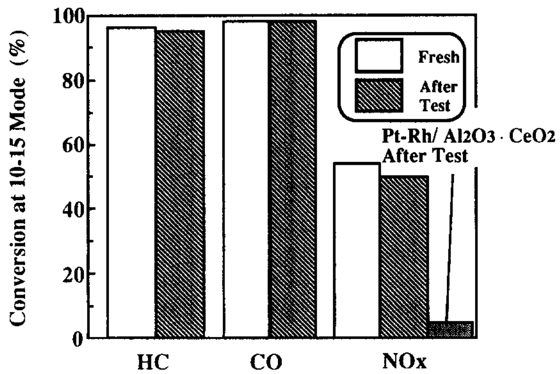

Fig. 13. Performance after endurance test.

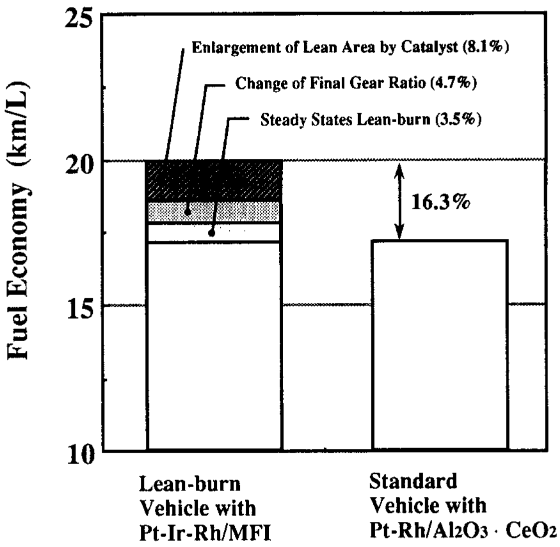

Fig. 14. Fuel economy of lean burn vehicle. Test mode, 10–15 mode; test vehicle, 1994 Familia Z-LEAN (1250 kg).

6. Conclusion

Various compositions of precious metals and zeolite support catalyst were studied with regard to performance, heat resistance, durability etc. It is concluded that: (1) the amount of NOx and HC adsorption and the desorption profile of catalyst affects the lean NOx conversion; and (2) Pt–Ir–Rh/MFI zeolite catalyst has a high performance and durability for practical use.

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