

Development of Lean NO_x Catalyst with High Thermal Durability

Hiroki HOSOE*

Masahiro SAKANUSHI*

Kimihiro TOKUSHIMA*

Tadao NISHIYAMA*

Masato KANEEDA**

Shogo KONYA***

ABSTRACT

A new metal substrate was developed to prevent the migration of alkali metals which work as NO_x adsorbents and maintain a higher NO_x conversion rate after thermal aging. A higher NO_x conversion rate was expected after thermal aging because the metal substrate contains almost no silicon (Si), however, the NO_x conversion rate after thermal aging fell below that of the cordierite substrate. This was not due to the migration of alkali metals to the metal substrate, but due to the chromium (Cr) in the metal substrate migrating to the washcoat and generating complex compounds formed with alkali metals. To help prevent this migration, the conventional metal substrate was heat-treated in air at 1100 °C to make an α -alumina barrier on the surface. This newly developed substrate showed no migration of alkali metals and almost no migration of Cr. When this substrate was used, the NO_x conversion rate after heat treatment at 830 °C for 280 hours was 31% higher than that of the conventional cordierite substrate.

1. Introduction

Calls for a reduction of the burden placed on the environment by automobiles are increasing. Carbon monoxide (CO), hydrocarbon (HC), and nitrogen oxide (NO_x) emissions have been subject to regulations for some time. Trends in the reduction of carbon dioxide (CO₂) emissions, which are not directly harmful to the human body but are a factor in global warming, have gathered at an increasing pace.

To reduce CO₂ emissions, it is necessary to increase fuel efficiency, of which lean combustion remains an effective means of achieving this goal. However, three-way catalysts cannot be used to convert NO_x in a lean burn engine, so it is necessary to use a lean catalyst that can adsorb and reduce NO_x when lean combustion is used.

Countries worldwide are establishing increasingly stringent regulations concerning CO, HC, and NO_x emissions. Because the performance of conventional lean

NO_x catalysts declines with thermal aging, the number of gasoline lean burn engines on the market has decreased as emissions regulations have become increasingly stringent.

The issue of thermal aging related performance decline in lean NO_x catalysts using cordierite substrates, which is caused by a chemical reaction between the silicon (Si) in the substrate and adsorbent alkali metals in the catalyst, was addressed by this work. The research discussed in this paper examined the causes of performance decline in a lean NO_x catalyst using a metal substrate containing almost no Si, in which there would be no migration of alkali metals to the substrate. The cause was identified as the migration of chromium (Cr) from the substrate to the washcoat, so a method of preventing the migration of Cr was developed. A lean NO_x catalyst using the developed substrate displayed a 31% higher NO_x conversion rate following thermal aging at 830 °C for 280 hours than a conventional catalyst using a cordierite substrate.

* Automobile R&D Center

** Hitachi, Ltd.

*** NIPPON STEEL CORPORATION

2. NOx Conversion Technology for Lean Burn Engine

Three-way catalysts were developed for use in gasoline engines in the 1970s. These catalysts provided a one-stage treatment of CO, HC, and NOx at stoichiometric air/fuel (A/F) ratios. Used in combination with high oxygen storage capacity (OSC) materials which broaden the conversion window and the precision A/F ratio control, they are the main technology used to convert exhaust gases in gasoline engines.

The issue of global warming has increased in severity, generating demands for the reduction of CO₂ emissions, which does not directly harm the human body but contributes to global warming, to increase in intensity. The automotive industry is no exception to this trend. A variety of techniques, including the achievement of weight savings and the reduction of friction, have been used to increase fuel efficiency and thus reduce CO₂ emissions from automobiles. The lean burn technology is an effective method to increase fuel efficiency. The development of the direct injection engine technology was promoted in the latter half of the 1990s.

However, while three-way catalysts display excellent NOx conversion performance at stoichiometric A/F ratios, they are virtually unable to convert NOx in lean burn at an oxygen concentration of 0.5% and above. A replacement NOx conversion technology able to function in lean burn is therefore necessary.

The following catalysts are able to convert NOx in lean burn:

- (1) NO direct decomposition catalysts
- (2) HC-SCR (HydroCarbon-Selective Catalytic Reduction) catalysts
- (3) NOx adsorption and reduction catalysts

Of these, neither (1) nor (2) possess sufficient NOx conversion performance to meet the 2005 emission control standards in Japan.

Type (3), lean NOx catalysts, use adsorbent materials to adsorb NOx in lean burn and convert the adsorbed NOx by means of intermittent rich spikes⁽¹⁾. Figure 1 shows the mechanism of NOx conversion in lean NOx catalysts. With a variety of modifications⁽²⁾, this type of

catalyst was used in the Stream with direct-injection system, and reduced NOx emissions by 50% compared to the 2005 emission control standards in Japan. The majority of stoichiometric gasoline engines have reduced NOx emissions to 75% of the level stipulated in the 2005 emission control standards. However, there are no catalysts that display a high NOx conversion rate in lean burn gasoline engines, and the 75% reduction has not been achieved yet using this technology. The development of a catalyst able to reduce NOx emissions by 75% compared to the 2005 emission control standards even in lean burn is therefore a desirable goal from the perspective of increased fuel efficiency.

3. Development of Metal Substrate for Lean NOx Catalyst

3.1. Issues of Cordierite Substrate and Study of Replacement Substrate

As indicated in Section 2, there are three main types of NOx-converting catalysts. The enhancement of the NOx conversion performance of one of these, the lean NOx catalyst, represents the most practical method of complying with future stringent emissions regulations.

The following represents methods to keep the performance of the conventionally used catalysts that support NOx-adsorbing materials on a cordierite substrate:

- (1) Prevention of sintering of precious metals
- (2) Prevention of sulfur poisoning
- (3) Prevention of migration of alkali metals to substrate

Issue (1) is also an issue in conventional three-way catalysts, and is not easy to settle. In the case of (2), performance can be recovered by means of a sulfur purge, and this issue is expected to be settled by the use of lower-sulfur fuels.

Issue (3) is specific to lean NOx catalysts. This phenomenon occurs because of the use of alkali metals as NOx-adsorbing materials in these catalysts. At temperatures of 700 °C and above, the alkali metals migrate to the cordierite substrate. To provide an example, in the case of potassium, the following reaction occurs:

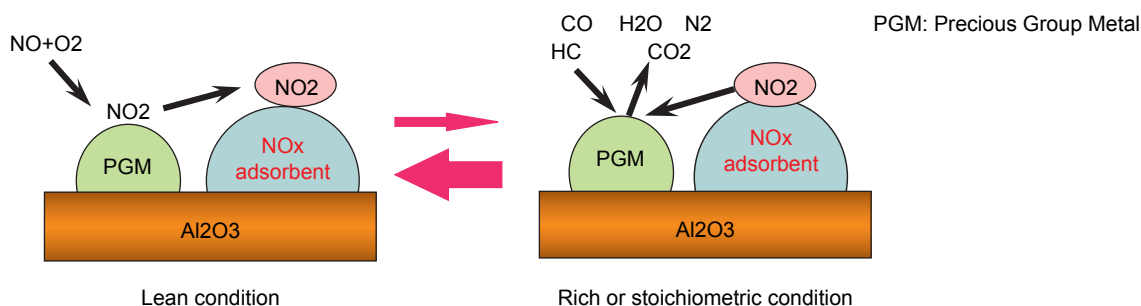


Fig. 1 NOx Purification mechanism of lean NOx catalyst

Figure 2 shows the results from an electron probe micro-analyzer (EPMA) image of potassium in a catalyst before and after thermal aging. These results show that the amount of alkali metals in the washcoat has been reduced, and that the alkali metals have migrated to the substrate due to thermal aging.

No method of reversing this reaction, as in the case of the use of sulfur purge when sulfur poisoning occurs, has been determined. The alkali metals that have undergone this reaction form complex compounds, which reduce its NO_x adsorption performance, causing the performance of the lean NO_x catalyst to decline. In addition, the compounds formed in the substrate have a different coefficient of thermal expansion from cordierite, and this can cause the substrate to crack. Figure 3 shows the surface of a catalyst following aging for 300 hours at 830 °C as an example. A crack due to thermal aging is visible on the external wall. To avoid this cracking of the substrate, it is necessary to restrict the supported amount of alkali metals.

The reason for the migration of alkali metals to the substrate is the fact that alkali metals react with Si, as Eq. (1) shows. Different methods have been proposed to

prevent this: specific elements can be added to stabilize the NO_x-adsorbing material⁽²⁾, or a K-capture layer can be formed between the substrate and the catalyst to prevent the alkali metals from reaching the substrate⁽³⁾.

In addition to cordierite substrates, metal substrates are also in mass production. These include substrates for three-way catalysts and the like. Metal substrates use 20Cr-5Al ferrite stainless steel alloy. Because the only Si found in these substrates occurs in the brazing material bonding the metal foil, it was considered that they might be effective in preventing the migration of alkali metals, and thus enhancing performance.

3.2. Results of Tests using Metal Substrates and Cause of Performance Decline

Based on the study mentioned above, lean NO_x catalyst was coated on a 20Cr-5Al substrate and subjected to thermal aging at 830 °C, after which its NO_x conversion rate was measured.

Figure 4 shows the results of these tests and the results of a lean NO_x catalyst supported on a conventional cordierite substrate as a comparison. Following thermal aging for 300 hours at 830 °C, the performance of the lean

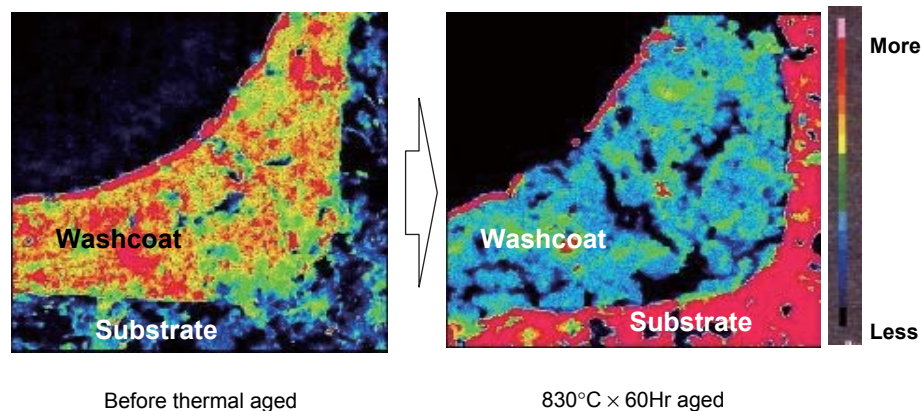


Fig. 2 EPMA map of potassium before and after thermal aging



Fig. 3 Surface crack after 830°C x 300Hr aging

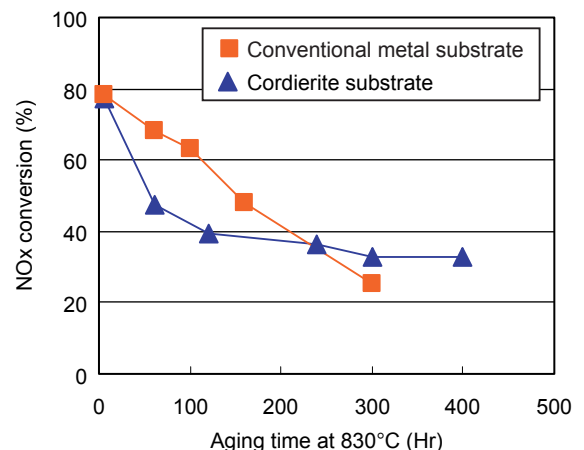


Fig. 4 NO_x Conversion with respect to aging time

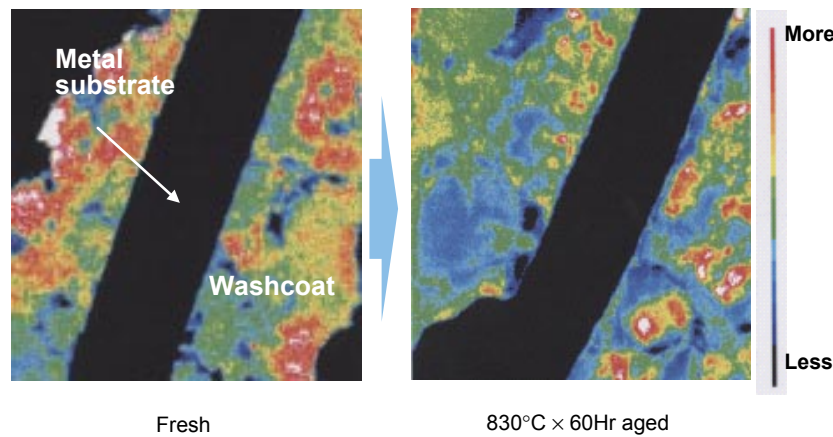


Fig. 5 EPMA map of potassium before and after aging

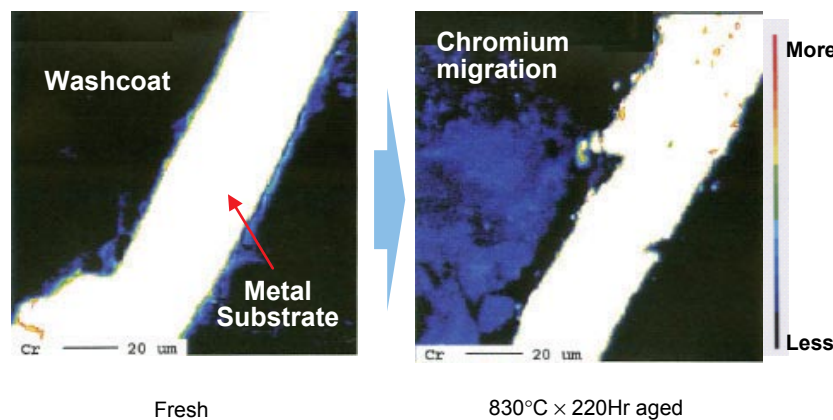


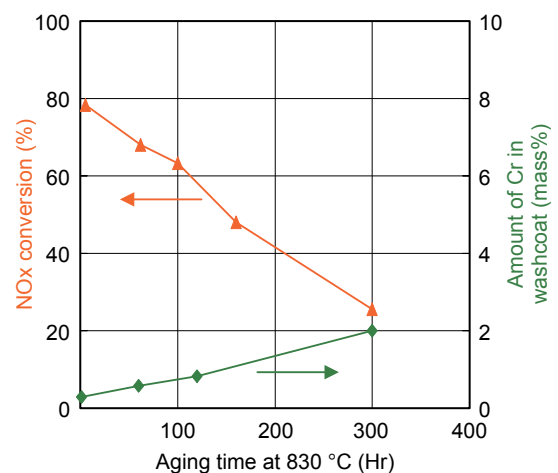
Fig. 6 EPMA map image of chromium before and after aging

NO_x catalyst supported by the 20Cr-5Al substrate declined to a level below that of the lean NO_x catalyst supported on the cordierite substrate. In addition, while the rate of performance decline with thermal aging time in the cordierite-supported catalyst was gradual, the metal-supported lean NO_x catalyst displayed an almost linear decline in performance with time.

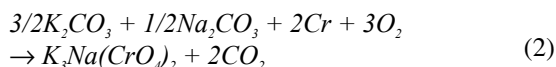
The catalyst and substrate were subjected to the EPMA analysis in order to determine the cause of this unexpected decline in performance. The results are shown in Figs. 5 and 6. As Fig. 5 shows, the analysis of the components of the substrate demonstrated that no alkali metals had migrated to the metal substrate. There was also no migration of other catalyst components to the substrate. However, as shown in Fig. 6, the results of analysis of the catalyst components indicated that Cr from the metal substrate had migrated to the washcoat. The relationship between the amount of Cr migration and the NO_x conversion rate is shown in Fig. 7. The decline in the rate of NO_x conversion is almost exactly proportional to the amount of Cr migration.

The washcoat was examined in isolation using powder X-ray diffractometry (XRD). The results showed that the

alkali metals and Cr had reacted to form chromium compounds. The XRD analysis results of the washcoat are shown in Fig. 8. These results indicate the following mechanism of performance decline in a lean NO_x catalyst

Fig. 7 NO_x conversion and amount of Cr in washcoat with respect to aging time

using a metal substrate: thermal aging causes the Cr in the metal substrate to migrate to the washcoat, generating a reaction of the type shown in Eq. (2), and complex oxides form in the alkali metals, making its adsorption performance to decline.



3.3. Development of a Metal Substrate with Limited Cr Migration

As discussed above, when a catalyst is supported by a conventional metal substrate, the rate of NO_x conversion declines as Cr migrates to the washcoat, where it forms complex compounds. A new method was therefore necessary to prevent Cr migration.

The metal substrate in a conventional metal substrate is formed from Fe-20Cr-5Al alloy. 5 mass% Al is used to increase the oxidation resistance of the metal substrate because the Al is preferentially oxidized and forms a protective alumina film when the metal substrate is exposed to high-temperature oxidizing air.

The present research project proceeded to examine the

possibility of using this protective alumina film as a barrier to prevent Cr diffusion after thermal aging in a lean NO_x catalyst. A conventional metal substrate was oxidized at 1100 °C in air, resulting in the formation of α alumina on the surface. Figure 9 shows a scanning electron microscope (SEM) image of this metal substrate (α-treated). The image shows that a uniform α alumina barrier has formed between the washcoat and the metal substrate.

To test the effectiveness of the α alumina barrier in controlling the migration of Cr, the catalyst was aged at 830 °C and its NO_x conversion performance was measured. Figure 10 shows EPMA maps of a conventional metal substrate and an α-treated metal substrate following thermal aging. Cr had migrated into the washcoat in the conventional metal substrate, but no Cr migration was observed in the α-treated metal substrate.

Figure 11 shows NO_x conversion rates for a cordierite substrate, a conventional metal substrate and an α-treated metal substrate following thermal aging. The rate of performance decline was slow in the case of the α-treated metal substrate, and it displayed a 31% higher rate of NO_x

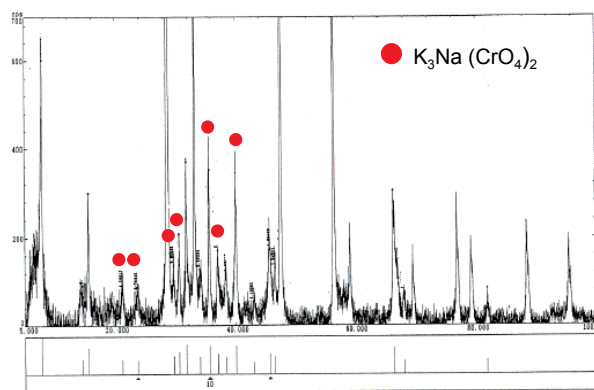


Fig. 8 XRD chart of washcoat after 830°C x 220Hr aging

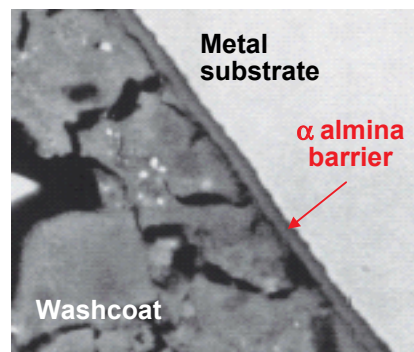


Fig. 9 SEM image of metal substrate with alpha alumina barrier

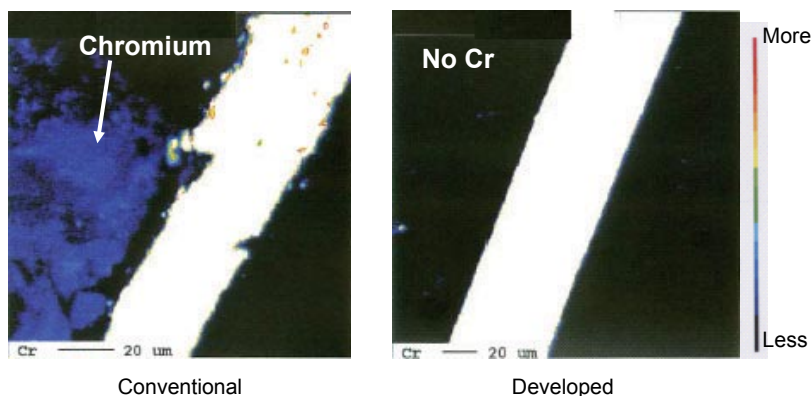


Fig. 10 EPMA map of chromium after 830°C x 220Hr aging

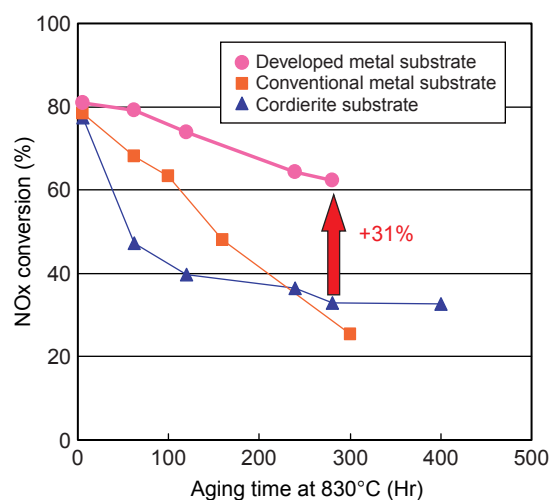


Fig. 11 Effect of metal substrate with α alumina barrier

conversion than the cordierite substrate following aging at 830 °C for 280 hours.

The developed α -treated alumina layer also displays reliable adhesion. Durability tests reproducing an automotive environment were conducted and no cracks were observed between the metal substrate and the α alumina film, indicating the developed substrate possesses sufficient durability.

4. Conclusion

A new catalyst substrate was developed by the thermal treatment of a mass-produced metal substrate at 1100 °C in air to create a fine α alumina film on the surface. The use of this substrate almost entirely controls the migration of Cr to the washcoat, which is the cause of performance decline in lean NO_x catalysts when a metal substrate is used. The developed substrate displays a 31% higher rate of NO_x conversion than a cordierite substrate following aging at 830 °C for 280 hours.

The development of the substrate led to the following findings:

- (1) Because metal substrates contain virtually no Si, alkali metals do not migrate to the substrate.
- (2) The NO_x conversion rate of a lean NO_x catalyst using a metal substrate declines because Cr in the metal substrate migrates to the washcoat and forms complex compounds with the alkali metals.
- (3) Thermal treatment of a metal substrate to precipitate a fine α alumina layer on the surface almost completely controls the migration of Cr, and the use of the substrate enhances the performance of lean NO_x catalysts.

References

- (1) Ohno, H., Takanohashi, T., Takaoka, N., Kuroda, O.,

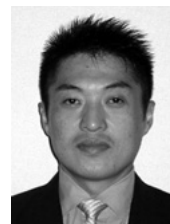
Iizuka, H.: NO_x Conversion Properties of a Mix Oxide Type Lean NO_x Catalyst, SAE Paper, 2000-01-1197 (2000)

- (2) Kaneeda, M., Kuroda, O., Iizuka, H., Higashiyama, K., Hiratsuka, T., Shinotsuka, N., Ohno, H., Takanohashi, T., Satoh, N.: Improvement of Thermal Resistance of Lean NO_x Catalyst, SAE Paper, 2003-01-1166 (2003)
- (3) Iwachido, K., Tanada, H., Watanabe, T., Yamada, N., Nakayama, O., Ando, H., Hori, M., Taniguchi, S., Noda, N., Abe, F.: Development of the NO_x Adsorber Catalyst for Use with High-Temperature Condition, SAE Paper, 2001-01-1298 (2001)

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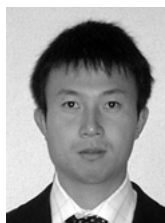
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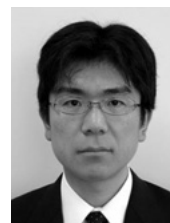
Masahiro SAKANUSHI



Kimihiro TOKUSHIMA



Tadao NISHIYAMA



Masato KANEEDA



Shogo KONYA