Special Feature: Automotive Exhaust Catalyst

NO$_x$ Storage and Reduction Catalysts for Gasoline-fueled Automotive Exhaust

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■**ABSTRACT**‖ This report reviews nitrogen oxide (NO$_x$) storage and reduction reactions and the technologies used by the Toyota group alliance to improve the durability of NO$_x$ storage and reduction type catalysts against both thermal damage and sulfur poisoning. Catalysts for NO$_x$ storage and reduction oxidize nitrogen monoxide (NO) emitted from automotive lean-burn engines to nitrogen dioxide (NO$_2$), which is then stored on doped NO$_x$ storage materials such as barium and/or potassium compounds as nitrate ions (NO$_3^-$). In a reducing atmosphere provided by a suitable engine management system, the nitrates formed are subsequently reduced and decomposed into NO$_x$ via reactions between reducing agents in the exhaust gas, such as hydrogen, carbon monoxide, and hydrocarbons. The emitted NO$_x$ is finally reduced and detoxified to nitrogen. To meet stringent emission regulations for automotive exhaust pollutants, NO$_x$ storage and reduction catalysts must have excellent activity for NO$_x$ removal and an extremely long lifetime. Thermal stress causes a decrease in the number of active sites due to sintering of the precious metals in the catalyst, which decreases the specific surface area of the support and leads to solid-phase reaction between the NO$_x$ storage material and the support. Sulfur is also present in exhaust gas derived from gasoline fuel, and it competes with NO$_x$ for storage and reacts with the doped NO$_x$ storage material to form sulfates. Once NO$_x$ storage materials are sulfated, their NO$_x$ storage capability is significantly deteriorated. We developed some novel solutions to overcome these issues by creating new materials for a sustainable environment.

■**KEYWORDS**‖ Automotive catalyst, NO$_x$ storage and reduction, Lean burn engine, Sulfur poisoning, Thermal deterioration

1. Introduction

There is an urgent demand for a decrease in carbon dioxide (CO$_2$) emissions from automobiles to prevent global warming. At the same time, the development of more fuel-efficient engines is also regarded as an additional benefit for the automobile industry. As a fuel-efficient option, the lean-burn gasoline engine has attracted much attention, due to its remarkable potential for improvement of fuel economy compared to conventional engine systems. However, the wide use of lean-burn engines is somewhat restricted by environmental regulations, because conventional three-way catalysts do not fully detoxify nitrogen oxides (NO$_x$) under excess oxygen conditions, although they do exhibit excellent catalytic activity for the removal of carbon monoxide (CO) and hydrocarbons (HC). Therefore, to meet stringent emission regulations for automotive exhaust pollutants, a new after-treatment system for lean-burn

gasoline engines is required.

Direct decomposition of NO$_x$, the generic term for nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$), into nitrogen (N$_2$) is ideal and thermodynamically favorable. However, excess oxygen (O$_2$) competes with NO$_x$ for adsorption on catalyst active sites and inhibits direct decomposition reactions of NO$_x$. Therefore, reducing agents such as hydrogen (H$_2$), CO, and HC are required to remove adsorbed oxygen from active sites on the catalyst surface. Catalysts with the ability to reduce NO$_x$ to N$_2$ by reaction with reducing agents in an oxidative atmosphere are called selective catalytic NO$_x$ reduction (SCR) catalysts and have been widely investigated for more than two decades. Well-known examples include copper ion-exchange zeolites (Cu/ZSM-5),[1-3] alumina,[4] base metals supported on alumina,[5] and precious metals supported on zeolites.[6] However, with respect to practical applications, these catalysts still have many problems. For example, not all SCR catalysts can completely remove NO$_x$ under

all oxidative atmospheres. Thus, SCR catalysts are not sufficiently reliable for actual utilization to achieve zero-pollutant-emission vehicles without modifications such as addition of urea as a NO_x reducing agent. Such additional equipment increases not only the capital cost, but also the operational costs of exhaust purification systems. Therefore, much research has been focused on improving the efficiency of conventional SCR catalysts and identifying novel catalysts and systems to replace them.

In this context, we developed a new concept for removal of NO_x from the oxidative exhaust gas produced by lean-burn engines at the end of the 1980s, the so-called NO_x storage and reduction (NSR) catalyst system. This system is currently being improved and is seen as one of the most feasible and attractive solutions to this technical challenge.[7,8] The NSR catalyst system was first applied in practice for a port-injection gasoline lean-burn engine in 1994[7,9] and then improved and applied in a direct-injection gasoline lean-burn engine in 1997.[10] After we reported this innovative system, many scientists have investigated this type of catalyst, which has resulted in more than 300 published research papers to date.[11-20]

A typical NSR catalyst consists of a precious metal such as platinum (Pt), alkaline and alkaline earth metal oxides such as barium (Ba) and/or potassium (K) compounds that act as the NO_x storage material, and a metal oxide such as alumina (Al_2O_3) as the support. Under an oxidative atmosphere, the NSR catalyst first oxidizes NO to NO_2 and then stores it as nitrate ions on the NO_x storage material. Under the subsequent reductive atmosphere, stored nitrate ions are released from the storage material as NO_x and are then reduced and detoxified to N_2.[21,22] In the NSR system, a fuel-rich spike (RS) is periodically delivered to the catalyst by the engine control system, so that reducing agents such as H_2, CO, and HC contained in the RS can convert stored nitrate ions to N_2 on the NSR catalyst.[4]

Sulfur (S) poisoning and thermal aging deteriorate the catalytic activity of NSRs. Therefore, for automotive exhaust purification, catalysts with excellent activity and sufficient lifetime (resistance to poisoning) over the entire period of use are required.

This report reviews NO_x storage and reduction reactions and the technology used by the Toyota group alliance to improve the durability of NSR catalysts. Meeting the challenge to create new materials has enabled us to develop a novel solution for a sustainable environment.

2. NO_x storage and reduction reactions

2. 1 NO_x purification mechanism[21]

An NSR catalyst comprising Pt and BaO supported on Al_2O_3 (Ba/Pt/Al_2O_3 catalyst) was used for experimental investigation. The concentration of N compounds measured using a quadrupole mass spectrometer (Q-Mass) is shown as a function of reaction time in **Fig. 1**.[22] When a reaction feed gas consisting of 0.2% NO and 5% O_2 in helium (He) was fed to the catalyst as a rectangular pulse from 0 to 120 s at 573 K, NO and NO_2 were the only N compounds detected in the outlet gas. However, the total amount of NO and NO_2 in the outlet gas was less than the amount of NO in the inlet gas, which indicated that some of the NO was stored on the catalyst under such oxidative conditions. Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) revealed that NO_x stored on the Ba/Pt/Al_2O_3 catalyst was in the form of nitrate ions. During the next 120 s, pure He gas was fed to the catalyst to purge NO_x from the gas phase and flush away N compounds that were weakly adsorbed on the catalyst surface. At the beginning of this period, a small amount of NO and NO_2 were detected in the outlet gas. After the 120 s period, the feed stream consisted of 5% O_2 and 10% H_2 in He, and a large amount of N_2 was detected in the outlet gas.

The results of this and other investigations revealed that NO_x purification on NSR catalysts proceeds
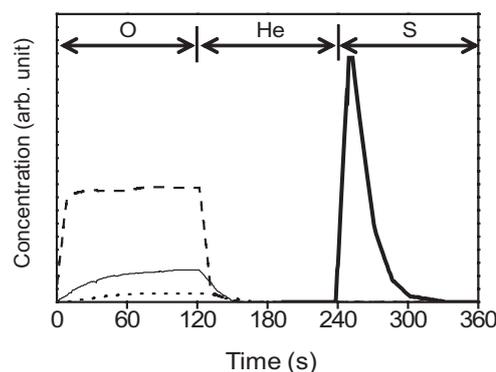
Fig. 1 Variation in N compounds on an NO_x storage and reduction catalyst: NO in the inlet gas (- - - -), NO in the outlet gas (———), NO_2 in the outlet gas (··········), and N_2 in the outlet gas (———). Catalyst: Ba/Pt/Al_2O_3; temperature: 573 K. O, He and S represent oxidizing, pure He, or stoichiometric gas flow, respectively.

according to the mechanism shown in **Fig. 2**. During NO_x storage under an oxidative atmosphere, NO is first oxidized to NO_2 over the precious metal, then combined with the storage material close to the precious metal, and finally stored as nitrate ions. During the subsequent reduction stage, stored nitrate ions are decomposed through reaction with the reducing agents and are then released from the storage material as NO_x to be eventually reduced to N_2.

2. 2 Temperature dependence of catalysis[23,24]

The change in the NO_x concentration in the outlet gas over time using a monolithic NSR catalyst consisting of an oxide support (mainly Al_2O_3), a ceria (CeO_2)-zirconia (ZrO_2)-based oxygen storage material, BaO and K_2O as NO_x storage materials, and supported Pt and rhodium (Rh) as precious metals is shown in **Fig. 3**. The reaction temperature was 523 K. Prior to the NO_x storage process, the NSR catalyst was pretreated with a simulated exhaust gas consisting of 0.62% O_2, 0.28% CO, 0.16% H_2, 90 ppm propylene (C_3H_6), 14.25% CO_2, and 5% water (H_2O) in N_2 to completely reduce and activate the precious metals and remove NO_x stored on the catalyst. The figure reveals the NO_x storage and reduction stages for the entire process. When an oxidative atmosphere consisting of 400 ppm NO, 7% O_2, 0.01% CO, 200 ppm C_3H_6, 11% CO_2, and 5% H_2O in N_2 was switched on at 0 s, the outlet NO_x concentration gradually increased with time and reached an approximately constant level around 1400 s. The difference in NO_x concentration between the inlet and outlet gases at this point could be attributed to the SCR of HC on the precious metals of the NSR catalyst.[25] The shaded area indicated by "a"

corresponds to the amount of NO_x stored on the catalyst. When a 3 s RS consisting of 400 ppm NO, 6% CO, 1.6% H_2, 1070 ppm C_3H_6, 11% CO_2, and 5% H_2O in N_2 was delivered to the catalyst, the NO_x concentration in the outlet gas transiently increased to a higher level than that in the inlet gas, rapidly decreased to nearly 0, and then gradually increased again with time to finally reach almost the same level as before the RS. Obviously, this response is closely related to the regeneration of NO_x storage sites by the reducing agents in the RS. The shaded area indicated by "b" corresponds to the amount of regenerated NO_x storage sites on the catalyst. The NO_x storage capacities indicated by the shaded areas "a" and "b" are denoted as the NO_x storage capacity and the RS-NO_x storage capacity, respectively.

Figure 4 shows the NO_x and RS-NO_x storage
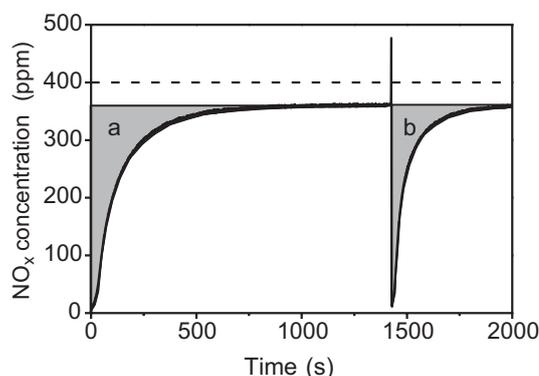
Fig. 3 NO_x concentration in the outlet and inlet gases during evaluation of NO_x storage and reduction. NO_x concentration in the outlet (——) and inlet gas (-----) at 523 K.
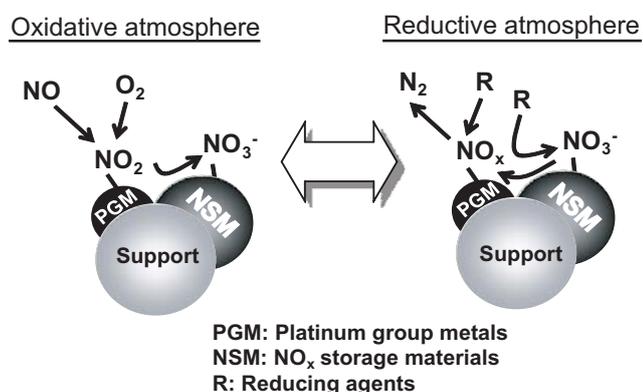
PGM: Platinum group metals
NSM: NO_x storage materials
R: Reducing agents

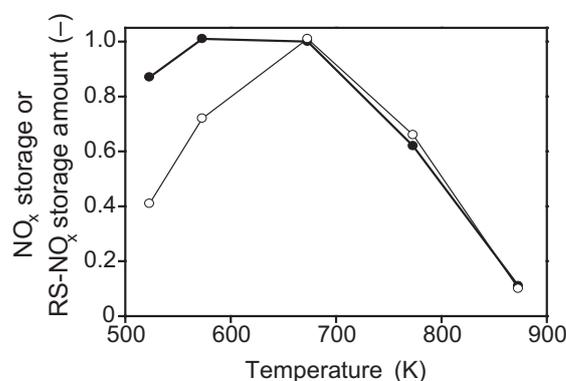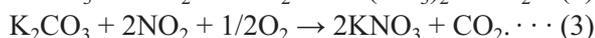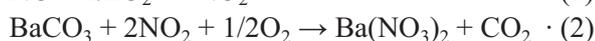**Fig. 2** NO_x purification mechanism on NSR catalysts.

Fig. 4 NO_x storage performance as a function of reaction temperature. NO_x storage capacity (●) and RS-NO_x storage capacity (○).

capacities against the reaction temperature. The NO_x storage capacity of the catalyst had maximum values at both 573 and 673 K, whereas the maximum RS-NO_x storage capacity was observed at 673 K. For temperatures greater than 673 K, the NO_x storage capacity was almost the same as the RS-NO_x storage capacity, which suggests that almost all NO_x storage sites on the catalyst are completely regenerated by a 3 s RS at >673 K. The thermodynamic equilibrium constants for the following three chemical reactions decrease with increasing reaction temperature, which indicates that the NO_2 partial pressure and nitrate formation from carbonate[25] decreased with increasing reaction temperature, as summarized in **Table 1**.

$$NO + 1/2O_2 \rightarrow NO_2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$
$$BaCO_3 + 2NO_2 + 1/2O_2 \rightarrow Ba(NO_3)_2 + CO_2 \cdot (2)$$
$$K_2CO_3 + 2NO_2 + 1/2O_2 \rightarrow 2KNO_3 + CO_2. \cdots (3)$$

This implies that the limitations due to thermodynamic equilibrium lead to a decrease in the NO_2 partial pressure and the amount of $Ba(NO_3)_2$ and KNO_3 with increasing temperature. Thus, thermodynamic limitations cause a decrease in the NO_x storage capacity at >673 K. We investigated improvement of the NO_x storage capability and nitrate stability for NSR catalysts at higher temperatures by utilizing interactions between the NO_x storage material and the support. This research revealed that an alkaline earth element added to Al_2O_3 yielded a mixed oxide with higher basicity than pure Al_2O_3 and effectively improved the storage material by stabilizing the nitrates formed, which thus enhanced the high-temperature NO_x storage capacity. Details of this research are reported elsewhere.[26]

The NO_x storage capacity at 523 K in Fig. 4 is approximately 15% less than that at 573 and 673 K. This decrease in NO_x storage capacity is assumed to be caused by inadequate catalytic activity at the lower reaction temperature. Some technical papers have reported that an increase in NO_2 partial pressure effectively enhances the NO_x storage capacity at low temperature,[18,27,28] and many investigations have focused on how to enhance NO oxidation reactions and/or NO_2 formation.[29-38]

At reaction temperatures lower than 623 K, the NO_x storage capacity on the catalyst is greater than the RS-NO_x storage capacity. The ratio of the RS-NO_x storage capacity to the NO_x storage capacity decreases with the reaction temperature, and is 72% at 573 K and 47% at 673 K. This result indicates that NO_x storage sites are not completely regenerated during the 3 s RS if the temperature is lower than 673 K. From these results, we can conclude that the reduction of stored NO_x is somewhat restricted at 673 K for the entire NO_x storage and reduction process. Further systematic investigations have revealed that the activities of the reagents used to reduce stored NO_x are different and decrease in the following order at <673 K: H_2>CO>C_3H_6. Similar results have been reported by other researchers.[39-43] In addition, our research has revealed that some of the NO_x storage sites are not regenerated, even when an excess of CO or C_3H_6 is supplied to the NSR catalyst, whereas all the NO_x storage sites could be fully regenerated when an adequate amount of H_2 was supplied.

The reduction of stored NO_3^- to N_2 progresses in two steps, as shown in Fig. 2; the release of NO_x from the nitrate and then reduction of the released NO_x to N_2 over a precious metal. It was confirmed that when CO or C_3H_6 was used as the reducing agent, the release rate of stored NO_x was the determining factor for the reduction of stored NO_x. The promotion of H_2 generation activity by certain on-board catalytic reactions, such as the water gas shift reaction and/or the steam reforming reaction, is expected to be a promising approach to improve the performance of NSR catalysts at these temperatures.

3. Deterioration of NSR function

Many systematic durability tests and analyses of NSR catalysts using actual or simulated exhaust gases have revealed that catalyst deactivation is predominantly due to thermal damage and/or sulfur poisoning.[14,21,44-46] For instance, **Fig. 5** shows the RS-NO_x storage capacity after durability tests under simulated oxidative and reductive exhaust gases alternated every

Table 1 Thermodynamic equilibrium constants for the formation of NO_2, $Ba(NO_3)_2$ and KNO_3 from 473 to 873 K.

	Temperature (K)				
	473	573	673	773	873
$K1$	2.84×10^2	21.6	3.53	0.918	0.326
$K2$	4.00×10^{12}	1.18×10^8	8.06×10^4	450	8.57
$K3$	8.54×10^{19}	3.42×10^{14}	9.48×10^{10}	2.83×10^8	3.49×10^6

$K1 = [NO_2]/([NO][O_2]^{1/2})$
$K2 = ([Ba(NO_3)_2][CO_2])/([BaCO_3][NO_2]^2[O_2]^{1/2})$
$K3 = ([KNO_3]^2[CO_2])/([K_2CO_3][NO_2]^2[O_2]^{1/2})$

30 s at 873 or 973 K for 100 min. The SO_2-aged catalysts used in these experiments were exposed to 480 and 500 ppm SO_2 under alternating oxidative and reductive atmospheres, whereas the SO_2-free-aged catalysts were not exposed to SO_2. Other components of the simulated exhaust gases for aging were 7.7% O_2, 1.43% CO, 0.47% H_2, 0.15% C_3H_6, 9.6% CO_2, and 3% H_2O in N_2 for oxidation and 4.5% CO, 1.5% H_2, 0.16% C_3H_6, 10% CO_2, and 3% H_2O in N_2 for reduction. The catalyst weight to reaction gas flow rate (W/F) was 2.0 mg min/cm^3. The NSR catalytic activity was evaluated according to the procedure described in Section 2.2, using simulated exhaust gas composed of 800 ppm NO, 6.6% O_2, 0.025% CO, 0.008% H_2, 0.02% C_3H_6, 11% CO_2, and 3% H_2O in N_2 for NO_x storage, and 11% CO_2, 5.6% CO, 1.9% H_2, 0.11% C_3H_6, 50 ppm NO, and 3% H_2O in N_2 for stored NO_x reduction. For catalysts aged at 873 K under an SO_2-free atmosphere, the NO_x storage capacity was approximately 80% of that of the fresh catalyst, whereas that of the SO_2-aged catalyst was approximately 40%, which indicates that catalyst deactivation at this temperature is mainly caused by sulfur poisoning. In contrast, after aging at 973 K, both catalysts had almost the same NO_x storage capacity, which was approximately 40% of that of the fresh catalyst, which indicates that thermal damage is the main reason for catalyst deactivation at this aging temperature. These results lead to the conclusion that sulfur poisoning is the predominant cause of NSR catalyst deterioration at lower temperature.

Thermal damage involves a decrease in the specific surface area of the support, sintering of the supported precious metals, and solid-phase reaction between the
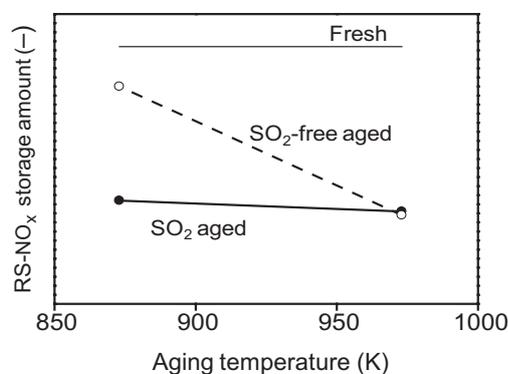

Fig. 5   Influence of aging temperature on NO_x storage and reduction.
RS-NO_x storage capacity of SO_2-aged (●) and SO_2-free-aged (○) catalysts.

NO_x storage materials and the support. These processes are generally thought to be irreversible deactivation phenomena and similar to issues observed for conventional three-way catalysts.

Sulfur poisons precious metals,[47,48] supports,[25] and NO_x storage materials.[21,47] DRIFTS, X-ray diffraction (XRD), and other analyses have revealed that adsorbed sulfur transforms NO_x storage materials from carbonates, nitrates, or oxides to sulfates, which drastically decreases the NO_x storage capacity,[21,25,47-49] because sulfates are more stable than nitrates. It has been deduced that approximately 1 mol of sulfur is emitted from an internal combustion engine when an automobile travels a distance of 100,000 km, assuming that the sulfur concentration in the gasoline fuel is 10 ppm and the fuel consumption of the automobile is 20 km/L. NSR catalysts are generally doped with less than 1 mol of NO_x storage materials; therefore, they are fully converted into bulk sulfates over a distance of several tens of thousands of kilometers if all of the sulfur emitted reacts with the NO_x storage materials. Sulfate formation on the storage material is thus a specific issue for NSR catalysts. Given these considerations, our research has focused on sulfur poisoning and thermal deterioration of NO_x storage materials, and approaches to overcome these problems are discussed in the following section.

4. Improvement in resistance to sulfur poisoning

4. 1 Strategies to solve sulfur poisoning

Sulfur poisoning of NO_x storage materials is a reversible deterioration of the material, because the sulfate formed can be decomposed to sulfur oxides (SO_x) or hydrogen sulfide (H_2S) when the temperature is increased in reductive atmospheres.[21] If an NSR catalyst is regenerated after sulfur poisoning, its NO_x storage ability can be partially restored.[44,47] The principal approach to reducing sulfur poisoning of NSR catalysts involves identifying how to accelerate sulfate decomposition with a smaller fuel consumption penalty. Our strategies to achieve this goal include smaller sulfate grain formation, hydrogen formation, a thin and homogeneous catalytic wash-coat layer, and addition of an acidic support. These concepts have already been practically applied using materials such as hematite,[50] Rh supported on ZrO_2,[25] a hexagonal monolithic substrate,[25] and titanium oxide (TiO_2),[51] respectively. Smaller particle size sulfates are more

easily decomposed than larger particles, because surface sulfates are more unstable than in the bulk. In addition, H_2 has stronger reducing ability for sulfate decomposition than CO and HC, similar to the situation for nitrate decomposition. A thin and homogeneous catalytic wash-coat layer reduces the distance for diffusion of reducing agents from the outer to the inner layer toward the cross-section direction of the catalytic converter, and increases the probability of interaction between the reducing agents and sulfates. An acidic support accelerates sulfate decomposition and the desorption rate of sulfur compounds. The effects of acidic supports and their shortcomings are described in the following subsections, using TiO_2 and related novel materials as examples.

4. 2　Effect of TiO₂ addition

The amount of sulfur deposited after durability tests has been reported to decrease with the increasing electronegativity of the support cation.[25] An acid support can destabilize the sulfates formed, because they are acidic chemical species. Nitrate is also acidic, and thus an excessive amount of acidic support decreases the NO_x storage capacity of the NSR catalyst. To balance NO_x storage and sulfur desorption, TiO_2 was selected as an additional support and used in combination with Al_2O_3 for practical application.[51] The concept was that sulfate on Al_2O_3 would be destabilized at the TiO_2-sulfate interface.

4. 3　Application of ZrO₂–TiO₂ solid solution as NSR supports[52,53]

One issue caused by TiO_2 addition during durability tests was the solid-phase reaction with K_2O. Mixed oxides formed by K_2O and TiO_2 caused a decrease in the NO_x storage capacity. We investigated the solid-phase reaction of alkaline and alkaline earth elements as NO_x storage materials with inorganic oxides as supports and found that ZrO_2 exhibited higher resistance to the formation of mixed oxides with K_2O. Therefore, we attempted to take advantage of the sulfur tolerance of TiO_2 and the solid-phase resistance of ZrO_2 and investigated different TiO_2/ZrO_2 ratios and preparation methods. We succeeded in preparing a novel Zr–Ti solid solution we named ZT and applied it as a NSR catalyst support. ZT exhibited a good balance between NO_x storage capacity, sulfur tolerance and resistance to solid-phase reaction.[53] The ZT support was synthesized by precipitation of a zirconyl nitrate $[ZrO(NO_3)_2 \cdot 2H_2O]$ and titanium chloride $(TiCl_4)$ solution neutralized with ammonia solution, followed by drying and calcination in air. The NSR catalyst was prepared by loading certain amounts of Pt, Rh, and K compounds. To evaluate ZT as the NSR catalyst support, no Al_2O_3 support material was used, and only K_2O was loaded as the NO_x storage material. The new system was compared with a TiO_2-supported catalyst. These catalyst systems are denoted as K/Pt–Rh/ZT and K/Pt–Rh/TiO_2, respectively. **Figure 6**(a) shows the amount of inactive K on sulfur-aged NSR catalysts as determined by chemical analyses. Sulfur aging was conducted at 873 K for 100 min as described in Section 3. ZT decreased the amount of inactive K due to solid-phase reaction. Figure 6(b) shows that the RS-NO_x storage capacity of the sulfur-aged K/Pt–Rh/ZT catalyst was approximately 3 times greater than that of the K/Pt–Rh/TiO_2 catalyst.
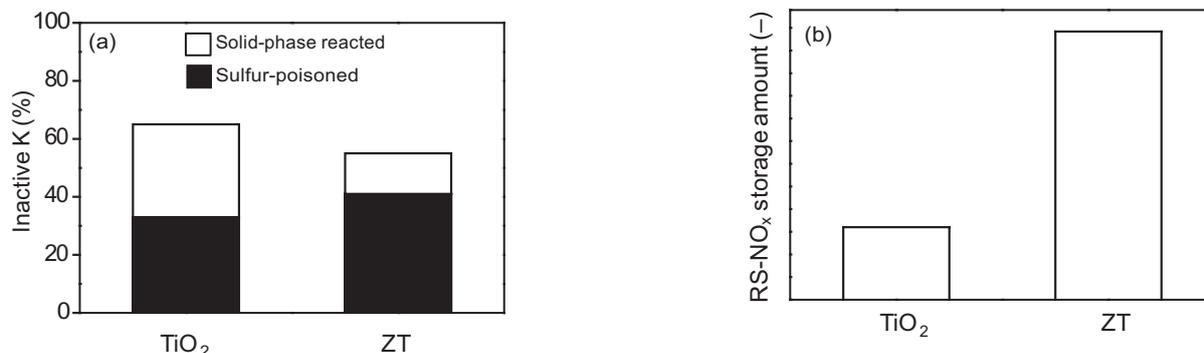

Fig. 6　Effect of TiO_2 and Zr–Ti mixed oxide support material on sulfur aging.

5. Enhancement of the NO_x storage performance at high temperature[54]

5. 1 Background and strategy for high-temperature performance

Conventional NSR catalysts for lean-burn engines are mainly operated at around 673 K,[55] because these catalysts have a maximum NO_x removal efficiency from 573 to 673 K. As shown in Fig. 4, our previous study revealed that the NO_x storage amount in a lean atmosphere was the same as the NO_x reduction amount from the subsequent RS over 673 K[24]; thus, the NSR capability above 673 K was restricted by the NO_x storage amount. In the near future, a motor vehicle with a lean-burn gasoline engine will possibly cruise on the highway at 100 km/h or faster, and thus NSR catalysts will be required to function at temperatures of 873 K or higher. Therefore, it is very important to explore a new approach to enhance the high-temperature NSR performance of catalysts in the lean phase.

Considering that the stability of stored NO_x could be increased by adopting more basic elements,[21,51] one promising approach to obtain better NO_x storage ability in the high-temperature range would involve enhancement of the basicity of the potassium NO_x storage material. It is well known that the electronic states of metals are affected and changed by interaction with the support oxides or additives in supported metal catalysts,[56-58] which suggests that the basicity of the potassium NO_x storage material could be enhanced if it was on a support with a higher basicity than γ-Al_2O_3. Mixed oxides composed of an alkaline earth metal and aluminum oxides were considered as support candidates, and the $MgAl_2O_4$ spinel was chosen as a specific example for this investigation. This research is mainly concerned with enhancement of the high-temperature NO_x storage capability at 873 K. We attempted to determine the feasibility of this approach by employing the $MgAl_2O_4$ spinel as a support material to enhance the basicity of the potassium NO_x storage material for improved NO_x storage performance at high-temperature.

5. 2 Influence of the $MgAl_2O_4$ support on high-temperature NO_x storage and NO_x storage sites

The catalysts employed in this study were K/Pt/$MgAl_2O_4$ and K/Pt/Al_2O_3, with $MgAl_2O_4$ (110 m^2/g) and γ-Al_2O_3 (150 m^2/g) supports, respectively. The catalysts were 50 mm long monolithic structures with 30 mm diameters.[51] The Pt loading was constant at 0.35g, while the potassium loading of K_2O was varied at 1.0, 2.0, and 3.3g. The NO_x storage performance was determined from the ratio of the NO_x storage amount on each catalyst to that on the fresh K/Pt/Al_2O_3 catalyst, which contained 1.0g K_2O as a reference. The NO_x storage amounts at 873 K under an oxidative atmosphere consisting of 7% O_2, 400 ppm NO, 11% CO_2, and 5% H_2O in N_2 versus the amounts of K_2O on the fresh K/Pt/$MgAl_2O_4$ (black circles) or K/Pt/Al_2O_3 (white circles) catalysts are shown in **Fig. 7**. The NO_x storage amount on both catalysts increased with the amount of K_2O. The NO_x storage amount on the K/Pt/$MgAl_2O_4$ catalyst was higher than that on the K/Pt/Al_2O_3 catalyst for all amounts of K_2O, although the difference decreased with increasing amount of K_2O.

In our previous study, the NO_x storage amount on a barium compound was negligible at 873 K, even for a fresh catalyst.[23] The Pauling electronegativities for barium and magnesium are 0.9 and 1.2, respectively; therefore, the basicity of magnesium is lower than that of barium. In addition, the magnesium in this study completely formed an oxide with alumina, whereas the barium used in the previous study was supported as a carbonate or nitrate on alumina. All catalysts had increased amounts of NO_x storage with increasing amounts of K_2O. Moreover, when the NO_x storage amounts shown in Fig. 7 were extrapolated to a zero
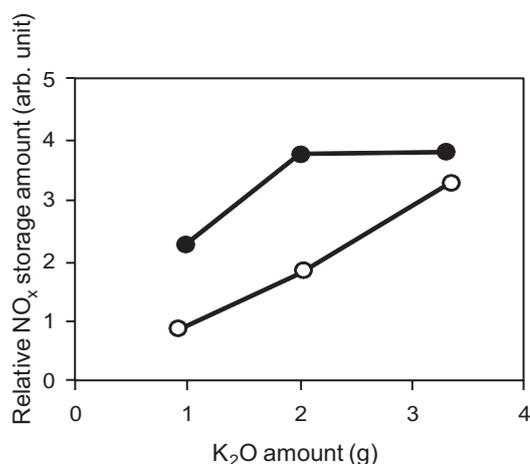
Fig. 7 NO_x storage performance of the fresh K/Pt/$MgAl_2O_4$ and K/Pt/Al_2O_3 catalysts at 873 K as a function of the K_2O loading.
K/Pt/$MgAl_2O_4$ catalyst:●, K/Pt/Al_2O_3 catalyst:○

K_2O loading, the amount of NO_x storage became negligible, which indicates that the NO_x storage sites on these catalysts are the potassium compounds.

5. 3　Influence of the $MgAl_2O_4$ support basicity on NO_x storage

CO_2 desorption patterns were measured under flowing N_2 for characterization of the basicity of the $MgAl_2O_4$ (heavy line) and γ-Al_2O_3 (thin line) supports and the results are shown in **Fig. 8**. The peak temperature for CO_2 desorption from $MgAl_2O_4$ was 450 K, whereas that for γ-Al_2O_3 was 440 K. In addition, the concentration of CO_2 desorbed from $MgAl_2O_4$ was much higher (2.5 times) than that from γ-Al_2O_3, although the BET specific surface area of the former support (110 m^2/g) was approximately 2/3 of the latter (150 m^2/g). These results indicate that the $MgAl_2O_4$ support has stronger basicity and more basic sites than the γ-Al_2O_3 support.

Figure 9 shows NO_x-temperature programmed desorption (TPD) spectra obtained for the fresh catalysts containing 2.0g K_2O under the same lean atmosphere flow used for the NO_x storage experiments. The start and end desorption temperatures of the $K/Pt/MgAl_2O_4$ catalyst were higher than those for the $K/Pt/Al_2O_3$ catalyst, and the integral of the amount of NO_x desorbed from the former catalyst (2000 μmol) was also higher than that from the latter (1060 μmol), which demonstrates that the stability of the NO_x stored on the potassium NO_x storage material was significantly enhanced by loading on the $MgAl_2O_4$ support. Therefore, the NO_x storage amount on the $K/Pt/MgAl_2O_4$ was consistently higher than that on the $K/Pt/Al_2O_3$ catalyst for the same K_2O amount, as
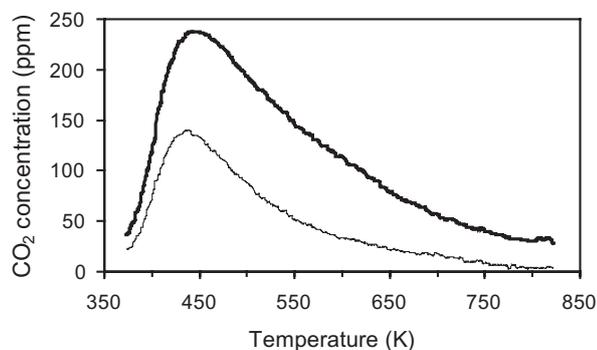
shown in Fig. 7. These results confirm the feasibility of this approach for both improvement of the stability of stored NO_x and enhancement of the NO_x storage capacity at high temperature by the addition of a basic oxide to the support material.

5. 4　Influence of the $MgAl_2O_4$ support on NO_x storage versus thermal aging

The amount of NO_x stored on the thermally aged $K/Pt/MgAl_2O_4$ (black circles) and $K/Pt/Al_2O_3$ (white circles) catalysts is shown as a function of the K_2O loading in **Fig. 10**. The catalysts were aged at 1023 K for 5 h under lean and rich feed gases composed of 6.0% O_2, 530 ppm NO, 0.025% CO, 0.2% C_3H_6, 10%
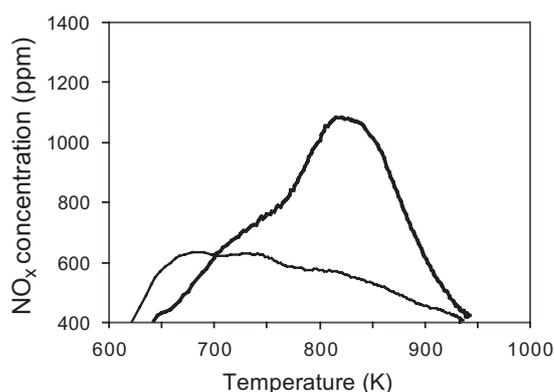
Fig. 9　NO_x-TPD spectra for fresh $K/Pt/MgAl_2O_4$ and $K/Pt/Al_2O_3$ catalysts.
$K/Pt/MgAl_2O_4$ catalysts: ▬▬ ,
$K/Pt/Al_2O_3$ catalysts: ───

Fig. 8　CO_2-TPD spectra of the $MgAl_2O_4$ and γ-Al_2O_3 supports.
$MgAl_2O_4$: ▬▬ , γ-Al_2O_3: ───
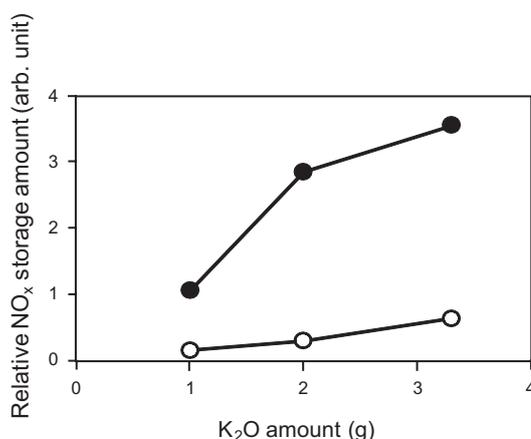
Fig. 10　NO_x storage performance at 873 K for thermally aged (1023 K, 5 h) $K/Pt/MgAl_2O_4$ and $K/Pt/Al_2O_3$ catalysts as a function of the K_2O loading.
$K/Pt/MgAl_2O_4$ catalyst:●, $K/Pt/Al_2O_3$ catalyst:○

CO_2, and 3% H_2O in N_2, and 6.0% CO, 530 ppm NO, 0.2% C_3H_6, 10% CO_2, and 3% H_2O in N_2, respectively. The amount of NO_x storage on the $K/Pt/MgAl_2O_4$ catalyst at all K_2O loadings was higher than that on the $K/Pt/Al_2O_3$ catalyst, and was the same as that for the fresh catalysts. However, in contrast to the fresh catalysts, the difference in NO_x storage between these two thermally aged catalysts increased with increased K_2O loading.

The NO_x storage residual ratios are illustrated in **Fig. 11** as a function of the K_2O loading for comparison of the thermal stability of the two catalysts. The NO_x storage residual ratio is the percentage ratio of the NO_x storage amount on the thermally aged catalyst to that on the fresh catalyst. The NO_x storage residual ratios for the $K/Pt/MgAl_2O_4$ catalyst (black circles) are consistently higher than those of the $K/Pt/Al_2O_3$ catalyst (white circles). The NO_x storage residual ratio on the $K/Pt/MgAl_2O_4$ catalyst increased with the K_2O loading, whereas that for the $K/Pt/Al_2O_3$ remained almost unchanged with increased K_2O loading. The NO_x storage residual ratio for the $K/Pt/MgAl_2O_4$ catalyst containing 3.3g K_2O was almost 100%, which indicates that this catalyst did not deteriorate as a result of the thermal aging treatment.

The NO_x-TPD spectra obtained for thermally aged catalysts containing 2.0g K_2O are shown in **Fig. 12**. As for the fresh catalysts, the start and end desorption temperatures of the $K/Pt/MgAl_2O_4$ catalyst (heavy line) were higher than those for the $K/Pt/Al_2O_3$ catalyst (thin line), and the integral of the amount of NO_x desorbed from the former catalyst (630 μmol) was also higher than that from the latter catalyst (45 μmol). The

ratio of the amount of desorbed NO_x from the thermally aged $K/Pt/MgAl_2O_4$ catalyst to that from the fresh catalyst was 53%, while it was only 7% for the $K/Pt/Al_2O_3$ catalyst. These results indicate that the durability of the $K/Pt/MgAl_2O_4$ catalyst for NO_x storage is significantly superior to that for the $K/Pt/Al_2O_3$ catalyst.

It has been reported that the NO_x storage function deteriorates when potassium reacts with the support material during durability tests,[55] which implies that the solid-phase reaction between the potassium NO_x storage material and $MgAl_2O_4$ somehow differs from that with the γ-Al_2O_3 support. Both these supports have the spinel structure; however, all of the cation sites of $MgAl_2O_4$ are occupied by Mg^{2+} or Al^{3+}, whereas approximately 11% of the cation sites of γ-Al_2O_3 are vacant. In other words, the $MgAl_2O_4$ support does not have any lattice defects and should have higher resistance to solid-phase reaction with potassium than pure γ-Al_2O_3. XRD analyses were conducted on the thermally aged catalysts, but no apparent XRD peaks were assigned to potassium compounds. The potassium compounds may be present in an amorphous state and would thus be undetected by XRD analysis. Further investigation is necessary to reveal the differences in the state of potassium on the different support materials and the influence of the $MgAl_2O_4$ support on the stability of the potassium NO_x storage material.

6. Conclusions

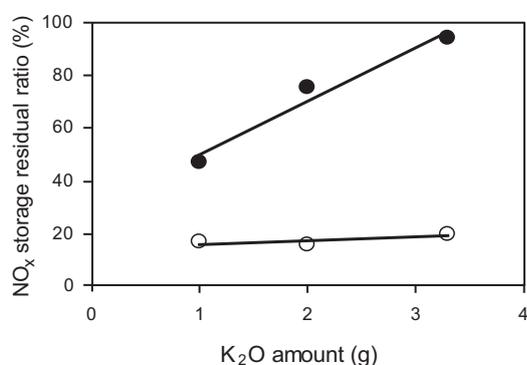This article has reviewed more than 15 years of our research efforts on the removal of NO_x emitted by

Fig. 11 NO_x storage residual ratio of the $K/Pt/MgAl_2O_4$ and $K/Pt/Al_2O_3$ catalysts at 873 K as a function of the K_2O loading.
$K/Pt/MgAl_2O_4$ catalyst:●, $K/Pt/Al_2O_3$ catalyst:○
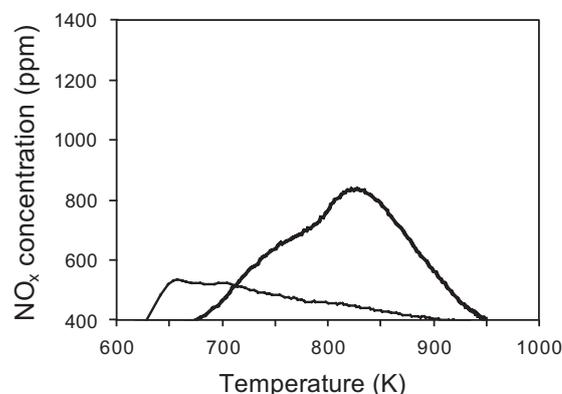
Fig. 12 NO_x-TPD spectra of the thermally aged (1023 K, 5 h) $K/Pt/MgAl_2O_4$ and $K/Pt/Al_2O_3$ catalysts.
$K/Pt/MgAl_2O_4$ catalysts: ▬▬ ,
$K/Pt/Al_2O_3$ catalysts: ——

lean-burn internal combustion engines using NSR catalysts. Some of the technologies identified from the result of reaction analyses have contributed to the design of some advanced NSR catalysts for practical application.

Engine operation conditions are dependent on the driving situation, and thus an automotive exhaust catalyst must have excellent performance over a wide range of transient temperatures, atmospheres and gas flow rates. NSR catalysts are designed to utilize the transient atmosphere conditions and principally oxidize NO to NO_2 in oxidative automotive exhaust gases and store it as nitrates under oxidative conditions. Stored nitrates are decomposed and released as NO_x when the exhaust atmosphere changes from oxidative to reductive under engine management control. The NO_x emitted is finally reduced and detoxified to N_2. This novel concept for NO_x removal was prompted by careful monitoring of emissions, and the NO_x removal observed during the emission test mode was better than that expected from that under steady lean conditions. We propose that such an innovative design could not have been achieved in laboratory experiments or by computer simulations. This highlights the importance of making observations under realistic conditions to overcome the difficulty of NO_x removal under oxidative conditions.

Since the first practical application of an NSR catalyst, our investigations have been aimed at improvement of the catalyst and the identification of guiding principles for the design of more advanced NSR catalysts, as described here; for instance, utilizing novel ZrO_2-TiO_2 $MgAl_2O_4$ as supports.

In addition to the regulation of NO_x, CO and HC emissions, laws on CO_2 emission or fuel consumption has been initiated in many countries. In principle, automotive catalysts cannot directly reduce CO_2 emission; however, they can indirectly contribute to solving this problem via pollutant purification for fuel-efficient cars. Further research and development of NO_x removal technology for lean-burn exhaust represents a promising strategy to increase sustainability.

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