

Development of Di-Air - A New Diesel deNOx System by Adsorbed Intermediate Reductants

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ABSTRACT

An unprecedented phenomenon that achieves high NOx conversion was found over an NSR catalyst. This phenomenon occurs when continuous short cycle injections of hydrocarbons (HCs) are supplied at a predetermined concentration in lean conditions. Furthermore, this phenomenon has a wider range of applicability for different catalyst temperatures (up to 800 degrees Celsius) and SVs, and for extending thermal and sulfur durability than a conventional NOx storage and reduction system. This paper analyzes the reaction mechanism and concludes it to be highly active HC-deNOx by intermediates generated from adsorbed NOx over the base catalysts and HCs partially oxidized by oscillated HC injection. Subsequently, a high performance deNOx system named Di-Air (diesel NOx aftertreatment by adsorbed intermediate reductants) was demonstrated that applies this concept to high speed driving cycles.

INTRODUCTION

Clean vehicles with low CO₂ emissions are being promoted as a countermeasure to global warming, and one effective approach to help address this issue is to popularize highly fuel efficient diesel vehicles and lean burn GDI vehicles. As part of this approach, limiting NOx emissions is a critical issue for diesel and GDI engines operated in lean conditions. In order to meet increasingly stringent emissions regulations in all countries, the development of a high performance deNOx system has become an important requirement.

One representative deNOx system, called a NOx storage reduction catalyst (NSR) system, was first introduced in 1994 [1] and it continues to be used on a large number of diesel vehicles. However, in order to meet post-Euro6 and real driving emissions regulations in the future, the development of a system that can convert NOx under wider temperature ranges and gas flow conditions is critical.

One drawback of the NSR system is a decline in NOx conversion in high gas flow conditions. This is mainly attributed to poor NOx storage speed in lean conditions and low use efficiency of the reductant in

rich conditions. In recent years, a system that utilizes NH₃ generated in rich operation to assist NOx reduction in lean conditions has been developed to address this issue [2-4]. This system is expected to improve NOx conversion in the area where NOx storage speed is insufficient. As a result, progress is being made to develop a feasible system that can store both NOx and useful reductants in catalysts.

NOVEL DENOX CONCEPT UTILIZING RECENT STUDIES OF NOx BEHAVIOR OVER NSR

Recent progress in kinetic measuring techniques has made the analysis of reactions over catalysts in transient conditions possible. As an example, Breen et al. analyzed the fast transient behavior of gas components in rich/lean conditions over an NSR catalyst, and found that N₂ is formed not only in rich conditions but also during a number of seconds after switching from rich to lean [5]. Taking this into account, the research described in this paper aimed to make the most of this NOx reduction effect in lean conditions by increasing the frequency of rich/lean cycles through supplying the reductant over short periods. In order to increase the number of rich periods with only a small fuel penalty, it is necessary to form rich conditions more frequently in a shorter period of time. Therefore, a direct HC injection system using a fuel injector decoupled from the engine was adopted as the reductant supplying method instead of a rich in-cylinder system, which may cause concerns about drivability and oil dilution. The system layout is shown in Fig. 1.

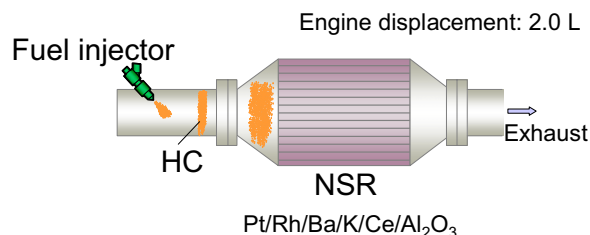


Fig. 1 Engine exhaust layout (catalyst volume: 0.8 L)

UNPRECEDENTED PHENOMENON OVER NSR CATALYST

The following development was carried out based on the above-mentioned concept. When HCs were supplied to an NSR by continuous short cycle injections at a predetermined concentration, it was found that NO_x could be reduced throughout a wider temperature range than with conventional storage and reduction. As an example, Fig. 2 shows the NO_x conversion performance with a catalyst bed temperature of 650°C.

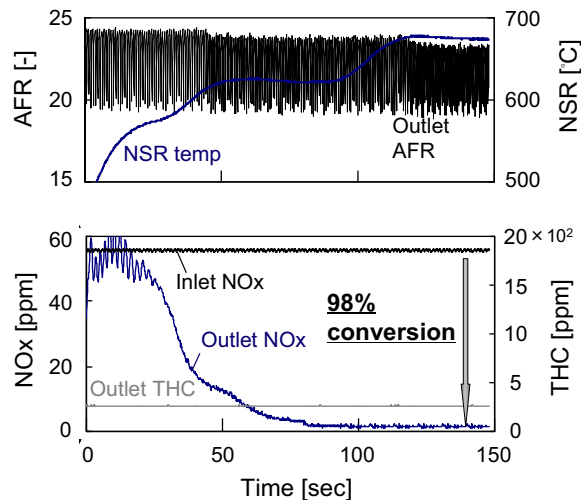


Fig. 2 NO_x conversion profile at PM regeneration (SV=56,000 h⁻¹, inlet gas temperature = 340°C, system layout = same as Fig. 1, injection frequency $f = 1\text{--}2.5$ Hz depending on NSR temperature)

Because a catalyst temperature of 650°C is above the decomposition temperature of nitrates, a catalyst cannot store NO_x. Moreover, the AFR (Air fuel ratio) sensor output from the catalyst outlet indicated a lean atmosphere, and HC and CO emissions were at very low levels. Therefore, it was suggested that this method demonstrates different conversion behavior from conventional storage and reduction that uses the rich/lean cycle. Taking into consideration that Breen et al. used CO and H₂ as reductants, this may be a unique phenomenon that occurs only when HCs are supplied. Since many researchers have focused on C₃H₆ as a reductant of hydrocarbons even though diesel fuel (long-chain HCs) is the reducing agent in actual cases, little detailed work has been published in the literature regarding the reaction between long-chain HCs and NO_x. Consequently, an investigation was carried out following the steps shown below to clarify this peculiar conversion phenomenon and verify its potential applications.

- Performance study of the discovered deNO_x phenomenon
- Analysis of its reaction mechanism
- Examples of application of the discovered deNO_x phenomenon to high speed driving cycles

PERFORMANCE STUDY OF DISCOVERED DENOX PHENOMENON

The performance of the discovered deNO_x phenomenon was studied by comparing it with conventional storage and reduction using an NSR catalyst in terms of the impact of space velocity (SV), thermal stress, and sulfur poisoning.

IMPACT OF SPACE VELOCITY

Figure 3 shows the relationship between SV and the NO_x conversion rate.

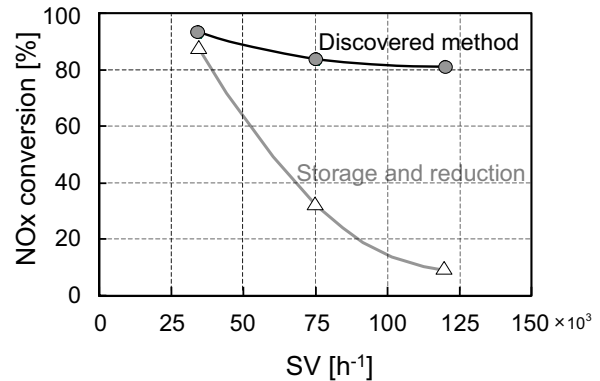


Fig. 3 Comparison of SV sensitivity between conventional storage and reduction method and the discovered method (injection frequency $f = 0.5$ Hz, system layout = same as Fig. 1, NSR temperature = 370–420°C, inlet NO_x = 98 ppm, fuel penalty = 2% in both methods, same NSR catalyst used for the comparative evaluations)

As the SV increases, the conversion rate of the storage and reduction method declines mainly because the use efficiency of the reductant and the NO_x storage speed are lowered. In contrast, the conversion rate with the discovered method was found to decline only slightly even at a high SV range. This feature has the potential to make aftertreatment systems more compact.

IMPACT OF THERMAL STRESS

Figure 4 shows the conversion rate before and after the equivalent of 160,000 km of aging.

The conversion rate of the storage and reduction method is greatly lowered after aging mainly due to the influence of platinum group metal (PGM) sintering caused by thermal stress and deterioration of the storage material, especially at low temperature ranges. In comparison, the discovered method was found to be hardly affected by these factors and could maintain a high conversion rate up to high temperatures of 800°C, even after aging.

ANALYSIS OF REACTION MECHANISM

SPECIFICATION OF REQUIRED CONDITIONS

This phenomenon is presumed to occur only when oscillated HC injection is supplied, but it was unclear how much oscillation is necessary to achieve high NO_x conversion. Therefore, the conversion rate sensitivity was studied under different oscillation amplitudes. Figure 6 shows the NO_x conversion behavior when the amplitude of oscillation was changed by post injection and by a fuel injector. The evaluation was performed at high temperature and high SV conditions to eliminate the influence of NO_x storage as much as possible (catalyst bed temperature = 550°C, SV = 75,000 h⁻¹).

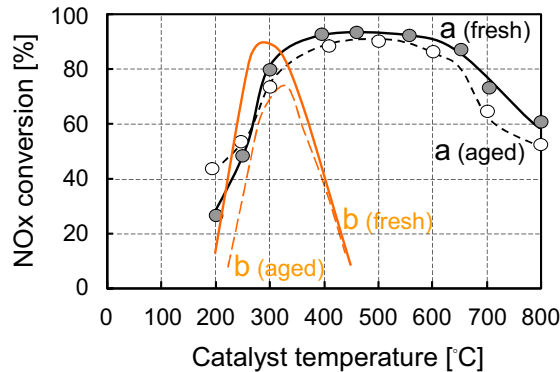


Fig. 4 Comparison of thermal durability between conventional storage and reduction method and the discovered method (a = discovered method, b = storage and reduction method, aging conditions = 700°C × 33 hours, injection frequency $f = 0.3\text{--}2.5$ Hz, SV = 45,000 h⁻¹, inlet NO_x = 60 ppm, using the same catalyst)

IMPACT OF SULFUR POISONING

Figure 5 shows the decline in conversion rate due to sulfur poisoning.

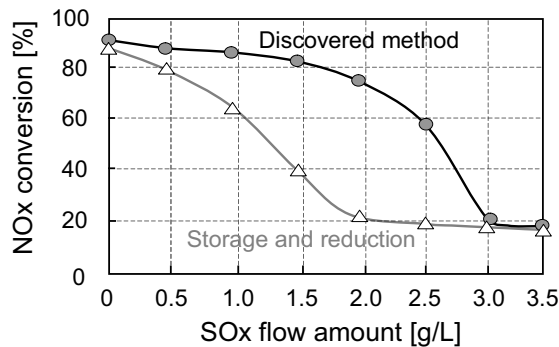


Fig. 5 Comparison of sulfur poisoning sensitivity between conventional storage and reduction method and the discovered method (both methods are regenerable) (SV = 50,000 h⁻¹, NSR temperature = 380°C, inlet NO_x = 60 ppm, fuel penalty = 2% in both methods)

The conversion rate declines due to sulfur poisoning with both methods. However, the decline with the discovered method is lower in terms of the amount of sulfur flow than the storage and reduction method. Moreover, sulfur regeneration is capable of recovering the conversion rate with both methods.

To summarize these results, although the discovered method uses an NSR catalyst, it has distinctly different properties from conventional storage and reduction. It has a wide range of applicability for catalyst temperature and SV, and its extended durability has the potential to help resolve issues in the conventional NSR system. Therefore, the reaction mechanism that would be necessary to develop a novel after-treatment system was analyzed.

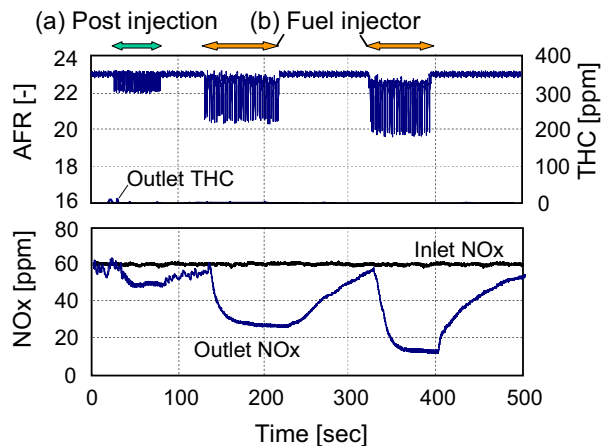


Fig. 6 Changes in outlet NO_x concentration as function of HC oscillation amplitude (SV = 75,000 h⁻¹, NSR temperature = 550°C, a = post injection, b = fuel injector, injection frequency $f = 0.5$ Hz)

As shown in Fig. 6, it was found that a small amplitude using post injection was not enough and a larger one using a fuel injector was necessary to achieve high NO_x conversion. This indicated that transient HC oxidation behavior is an important factor in this phenomenon. Subsequently, the relationship between NO_x conversion and transient CO₂ behavior generated from HC oxidation over a catalyst was investigated. Transient CO₂ behavior was investigated at the outlet of each section of three equal-length catalysts as shown in Fig. 7.

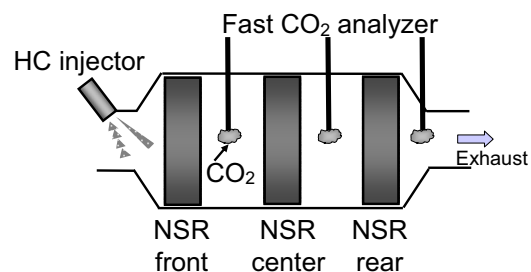


Fig. 7 Evaluation apparatus setup using fast CO₂ analyzer with catalysts divided into three equal-length sections