

Reaction Mechanism Analysis of Di-Air-Contributions of Hydrocarbons and Intermediates

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ABSTRACT

The details of Di-Air, a new NO_x reduction system using continuous short pulse injections of hydrocarbons (HC) in front of a NO_x storage and reduction (NSR) catalyst, have already been reported. This paper describes further studies into the deNO_x mechanism, mainly from the standpoint of the contribution of HC and intermediates.

In the process of a preliminary survey regarding HC oxidation behavior at the moment of injection, it was found that HC have unique advantages as a reductant. The addition of HC lead to the reduction or metallization of platinum group metals (PGM) while keeping the overall gas atmosphere in a lean state due to adsorbed HC. This causes local O₂ inhibition and generates reductive intermediate species such as R-NCO.

Therefore, the specific benefits of HC were analyzed from the viewpoints of 1) the impact on the PGM state, 2) the characterization of intermediate species, and 3) Di-Air performance compared to other reductants. As a result, the operando dispersive X-ray adsorption fine structure (DXAFS) method was used to find that HC prolong the metallic state of Pt compared to CO and H₂ during a period of time lasting a number of seconds under a lean atmosphere. Moreover, adsorption species and the catalyst outlet gas compositions during the period when lean gases of NO + O₂ are supplied to the metalized PGM were investigated using FTIR and a mass spectrometer. As a result, under lean conditions, intermediate species such as R-NCO were generated for a number of seconds after the supply of NO + O₂, and these species were changed into N₂.

In addition, temperature programmed desorption (TPD) results showed that HC intermediate species were more thermally stable and that their adsorption energy was larger compared to that of CO and bulk nitrates stored in a conventional NSR. This result also suggests that these characteristics of HC intermediate species contribute to high NO_x conversion under high temperature conditions. Moreover, it was found that HC is superior to other reductants, such as CO and H₂, only when small amounts of reductant are continuously supplied at short intervals under high temperature conditions. This result is different from past experience, which concluded that H₂ was the best reductant in any case. It was concluded that these observations explain the reason why the Di-Air system can achieve high NO_x conversion at high temperatures.

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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 NO_x 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 deNO_x system has become an important requirement.

One representative deNO_x system, called a NO_x storage reduction catalyst (NSR) system has a drawback in that the NO_x conversion rate declines in high gas flow and high temperature conditions. This drawback must be resolved to meet driving emissions regulations in the future.

A new NO_x reduction method called Di-Air has been proposed recently as an effective approach to resolving this issue [1]. This method supplies continuous short cycle injections of HC toward an NSR catalyst as shown in Fig. 1, and purifies NO_x using reductive intermediate species generated from partially oxidized HC and adsorbed NO_x in a catalyst. Di-Air can be utilized to achieve high NO_x conversion during high speed driving cycles and PM regeneration [2], in which conversion of a conventional NSR system is critically low.

However, the benefits of the characteristic aspects of NO_x conversion by Di-Air, namely (1) the supply of HC as a reductant, (2) the use of intermediate species for reduction, and (3) the intermittent supply of HC, have yet to be fully explained in terms of catalytic kinetics or adsorption chemistry. This paper describes the study that was performed to investigate the contribution of HC and intermediate species to the Di-Air reaction mechanism from the following three viewpoints.

- 1). The impact of HC on the platinum group metal (PGM) state
- 2). The characterization of the intermediate species
- 3). Di-Air performance compared to other reductants

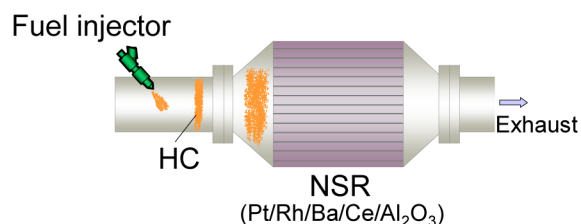


Figure 1. System layout of Di-Air.

BENEFITS OF OSCILLATED HC INJECTION

As shown in Fig. 2, one of the conditions for efficient NO_x conversion by Di-Air is to supply HC at a certain oscillation amplitude. This is because the intermediate species required for NO_x conversion can be generated efficiently by making the oscillation amplitude larger and instantly increasing the HC:O₂ ratio [1]. It has been found that partially oxidized HC, which act as the source of the intermediate species, are more easily generated as the HC supply concentration increases since full oxidation is inhibited under these conditions. However, the detailed oxidation behavior had yet to be observed.

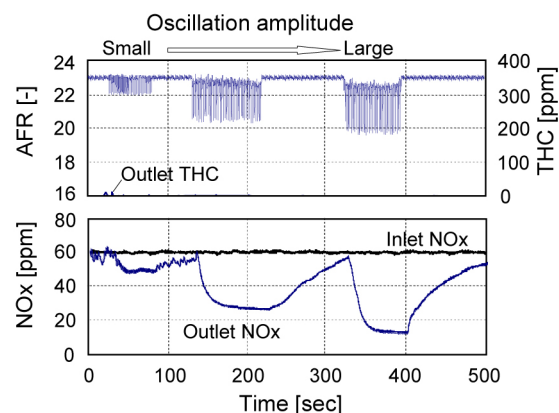


Figure 2. Influence of HC oscillation amplitude on NO_x conversion. (SV = 75,000h⁻¹, NSR temperature = 550°C, injection frequency = 0.5Hz).

Therefore, the detailed oxidation behavior of HC was investigated using a fast CO₂/CO analyzer (the NDIR500 manufactured by Cambustion Ltd. with a response rate of 8 msec) and a fast HC analyzer (the HFR500 manufactured by the same company with a response rate of 1 msec). The HC oscillation amplitude was varied within a range that maintains the catalyst outlet gas in a lean state. The MEXA-1600 analytical emissions system was located in front of the fuel injector to measure the raw O₂ concentration from the engine. The O₂ concentration during the injection was calculated from the raw O₂ concentration in front of the catalyst and the CO₂ concentration after the catalyst using Equation (1). The O₂ storage capacity was not considered in the formula because lean conditions were kept during the injections.

Engine displacement: 2.0 L

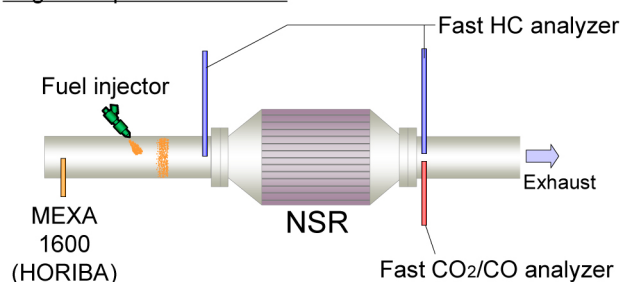
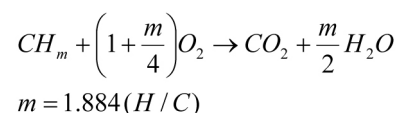


Figure 3. System layout for investigating HC oxidation behavior.



(1)

Figure 4 shows the results of the investigation. The figure compares two injection patterns: with a small HC oscillation amplitude (the left graph in Fig. 4) and with a large HC

oscillation amplitude (the right graph in Fig. 4). In both cases, the duration of CO₂ generation (α) is longer than the duration of HC supply (β) and occurs after a time delay. Even in the right graph that has a larger supply amplitude, oxidation does not occur immediately, and the HC is oxidized over a period of time while a lean atmosphere is maintained. This result indicates that HC supplied by oscillation inhibits the oxidation reaction by first being adsorbed over the catalyst.

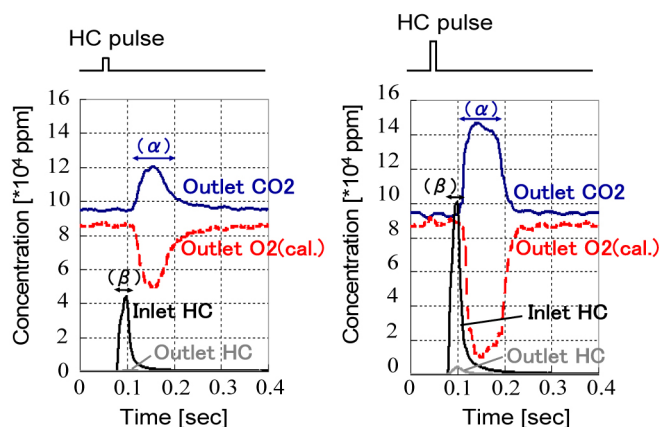


Figure 4. Comparison of HC oxidation behavior. ($SV = 53,000h^{-1}$, NSR temperature = $420^{\circ}C$, inlet $O_2 = 8.6\%$, injection amounts = $60mm^3$: left, $120mm^3$: right).

In this process, considering the amounts of HC compared to the adsorption sites, HC is also expected to be adsorbed in the vicinity of the PGM and to suppress conversion into oxidized PGM (Figure 5). Accordingly, one of the benefits of oscillated HC is to scavenge oxygen in the vicinity of the PGM while maintaining an overall lean gas atmosphere, which allows local metallization of the PGM. Therefore, this paper first focuses on the characteristics of PGM metallization by HC.

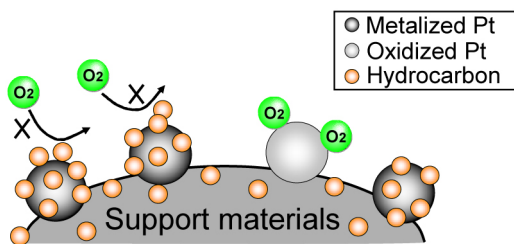


Figure 5. Image of oscillated HC adsorption by Di-Air injection.

METALLIZATION PERIOD OF PGM BY HC

One typical reduction method that utilizes the metallization of PGM is hydrocarbon selective catalytic reduction (HC-SCR) that reduces NO_x in the presence of excessive oxygen. The reduction mechanisms of HC-SCR

with PGM catalysts mainly include: 1) NO dissociation on the surface of metallic PGM, 2) reduction by intermediate species such as isocyanates ($-NCO$), and 3) reduction through an oxidation scheme from NO to NO₂. Various research cases have already been reported about the mechanisms of these reactions [3,4,5,6]. Although still controversial, the mainstream theory is that the first key factor in each reaction is the metallization of PGM. For example, Halkides et al. compared the behavior of N₂ when NO was supplied after pre-treatment with C₃H₆ or H₂ on a Rh/TiO₂ catalyst. In the case of C₃H₆ pre-treatment, an approximately twice as long N₂ generation period was found compared with H₂ pre-treatment. Therefore, it was inferred that C₃H₆ has twice the capability to scavenge adsorbed oxygen atoms as H₂ [7]. However, since the experiments performed by Halkides et al. were mainly carried out at low temperatures of approximately $250^{\circ}C$, this does not define the characteristics in the high-temperature region of $300^{\circ}C$ to $650^{\circ}C$ that forms the main Di-Air conversion window. In addition, conventional experiments have mainly observed the gas composition behavior using mass spectrometers and the like, and there are few examples of direct observation of the PGM state. Therefore, the effect of various reductants on PGM under high temperatures was investigated using the operando dispersive X-ray adsorption fine structure (DXAFS) method, which is capable of observing the PGM state directly with high temporal resolution [8].

DXAFS Experiment

The DXAFS experiment was performed using the PF-AR Beamline NW2 of the High Energy Accelerator Research Organization in Tsukuba, Japan. The storage ring energy was 6.5 GeV with the initial current of 200 mA. As shown in the optical layout in Fig. 6, a polychromatic beam generated by a bent-crystal polychromator is concentrated on the sample and then dispersed to the detector. This method is capable of simultaneously detecting beams with multiple energy levels and recording the absorption behavior of each level. The energy was adjusted to approximately the L₃ absorption edge of Pt.

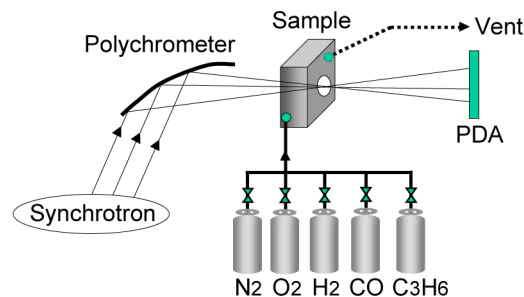


Figure 6. Optical layout of operando DXAFS method.

Figure 7 shows the experimental flow. First, a 1% H₂ gas flow was applied for ten minutes at a catalyst temperature of