

NO_x Trap Three-Way Catalyst (N-TWC) Concept: TWC with NO_x Adsorption Properties at Low Temperatures for Cold-Start Emission Control

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ABSTRACT

A new concept for trapping NO_x and HC during cold start, the NO_x Trap Three-Way Catalyst (N-TWC), is proposed. N-TWC adsorbs NO_x at room temperature, and upon reaching activation temperature under suitable air-fuel ratio conditions, it reduces the adsorbed NO_x. This allows a reduction in NO_x emissions during cold start. N-TWC's reduction mechanism relies on NO_x adsorption sites which are shown to be highly dispersed palladium on acid sites in the zeolite. Testing on an actual vehicle equipped with N-TWC confirmed that N-TWC is able to reduce emissions of NO_x and HC during cold start, which is a challenge for conventional TWCs.

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INTRODUCTION

Various efforts have been made to improve the efficiency of internal combustion engines in order to reduce CO₂ emissions and reduce consumption of petroleum resources. However, because they reduce the exhaust temperature, improvements to the efficiency of internal combustion engines are disadvantageous to the activation of exhaust catalysts such as three-way catalytic converters (TWCs), and are a primary cause of increased tailpipe emissions. Higher-efficiency internal combustion engines therefore require combination with exhaust systems that can reduce NO_x and HC at low exhaust temperatures.

Figure 1 shows the NO_x and HC emission profiles in a FTP-75 test cycle using a gasoline-powered vehicle equipped with a conventional TWC system. NO_x and HC emissions during cold start are 0.2 g, which accounts for approximately 40% of emissions of NO_x and HC over the entire test cycle (0.5 g). In other words, NO_x and HC emissions cannot be reduced when the TWC is below the activation temperature.

HC traps using zeolites are a well-known countermeasure against HC emissions during cold start [1,2]. Zeolites, oxides made of silicon oxide, have a regular three-dimensional pore structure. Emissions of HC can be reduced by trapping the HC in the zeolite pores during cold start, then releasing and reducing it after catalytic activation. However, such systems tend to be complicated because they require a mechanism that re-circulates the HC as it is desorbed from the HC trap upstream of the warmed-up three-way catalyst in order to reduce the HC adsorbed in the HC trap [3].

A well-known NO_x adsorption catalyst is a NO_x storage catalyst (NSC) [4]. An NSC initially oxidizes NO in an oxidative atmosphere, and then uses an adsorbent such as barium to adsorb the NO as

nitrates or nitrites. Finally, the oxidative atmosphere is switched to a reducing atmosphere (rich-spike), and the adsorbed NO_x is reduced into N₂. Lean NO_x catalyst using cerium oxide as the NO_x adsorbent has been proposed as a way to improve the NO_x reduction efficiency at low exhaust temperatures [5,6]. In recent years, NO_x adsorption catalysts using Ag/Al₂O₃ as the NO_x adsorbent have also been proposed [7,8]. However, NO_x cannot be adsorbed at room temperature in any of these methods.

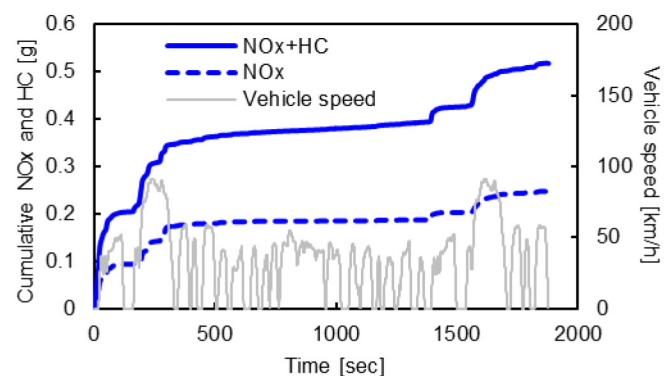


Figure 1. NO_x and HC emission profile in FTP-75 test cycle with conventional TWC system

As a result of investigations into materials for adsorbing NO_x and HC during cold start, a NO_x adsorption catalyst was found that works at room temperatures. Furthermore, this catalyst is able to reduce NO_x emissions during cold start thanks to a combination of properties that not only adsorb NO_x but also purify the adsorbed NO_x under stoichiometric air-fuel ratio conditions. This paper proposes a new concept for a three-way catalyst system that utilizes these properties.

N-TWC Concept

Figure 2 shows a working image of the NO_x Trap TWC (N-TWC) concept proposed in this paper. The N-TWC consists of palladium supported on zeolite. The N-TWC has two special properties. The first is adsorption of NO_x and HC during cold start and storage until a temperature is reached that activates the three-way catalytic reaction. The second is purification of the NO_x that was adsorbed during the warm-up process using reducing agents in the exhaust (CO and HC) or the adsorbed HC. Thanks to the combination of these two properties, N-TWC is able to reduce NO_x emissions during cold start. This paper reports on the following topics in particular:

Elucidation of the NO_x adsorption mechanism and structural characterization of the NO_x adsorption sites.

Confirmation of the effectiveness of the N-TWC concept.

Adsorption at the Cold Start Reaction during the Warm Up

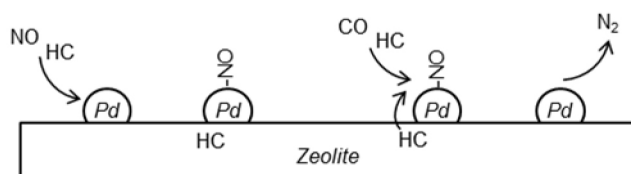


Figure 2. Adsorption and reaction scheme on N-TWC

EXPERIMENTAL METHODS

Preparation Methods of Catalyst Powder and Honeycomb Catalyst

ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=50$), an MFI-type zeolite, was used as the support for catalyst preparation. Noble metal supported on ZSM-5 (Pd/ZSM-5, Pt/ZSM-5, and Rh/ZSM-5) was prepared by impregnation method using solutions of the noble metal precursors. The metal loading was 1 wt.% in each samples. ZSM-5 without noble metals was also prepared as a comparison. The catalysts with different Pd loadings of ZSM-5 were prepared, supporting Pd at 0.2, 0.5, and 2.4 wt.% each. The catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ for the ZSM-5 were also prepared, with $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 23, 30, 80, and 300 and a Pd loading of 1 wt.%. Pd supported on oxides (Pd/ Al_2O_3 , Pd/ SiO_2 , and Pd/ CeO_2) was prepared by impregnation method as simulated TWC. The Pd loading was 1 wt.% in each samples. In addition, Pt,Ba,Ce/ Al_2O_3 were prepared as typical NSC, with 1 wt.% Pt loaded and $\text{BaO}:\text{CeO}_2:\text{Al}_2\text{O}_3 = 1:2:2$ (oxide weight ratio). All catalyst powder was calcined at 600°C for 2 h using electric furnace.

The slurry water solutions which consist of obtained catalyst powder and alumina binder was prepared. The honeycomb catalysts were prepared by washcoating slurry water solutions to 400-cpsi cordierite honeycomb monoliths with a diameter of 2.54 cm and length of 6 cm. The washcoated honeycomb catalyst was calcined using electric furnace and the washcoat amount was 200 g/L.

Method for Evaluating NO_x Adsorption Efficiencies

The NO_x adsorption efficiencies were evaluated in the laboratory reactor shown in Figure 3. A gas mixture was supplied to the honeycomb catalyst placed in the heating section of the laboratory reactor. After passing through the honeycomb catalyst, each gas component was measured using the following methods of analysis:

THC (Total hydrocarbon): FID (Flame Ionization Detector);

CO₂, CO: NDIR (Non-Dispersive Infra-Red spectroscopy);

O₂: MPA (Magneto-Pneumatic Detector);

NO_x: CLD (Chemi-Luminescent Detector);

NO, NO₂, NH₃, N₂O: FT-IR (Fourier Transform Infra-Red spectroscopy).

The gas mixture was prepared by mixing gasses from cylinders of different composition adjusted using a mass flow controller. The total gas flow rate was adjusted to 20 L/min, with a Gas Hourly Space Velocity (GHSV) of 40000 h⁻¹. All the honeycomb catalysts were pretreated at 600°C in a flow of 10% O₂ and balance N₂ in order to remove adsorbed species on the catalyst surface. The pretreated honeycomb catalysts were subjected to NO adsorption treatment at 50°C in a flow of 400 ppm NO, 2% O₂, balance N₂. The NO storage capacity ($\text{g}_{\text{NO}}/\text{L}_{\text{cat}}$) was measured as the weight of NO adsorbed per 1 liter of honeycomb catalyst. The NO storage capacity ($\text{g}_{\text{NO}}/\text{L}_{\text{cat}}$) was obtained by integrating the weight of both NO and the NO₂ desorbed during the period in which the honeycomb catalyst that had adsorbed the NO was heated by 20°C/min up to 600°C in a flow of N₂.

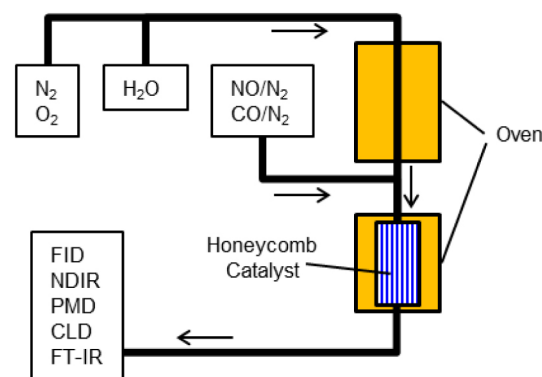


Figure 3. Construction of laboratory reactor

Method for Evaluating NO_x Reduction Efficiencies

After NO adsorption, the reduction efficiencies for the NO_x adsorbed by the catalyst were measured by comparing amounts of adsorption and desorption at two different oxygen excess ratios ($\lambda = 0.9$ and 2.0) when the temperature was raised by 20°C/min. The value of λ for the CO oxidation reaction ($\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$) was calculated using the concentrations of oxygen and CO as shown in equation (1). The two conditions were 1000 ppm CO, 0.045% O₂, balance N₂ ($\lambda=0.9$); and 1000 ppm CO, 0.1% O₂, balance N₂ ($\lambda=2.0$).