

Development of a New Metal Substrate for Lean NO_x Trap

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ABSTRACT

This paper presents a new substrate for Lean NO_x Traps (LNT) which enables high NO_x conversion efficiency, even after long-term aging, when using alkali metals as the NO_x adsorber.

When a conventional metal honeycomb is used as the LNT substrate, the chromium in the metal substrate migrates into the washcoat and reacts with the alkali metals after thermal aging. In order to help prevent this migration, we have developed a new substrate where a fine γ -alumina barrier is precipitated to the surface of the metal substrate. The new substrate is highly capable of preventing migration of chromium into the washcoat and greatly enhances the NO_x conversion.

The durability of the new substrate and emission test using a test vehicle are also examined.

INTRODUCTION

Technology capable of satisfying both increasingly stringent fuel economy and emission regulations is in demand. In this context, LNT, which is capable of purifying NO_x under lean and rich operations [1,2], is an effective method of catalytic conversion that is even capable of satisfying future regulations. LNT can also be said to be the most effective exhaust gas aftertreatment technology for passenger cars with lean burn engines, due to the fact that no urea tank is needed as with selective catalytic reduction (SCR) and that the catalyst volume does not need to be that great. However, due to regulations becoming more stringent in every nation, and a trend toward an ever increasing emission

durability requirement, there is a demand for maintaining high performance of the catalyst even after severe thermal aging. LNT adsorption materials include ceria-based (OSC) adsorption materials capable of adsorbing NO_x in the 200 to 400 degree C range [3], adsorption materials that use alkali earth metals, such as barium, that have superior NO_x adsorption characteristics in the 250 to 450 degree C range, and finally adsorption materials that use alkali metals, such as potassium, that have excellent NO_x adsorbability in the 300 to 500 degree C range [4,5]. Although it has already been widely reported in many papers that the adsorption materials with the greatest NO_x conversion efficiency are those that use alkali metals, particularly potassium, the use of potassium is known to result in various issues. First, as with barium-based adsorption materials, they are susceptible to sulfur poisoning, and desulfation is not easy [6,7]. This means that it is necessary to perform desulfation operations periodically, which lead to a fuel penalty. Furthermore, with desulfation operations usually performed at temperatures above 650 degree C, thermal degradation of the catalyst can result. The second issue is that alkali metals can volatilize at high temperatures. A method of preventing alkali metals from volatilizing into the exhaust gas through the addition of a potassium-stabilizer intended to improve the problem has been reported [5]. The last and most significant issue is that when cordierite is used as the substrate, alkali metals migrate into the cordierite substrate at high temperature. This is due to the fact that the SiO₂ in the cordierite and the alkali metals react easily with each other, and various reactions have been reported [8]. While the first two issues reduce catalyst performance, the last issue not only degrades catalyst performance, but results in an issue whereby the substrate breaks due to decreased substrate strength

and an increase in the coefficient of thermal expansion [4]. Therefore, new substrates which don't cause alkali migration have been desired. Although most of the substrates currently on the market are cordierite substrates, Fe-20Cr-5Al metal substrates are also being used, but at very low levels. The main reason that metal substrates are used is that their pressure loss is lower than cordierite substrates, so they are often used in sport cars and other high-performance vehicles.

Although there have already been reports of using metal substrates for a LNT, the main issue has been the high-mobility of potassium. In our current research, we studied NOx conversion performance after severe aging and the reasons for decreased performance when using a metal substrate. In addition to degradation due to sintering of platinum group metals, we found that complex compounds are formed by migration of chromium in the metal substrate into the washcoat. We therefore applied a heat treatment to prevent the migration of the chromium and make an α -alumina barrier over the entire surface of the metal substrate. Effectively serving as a chromium diffusion barrier, the α -alumina barrier was able to almost completely prevent the migration of chromium into the washcoat and conversion performance was improved drastically as a result. In the case of this substrate, we confirmed that there was no peeling of the α -alumina barrier from the metal substrate and that it possessed sufficient durability after a high-temperature oxidation test. Finally, we were able to achieve good performance results in a real vehicle application test.

EXPERIMENTAL

LNT CATALYST

The catalyst included platinum group metals (PGM), alkali metals consisting mainly of potassium as the adsorbants, and transition metal oxides. These catalytic elements were supported on an alumina-coated honeycomb (400 cells) by an impregnation method. The alumina-coated honeycomb was impregnated with an impregnation liquid that contained the catalyst elements, then dried by a hot air flow, and baked in an electric furnace. The loading amount of PGM is about 2.1g/L, including all three kinds of precious metals (Pt, Pd and Rh).

CATALYST AGING CONDITIONS

Substrates were aged for up to 300 hours in a muffle furnace at 830 degree C under dry air conditions. The reason for setting the aging temperature at 830 degree C is that some of the alkali metals can melt around 850 degree C and we anticipated rapid degradation due to the reaction with the α -alumina used as the catalyst support material.

MODEL GAS COMPOSITION

We measured conversion performance using the following compositions to imitate lean and rich exhaust conditions. The gas compositions used are given in Table 1.

	Lean	Rich (NOx Purge)
CO	0.1%	0.95%
C ₃ H ₆	1260ppmC	1220ppmC
NOx	500ppm	480ppm
CO ₂	14%	13%
H ₂	0.33%	0.32%
O ₂	4.70%	0.40%
N ₂	balance	balance
H ₂ O	+10%	+10%
GHSV	36000/h	35000/h

Table.1 Simulated Exhaust Gas Composition for NOx Performance Measurements

NO_x CONVERSION RATE MEASUREMENT

The above model gas was introduced into a 50-mm long honeycomb with a 1-inch diameter. With lean and rich cycles of both 3 minutes, we confirmed that stable conditions were achieved after repeating numerous cycles. After then switching the gas from rich to lean, we defined the average NOx conversion of the first 1 minute as the NOx conversion. We then took measurements from 300 degree C up to 500 degree C at 50 degree C intervals. The average NOx conversion referred to later is the calculated average of the NOx conversion found at 300, 350, 400, 450 and 500 degree C.

RESULT AND DISCUSSION

DEGRADATION MECHANISM WHEN USING A CONVENTIONAL METAL SUBSTRATE

Figures 1 and 2 show the NOx conversion rate versus temperature following catalyst aging at 830 degree C. Although there is drastic degradation up to 60 hours of aging when using a cordierite substrate, the degradation after this point becomes saturated. On the other hand, when using a metal honeycomb, good performance is maintained even after 60 hours of aging, but NOx conversion decreases if aging proceeds beyond this point. If aging is conducted for 240 hours or more, the result is that the average NOx conversion worsens in the range from 300 to 500 degree C, even more than when using a cordierite substrate. (Fig. 3)

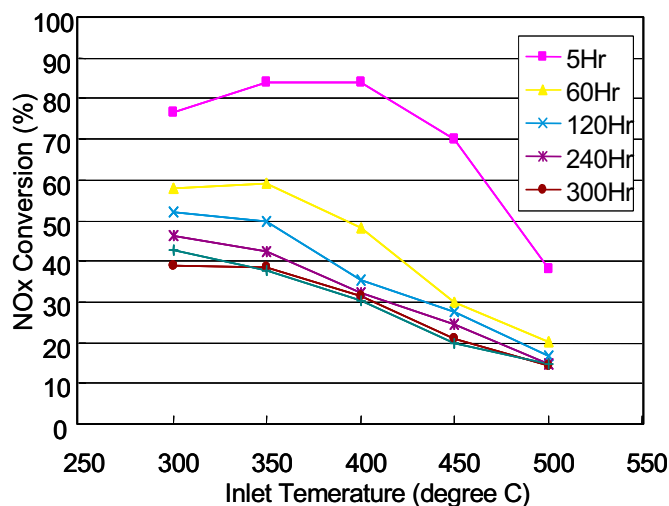


Fig.1 NOx Conversion of LNT on Cordierite Substrate Following Aging at 830C

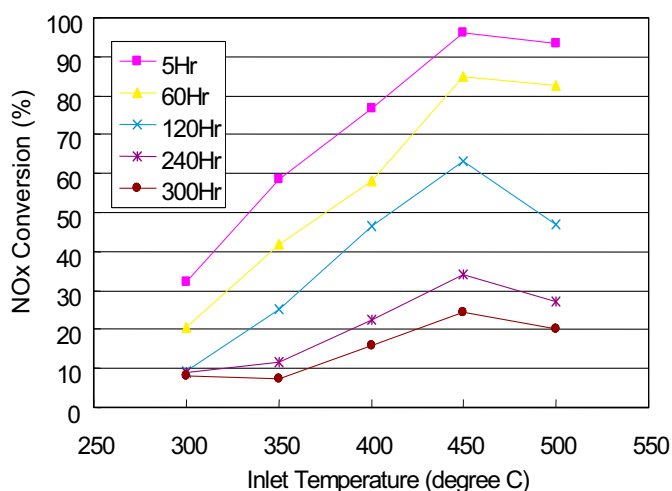


Fig.2 NOx Conversion of LNT on Conventional Metal Substrate Following Aging at 830 degree C

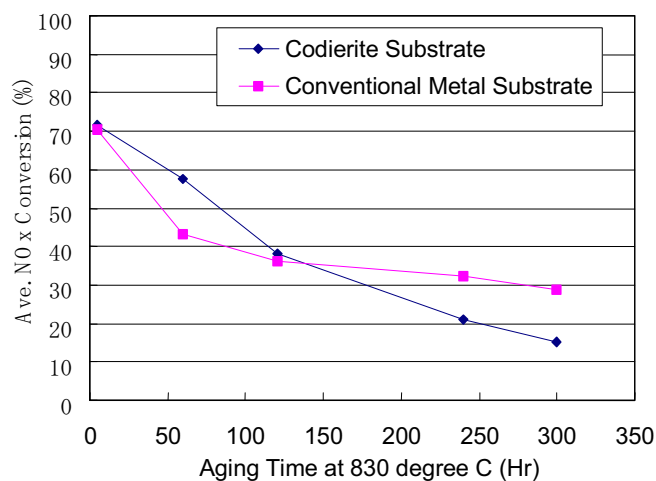


Fig.3 Average NOx Conversion of LNT on Different Substrate after Thermal Aging

In order to investigate the mechanism for the degradation, Electron Probe Micro-Analysis (EPMA) was

conducted. First, we observed whether alkali metals were migrating into the substrate. Although the metal substrate did not contain SiO_2 , metallic Si was included in part of the brazing metal. We also checked whether migration of alkali metals occurred there.

For comparison purposes, Fig. 4 shows the EPMA image of the potassium when using a cordierite substrate both when fresh and after 60 hours of aging at 830 degree C. After 60 hours, many of the potassium had already migrated. We can infer that this is one factor causing reduced performance at 60 hours. Figure 5 shows the scanning electron microscope (SEM) and EPMA image of the potassium when using a metal substrate. Even after 300 hours of aging, there were no alkali metals present in the foil or brazing material, and the migration of alkali metals didn't occur. Although we also checked whether there was migration of PGM and alkali metals other than potassium, we could not see the migration of any of the elements into the substrate.

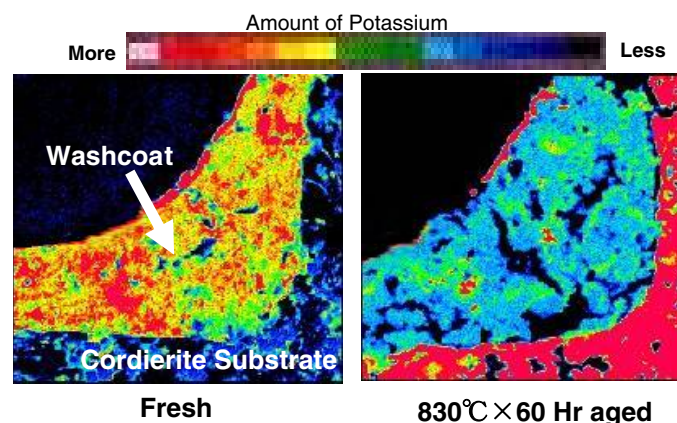


Fig.4 Alkali Migration to Cordierite Substrate

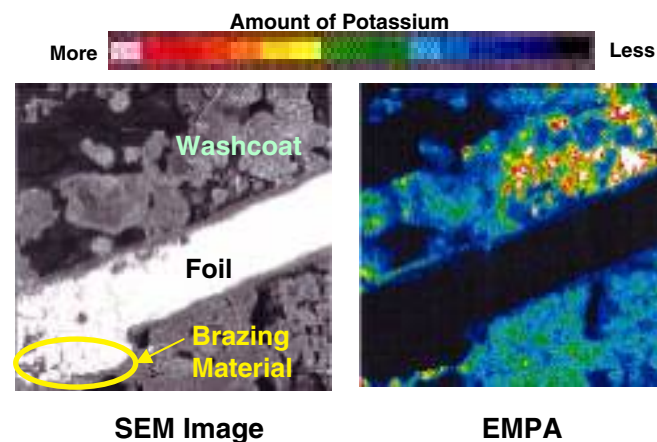


Fig.5 SEM and EPMA (K) Image after Thermal Aging (830 degree C x 300Hr)

EPMA of the substrate compounds were also conducted. Figure 6 shows the EPMA image of chromium when fresh and after 220 hours of thermal aging at 830 degree C. While chromium was only