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The new concept 3-way catalyst for automotive lean-burn engine: NO_x storage and reduction catalyst

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Abstract

The new concept 3-way catalysts for a lean-burn engine have been developed, and their NO_x purification mechanisms have been studied. The catalysts consist of precious metals, aluminum oxide and some other metal compounds such as NO_x storage compounds. NO_x is oxidized over the precious metals and stored as nitrate ion combined with NO_x storage compounds under oxidizing conditions. The stored NO_x is reduced to N_2 under stoichiometric and reducing conditions. The NO_x storage capacity is deteriorated by sulfur. The improved catalysts showed sufficient NO_x conversion durability in the Japanese 10–15 mode test.

Keywords: NO_x; Automotive lean-burn engine; Reduction

1. Introduction

Reducing CO_2 emission from automobiles is important in order to prevent the greenhouse effect. The gasoline fuel lean-burn engine is one of the key technologies to improve the fuel efficiency of a passenger car. However, the lean operating conditions have been limited, because the NO_x emitted under oxidizing conditions could not be purified using conventional 3-way catalysts. Namely, when the lean-burn engine was accelerated under lean conditions, NO_x emission became high. If the NO_x can be purified by a new catalyst, the lean operating conditions can be widened, and the fuel efficiency can also be improved.

Recently, catalysts for selective NO_x reduction under oxidizing conditions have been widely studied. The famous examples of these catalysts are the copper ion-exchanged zeolites (Cu-ZSM-5) [1–3], alumina [4], base metals supported on alumina [5], and precious metals supported on zeolites [6]. But, these catalysts have many problems for practical use such as low NO_x conversion, a narrow temperature window and insufficient durability.

The new concept 3-way catalysts consist of precious metals, aluminum oxide and some other metal compounds. The Japanese 10–15 mode regulated emission test using a passenger car

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equipped with a lean-burn engine revealed that the NO_x conversion of these catalysts under dynamic oxidizing conditions are higher than that under static oxidizing conditions [7]. These new catalysts are called 'NO_x storage and reduction catalysts (NSR catalysts)'. In the present report, the NO_x purification mechanism, their cause of deterioration and NO_x purification performance of the improved catalysts in vehicle tests were studied. The lean burn system with the NSR catalyst was explained in details in another article [7].

2. Experimental

Catalysts were prepared by impregnating precious metals (mainly Pt), and various alkaline and alkaline earth metals (mainly Ba) and rare earth oxides on supports. In many cases, the support used was alumina. Silica was used as a support, without a NO_x storage function.

NO_x conversion of the catalysts was measured using simulated exhaust gases by alternating between oxidizing and reducing conditions at every several minutes. The typical gas composition of simulated exhaust is shown in Table 1. The NO_x concentration was measured using a chemiluminescent NO_x analyzer built in MEXA (Horiba).

N-compounds (N_2, NO, NO_2) in simpler gases at 573 K were measured using a quadrupole mass spectrometer (ULVAC).

NO_x species stored on NO_x storage compounds, under a flow of a mixture of 0.1% NO/N_2, 10% O_2/N_2 and 3% H_2O at 673 K, were analyzed using diffuse reflectance FT-IR (Japan Spectroscopic).

The amount of NO_x stored at 623 K was measured using TG (Shimazu). The simulated gases used for this experiment were composed of 2% NO/N_2 and 50% O_2/N_2.

The vehicle test was carried out using a passenger car equipped with a 1.8 l lean-burn engine.

Table 1
Typical gas composition for NO_x storage and reduction reaction

	NO	O_2	C_3H_6	CO	H_2O	CO_2	N_2
reducing condition	70 ppm	0.6%	2000 ppm	0.5%	10%	14.5%	balance
oxidizing condition	700 ppm	4.0%	800 ppm	0.1%	10%	12.7%	balance

3. Results and discussion

3.1. NO_x purification phenomena of NSR catalyst

NO_x purification behavior, when the simulated gases were fed alternately under oxidizing and reducing conditions, is shown in Fig. 1. NO_x was removed under oxidizing conditions, and NO_x concentration in the outlet gas gradually increased with time. When the catalyst was exposed to the simulated gases under oxidizing conditions for a long period, NO_x concentration in the outlet gas almost became constant (Fig. 2). The concentration of N-compounds measured using a quadrupole mass spectrometer (Q-Mass) is shown in Fig. 3. When NO was fed to the catalyst as a rectangular pulse under oxidizing conditions, only NO and NO_2 were detected in the outlet gas. However, the total amount of NO and NO_2 in the outlet gas was smaller than that of NO in the inlet gas. Under stoichiometric conditions without N-com-

Fig. 1. NO_x purification behavior of NSR catalyst (- - - - -) inlet gas, (———) outlet gas, inlet gases were fed alternately at every 120 s under reducing and oxidizing conditions. Catalyst: Pt/Ba/Al_2O_3, temperature: 573 K, gas composition: under reducing condition (a) [NO] = 70 ppm, [O_2] = 0.6%, [C_3H_6] = 2000 ppm, [CO] = 0.5%, [H_2O] = 10%, [CO_2] = 14.5%, N_2 balance, under oxidizing condition (b) [NO] = 700 ppm, [O_2] = 4%, [C_3H_6] = 800 ppm, [CO] = 0.1%, [H_2O] = 10%, [CO_2] = 12.7%, N_2 balance.

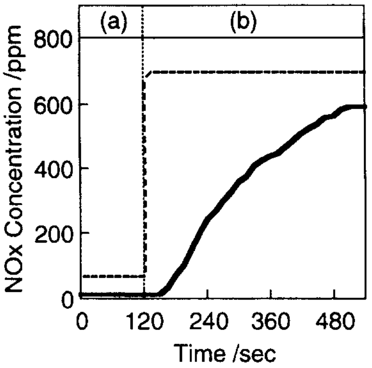

Fig. 2. NO_x purification behavior of the NSR catalyst exposed to simulated gases for a long period under oxidizing condition (- - -) inlet gas, (———) outlet gas. Catalyst: $Pt/Ba/Al_2O_3$, temperature: 573 K, gas compositions of (a) and (b) were the same as described in Fig. 1.

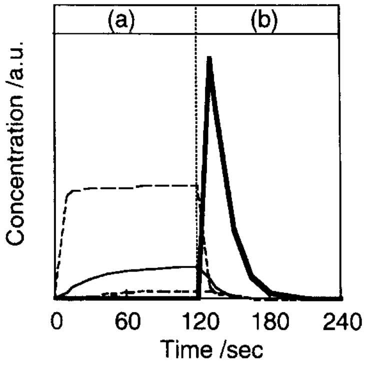

Fig. 3. N-compound behavior of NSR catalyst (1). (- - -) NO in inlet gas, (———) NO in outlet gas, (- - -) NO_2 in outlet gas, (———) N_2 in outlet gas. Catalyst: $Pt/Ba/Al_2O_3$, temperature: 573 K, gas composition: under oxidizing condition (a) $[NO] = 0.2\%$, $[O_2] = 5\%$, He balance, under reducing condition (b) $[O_2] = 5\%$, $[H_2] = 10\%$, He balance.

pounds in the inlet gas, N_2 was detected in the outlet gas. These results indicate that, NO_x was stored on the catalyst under oxidizing conditions, and that the stored NO_x was then reduced to N_2 under stoichiometric and reducing conditions.

NO_x storage mechanism

Fig. 4 shows the NO_x storage amount plotted as a function of O_2 concentrations in simulated gases. The NO_x storage amount was very low without O_2, and rapidly increased with increasing the concentration of O_2 and finally reached a constant value above 1% O_2. From these results, it was expected that NO_x was stored on the catalyst as an oxidized form. The stored NO_x species measured using diffuse reflectance FT-IR are shown in Fig. 5. From the absorption peak at about 1350 cm^{-1}, the stored NO_x species were assigned to nitrate ions. The molar ratio of the saturated storage amount of NO_2 to Ba was about 2. This result also suggests that NO_x reacted with Ba^{2+} to form $Ba(NO_3)_2$. The relation between electronegativity of each NO_x storage compound and the NO_x storage amount is shown in Fig. 6. The stronger the basicity of the NO_x storage compound was, the larger the quantity of the NO_x stored was. The more stable nitrates could be formed with the stronger basicity of the NO_x storage compounds. These results suggest that NO_x is oxidized on precious metals and finally stored on NO_x storage

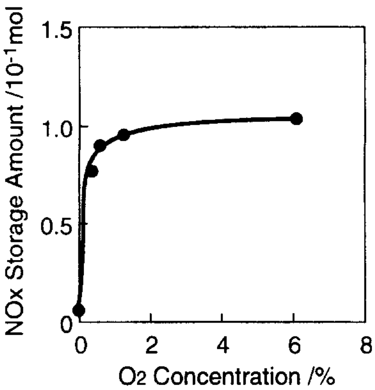

Fig. 4. Influence of the O_2 concentration on NO_x storage amount. Catalyst: $Pt/Ba/Al_2O_3$, temperature: 573 K, gas composition: $[NO] = 250$ ppm, $[O_2] = 0–6\%$, N_2 balance.

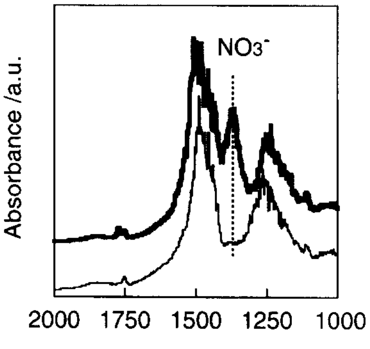

Fig. 5. FT-IR spectra of NO_x species stored on NO_x storage compound. (———) spectrum of catalyst (under N_2 flow), (———) spectrum of catalyst and NO_x species stored on NO_x storage compound (under $NO + O_2 + N_2$ flow), catalyst: $Pt/Ba/SiO_2$, temperature: 673 K. Spectrum of catalyst and stored NO_x species were measured under a gas composition of $[NO] = 0.1\%$, $[O_2] = 4\%$, $[H_2O] = 3\%$ and N_2 balance.

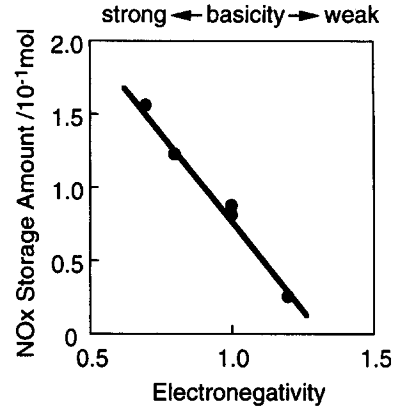

Fig. 6. Influence of basicity of NO_x storage compounds on NO_x storage amount. Catalyst: Pt/NO_x storage compound/Al_2O_3, temperature: 523 K, gas composition: $[NO] = 700$ ppm, $[O_2] = 4\%$, $[C_3H_6] = 800$ ppm, $[CO] = 0.1\%$, $[H_2O] = 10\%$, $[CO_2] = 12.7\%$, N_2 balance.

compounds to form nitrates. Misono and co-workers [8] and Arai and co-workers [9] have reported that complex oxides could store NO_x under oxidizing conditions. Arai and co-workers have also reported that NO_x was stored as nitrates. Similarly, NSR catalysts also stored NO_x as nitrates.

Combination of catalysts has been studied in order to prove the migration of NO_x from precious metals to NO_x storage compounds. One catalyst was prepared by supporting Pt and Ba on identical support particles, while another catalyst was prepared by supporting Pt and Ba on separate support particles and blending them. The NO_x storage ratio of these two catalysts are shown in Fig. 7. The former catalyst which had Pt and Ba supported on identical support particles, alone stored NO_x. This result suggests that the migration process of NO_x from precious metals to NO_x storage compounds was a very important step for NO_x storage, and that the migrated NO_x reacted with NO_x storage compounds neighboring on precious metals to form nitrates.

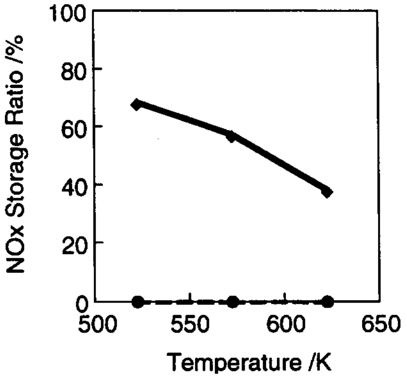

Fig. 7. Influence of arrangement of precious metal and NO_x storage compound on NO_x storage ratio. (——◆——) Pt and Ba were supported on identical SiO_2 particles, (- - -●- - -) Pt and Ba were supported on separate SiO_2 particles. Gas composition: $[NO] = 570$ ppm, $[O_2] = 8\%$, $[C_3H_6] = 1200$ ppm, $[CO] = 0.2\%$ $[H_2] = 500$ ppm, He balance.

NO_x reduction mechanism

Fig. 8 shows the concentration of N-compounds measured using Q-Mass under a different condition from as described in Fig. 3. In this figure, He was fed to the catalyst between oxidizing and stoichiometric conditions. During the He gas flow, a little NO and NO_2 were detected in the outlet gas. Subsequently, under stoichiometric conditions, N_2 was detected. From these results, nitrates formed under oxidizing conditions were supposed to be decomposed into NO_x by the reducing agent (HC, CO, H_2, etc.) activated on the precious metals. The influence of the reducing agents on NO_x conversion is shown in Fig. 9. The stoichiometric ratio in the case of NO_x reducing conditions was varied by changing the mixture ratio of CO, H_2 and C_3H_6. NO_x conversion was high under reducing conditions (stoichiometric ratio < 1), while it was low under oxidizing conditions (stoichiometric ratio > 1). NO_x conversion did not depend on the type of reducing agents,

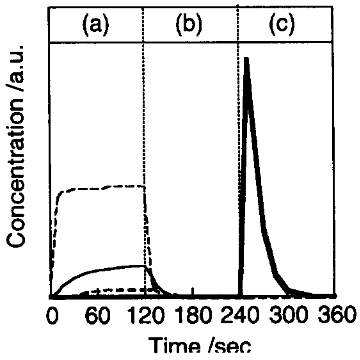

Fig. 8. N-compound behavior of NSR Catalyst (2). (- - -) NO in inlet gas, (———) NO in outlet gas, (- - -) NO_2 in outlet gas, (———) N_2 in outlet gas. Catalyst: Pt/Ba/Al_2O_3, temperature: 573 K, gas composition: under oxidizing (a) and under reducing (c) conditions were the same as described in Fig. 3., (b) $[He] = 100\%$.

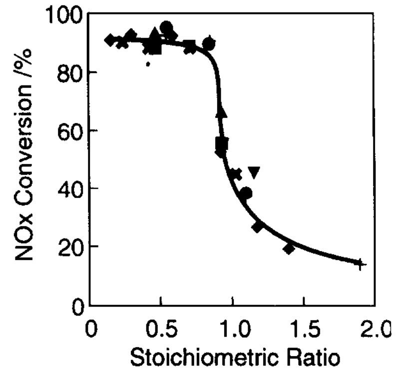

Fig. 9. Influence of various reducing agents and their combination on NO_x conversion. Catalyst: $Pt/Ba/Al_2O_3$, temperature: 523 K, combination of reducing agents and water ▼ C_3H_6, ● H_2, + H_2+H_2O, ■ CO, ▲ $CO+H_2O$, × $C_3H_6+CO+H_2O$, ◆ H_2+CO+H_2O. Stoichiometric ratio = $(2[O_2]+[NO])/([H_2]+[CO]+9[C_3H_6])$.

but depended on the stoichiometric ratio. This result suggests that the emitted NO_x is reduced to nitrogen on precious metals.

Summary of NO_x storage and reduction mechanism

The NO_x storage and reduction mechanism expected from the previously described results is shown in Fig. 10. NO_x is oxidized on precious metals and combined with neighboring NO_x storage compounds to form nitrates. The nitrates thus formed are decomposed into NO_x by reducing agents activated on precious metals under stoichiometric and reducing conditions. The emitted NO_x is reduced to N_2 on precious metals by reducing agents.

3.2. Important factors of NSR catalysts

Particle size of Pt

Based on the NO_x storage and reduction mechanism, the migration process of NO_x and activated reducing agents from precious metals to NO_x storage compounds was very important for NO_x purification. The influence of Pt particle size on NO_x conversion is shown in Fig. 11. Pt particle size was measured using X-ray diffraction (XRD). NO_x conversion was dependent on Pt particle size; the smaller the Pt particle size, the higher the NO_x conversion. It is expected that when the Pt particle size becomes smaller, Pt surface area increased; namely, the number of active sites for the NO_x oxidation reaction and reducing agent activation existing on the Pt surface increased. The interface between Pt and NO_x storage compounds was also increased. Therefore, migration of the reactants was promoted. NO_x conversion may have been effected by these two causes.

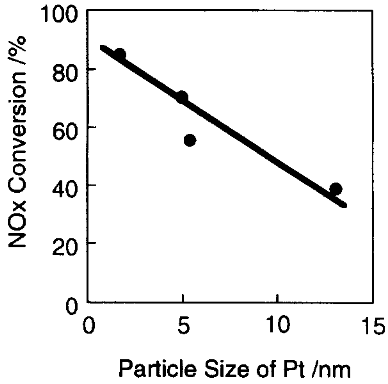

Fig. 11. Influence of the particle size of Pt on NO_x conversion. Catalyst: $Pt/Ba/Al_2O_3$, gas composition: oxidizing condition [NO] = 700 ppm, $[O_2]$ = 4%, $[C_3H_6]$ = 800 ppm, [CO] = 0.1%, $[H_2O]$ = 10%, $[CO_2]$ = 12.7%, N_2 balance, reducing condition [NO] = 70 ppm, $[O_2]$ = 0.6%, $[C_3H_6]$ = 2000 ppm, [CO] = 0.5%, $[H_2O]$ = 10%, $[CO_2]$ = 14.5%, N_2 balance. The particle size of Pt was measured using XRD.

Type of NO_x storage compounds

As described in section 3.1, the NO_x storage amount was dependent on the basicity of the NO_x storage compounds. In general, basic compounds

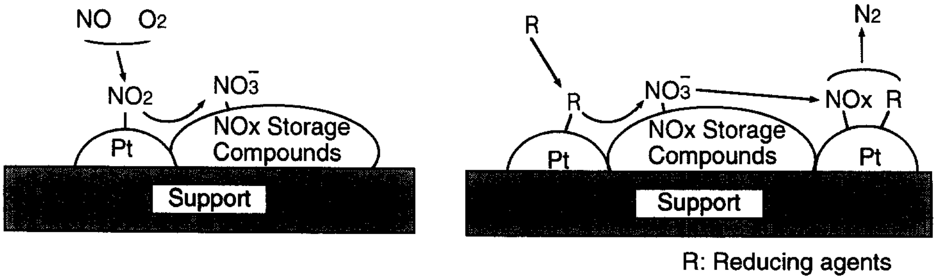

Fig. 10. NO_x storage and reduction mechanism of NSR catalysts.

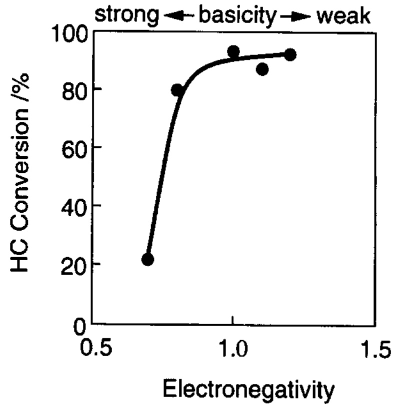

Fig. 12. Influence of basicity of NO_x storage compound on HC conversion. Catalyst: Pt/NO_x storage compound/Al_2O_3, HC conversion was measured in the Japanese 10–15 mode emission test.

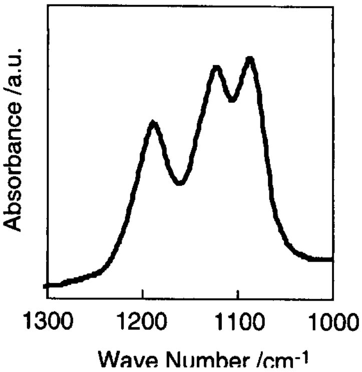

Fig. 13. FT-IR Spectrum of NSR catalyst after durability test. Catalyst: Pt/Ba/Al_2O_3.

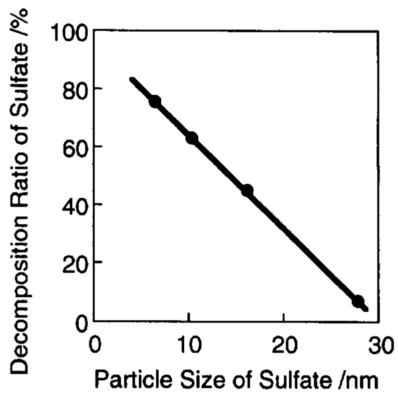

Fig. 14. Influence of sulfate particle size on its decomposition ratio. Decomposition condition: temperature: 973 K, time: 20 min, gas composition: $[C_3H_6] = 1\%/N_2$ balance. The particle size and the decomposition ratio of sulfate were measured using XRD.

have effects on the activity of Pt. For instance, the oxidation activity of HC is decreased. Also, in the case of the NSR catalyst, basicity of the NO_x storage compound affected HC conversion. HC conversion drastically decreased using too strong basic NO_x storage compounds (Fig. 12). The NSR catalyst must have not only NO_x storage ability under oxidizing conditions but also three-way activity under stoichiometric and reducing conditions. Therefore, the selection of basicity of the NO_x storage compounds is important for NSR catalysts.

3.3. The durability of the NSR catalysts

The durability of the catalyst was tested using real and simulated exhaust gases containing SO_2. The deterioration was expected to be caused by thermal aging and poisoning. If SO_2 was in the exhaust gas, the NO_x storage capacity would be drastically reduced. SO_2 is formed through the oxidation of sulfur compounds in the fuel. Sulfate ion was detected on the catalyst after the test using FT-IR (Fig. 13). SO_2 was expected to be oxidized on the precious metal and combined with the NO_x storage compounds to form sulfates. Sulfates are more stable than nitrates. Therefore, NO_x storage compounds were formed as sulfates, which could not store NO_x.

However, some of the sulfates neighboring on the precious metals were gradually reduced and decomposed under stoichiometric and reducing conditions. The relation between the sulfate particle size and their decomposition ratio is shown in Fig. 14. They were measured using XRD. The smaller the sulfate particle size, the easier the decomposition of the sulfates. Therefore, we tried to find the optimum chemical composition of the NO_x storage compounds that inhibits the growth in size of sulfate particles, and some additives were found. As a result, the improved NSR catalysts were able to decompose sulfates, and provided to practical use.

3.4. Performance of NSR catalysts in vehicle test

In the Japanese 10–15 mode using a passenger car equipped with a 1.8 l lean-burn engine, the improved fresh catalyst had 90% NO_x conversion, and after the durability test (equal to 100 000 km running, using Japanese regular gasoline containing 30 ppm of sulfur compounds), the catalyst had 60% NO_x conversion. This result indicates that NSR catalysts have sufficient durability using low sulfur level gasoline fuels.

4. Conclusions

The new concept three-way catalysts with a NO_x storage and reduction function for lean-burn engines have been developed. The catalysts are confirmed to have about 90% NO_x conversion at the initial stage in the Japanese 10–15 mode using a passenger car equipped with a lean-burn engine and have excellent durability.

The NO_x purification mechanism of NSR catalysts has been studied. NO_x is oxidized on precious metals and stored on neighboring NO_x storage compounds as nitrates under oxidizing conditions. Subsequently, the stored NO_x is reduced to N_2 by the following two steps: The first is decomposition of nitrates, and the second is the reaction with reducing agents on the precious metals.

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