Improvement of Catalysts for NO\textsubscript{x} Storage and Reduction for Gasoline-fueled Automotive Exhaust

Naoki Takahashi* and Haruo Imagawa
Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, JAPAN

(Received January 7, 2009)

Catalysts for nitrogen oxide (NO\textsubscript{x}) storage and reduction oxidize nitrogen monoxide (NO) emitted from automotive lean-burn engines to nitrogen dioxide (NO\textsubscript{2}) that is then stored on doped NO\textsubscript{x} storage materials such as barium and/or potassium compounds as nitrate ions (NO\textsubscript{3}\textsuperscript{-}). In a reducing atmosphere provided by a suitable engine management system, the nitrates formed are subsequently reduced and decomposed into NO\textsubscript{x} via reactions between reducing agents in the exhaust gas such as hydrogen, carbon monoxide and hydrocarbons. The emitted NO\textsubscript{x} is finally reduced and detoxified to nitrogen. To meet stringent emission regulations for automotive exhaust pollutants, NO\textsubscript{x} storage and reduction catalysts must have excellent NO\textsubscript{x} removal activity and an extremely long lifetime. These catalysts can deteriorate not only due to thermal stress, but also to sulfur poisoning. Thermal stress causes a decrease in the number of active sites through sintering of precious metals, decreases the specific surface area of the support and leads to solid-phase reaction between the NO\textsubscript{x} storage material and the support. Sulfur is present in exhaust gas derived from gasoline fuel and it competes with NO\textsubscript{x} for storage and reacts with the doped NO\textsubscript{x} storage material to form sulfates. Once NO\textsubscript{x} storage materials are sulfated, they drastically lose their NO\textsubscript{x} storage capability. This report reviews the technologies used to overcome these issues and to improve the durability of NO\textsubscript{x} storage and reduction catalysts against both thermal damage and sulfur poisoning. An advanced novel catalyst system for NO\textsubscript{x} removal with synergistic NO\textsubscript{x} storage and reduction with ammonia (NH\textsubscript{3}) functions is also described.

Keywords
Automotive catalyst, NO\textsubscript{x} storage and reduction, Lean burn engine, Sulfur poisoning, Thermal deterioration

1. Introduction

A decrease in carbon dioxide (CO\textsubscript{2}) emissions from automobiles is urgently required to prevent global warming. Meanwhile, 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 because of its remarkable potential to improve 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 cannot fully detoxify nitrogen oxides (NO\textsubscript{x}) under excess oxygen conditions, although they exhibit excellent catalytic activity for the removal of carbon monoxide (CO) and hydrocarbons (HC). 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\textsubscript{x}, the generic term for nitrogen monoxide (NO) and nitrogen dioxide (NO\textsubscript{2}), into nitrogen (N\textsubscript{2}) is ideal and thermodynamically favorable. However, excess oxygen (O\textsubscript{2}) competes with NO\textsubscript{x} for adsorption on catalyst active sites and inhibits direct decomposition reactions of NO\textsubscript{x}. Therefore, reducing agents such as hydrogen (H\textsubscript{2}), CO and HC are required to remove adsorbed oxygen from active sites on the catalyst surface. Catalysts with the ability to reduce NO\textsubscript{x} to N\textsubscript{2} by reaction with reducing agents in an oxidative atmosphere are called selective catalytic NO\textsubscript{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)\textsuperscript{1–3}, alumina\textsuperscript{4}, base metals supported on alumina\textsuperscript{5}, and precious metals supported on zeolites\textsuperscript{6}. From the point of view of practical use, these catalysts still have many problems. For example, not all SCR catalysts can completely remove NO\textsubscript{x} under all oxidative atmospheres. Thus, SCR catalysts are not sufficiently reliable for actual utilization to achieve zero-pollutant-emission cars without additional methods such as addition of urea as a NO\textsubscript{x} reducing agent. Such additional equipment increases not only the capi-

* To whom correspondence should be addressed.
* E-mail: e0790@mosk.tytlabs.co.jp
nal cost, but also the operation costs of an exhaust purification system. Therefore, researchers have focused much attention on improving the efficiency of conventional SCR catalysts and identifying novel catalysts and systems to replace SCR catalysts.

In this context, at the end of the 1980s we developed a new concept to remove NOx from oxidative exhaust gas from lean-burn engines, the so-called NOx storage and reduction (NSR) catalyst system. The system is currently being improved as one of the most feasible and attractive solutions to this technical challenge7,8). The NSR catalyst system was first applied in practice for a port-injection gasoline lean-burn engine in 19947,9), and then improved and applied for a direct-injection gasoline lean-burn engine in 199710). After this innovative information was reported by our research group, many scientists have investigated this type of catalyst and more than 300 research papers have been published since then11). 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, which act as the NOx storage material, and a metal oxide such as alumina (Al2O3) as the support. Under an oxidative atmosphere, an NSR catalyst first oxidizes NO to NO2 and then stores it as nitrate ions on the NOx storage material. Under the subsequent reductive atmosphere, stored nitrate ions are released from the storage material as NOx and are then reduced and detoxified to N221),22). In the NSR system, a fuel-rich spike (RS) is periodically delivered to the catalyst by the engine control system, and reducing agents such as H2, CO and HC contained in the RS convert stored nitrate ions to N2 on the NSR catalyst4).

Sulfur (S) poisoning and thermal aging deteriorate the NSR catalytic activity. For automotive exhaust purification, catalysts with excellent activity and a sufficient lifetime over the whole usage period are required.

This report reviews NOx storage and reduction reactions and the technology used by the Toyota group alliance to improve the durability of NSR catalysts and to design an advanced novel catalyst system for NOx removal with the NSR function. Meeting the challenge to create new materials or add functions based on analyses of the state and reactions of the NSR catalyst has enabled us to develop advanced new catalyst systems.

2. NOx Storage and Reduction Reactions

2.1. NOx Purification Mechanism23)

An NSR catalyst comprising Pt and BaO supported on Al2O3 (Ba/Pt/Al2O3 catalyst) was used for experiments. The concentration of N compounds measured using a quadrupole mass spectrometer (Q-Mass) is shown as a function of reaction time in Fig. 122). When reaction gas consisting of 0.2% NO and 5% O2 in helium (He) was fed to the catalyst as a rectangular pulse from 0 to 120 s at 573 K, NO and NO2 were the only N compounds detected in the outlet gas. However, the total amount of NO and NO2 in the outlet gas was less than the amount of NO in the inlet gas. Some of the NO was expected to be stored on the catalyst under these oxidative conditions. Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) revealed that NOx stored on the Ba/Pt/Al2O3 catalyst was in the form of nitrate ions. During the next 120 s, pure He gas was fed to the catalyst to purge NOx from the gas phase and flush away N compounds weakly adsorbed on the catalyst surface. At the beginning of this period, a small amount of NO and NO2 were detected in the outlet gas. After the 120-s period, the feed stream consisted of 5% O2 and 10% H2 in He and a large amount of N2 was detected in the outlet gas. The results of this and other investigations revealed that NOx purification on NSR catalysts proceeds according to the mechanism shown in Fig. 2. During NOx storage under an oxidative atmosphere, NO is first oxidized to NO2 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 decompose through reaction with the reducing agents and are released from the storage material as NOx, and are eventually reduced to N2.

2.2. Temperature Property23),24)

Figure 3 shows the evolution of NOx concentration in the outlet gas over time on a monolithic NSR catalyst consisting of an oxide support (mainly Al2O3), a ceria (CeO2)-zirconia (ZrO2)-based oxygen storage material, BaO and K2O as the NOx storage materials, and supported Pt and rhodium (Rh) as precious metals. The
reaction temperature was 523 K. Prior to the NO\textsubscript{x} storage process, the NSR catalyst was pretreated with simulated exhaust gas consisting of 0.62% O\textsubscript{2}, 0.28% CO, 0.16% H\textsubscript{2}, 90 ppm propylene (C\textsubscript{3}H\textsubscript{6}), 14.25% CO\textsubscript{2} and 5% water (H\textsubscript{2}O) in N\textsubscript{2} to completely reduce and activate the precious metals and remove NO\textsubscript{x} stored on the catalyst. The figure reveals the NO\textsubscript{x} storage and reduction stages for the entire process. When an oxidative atmosphere consisting of 400 ppm NO, 7% O\textsubscript{2}, 0.01% CO, 200 ppm C\textsubscript{3}H\textsubscript{6}, 11% CO\textsubscript{2} and 5% H\textsubscript{2}O in N\textsubscript{2} was switched on at 0 s, the outlet NO\textsubscript{x} concentration gradually increased with time and reached an approximately constant level around 1400 s. The difference in NO\textsubscript{x} concentration between the inlet and outlet gases at this point could be attributed to SCR of HC on the precious metals of the NSR catalyst.25) The shaded area “a” relates to the amount of NO\textsubscript{x} stored on the catalyst. When a 3-s RS consisting of 400 ppm NO, 6% CO, 1.6% H\textsubscript{2}, 1070 ppm C\textsubscript{3}H\textsubscript{6}, 11% CO\textsubscript{2} and 5% H\textsubscript{2}O in N\textsubscript{2} was delivered to the catalyst, the NO\textsubscript{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 and finally reached almost the same level as before the RS. Obviously, this is closely related to the regeneration of NO\textsubscript{x} storage sites by the reducing agents in the RS. The shaded area “b” relates to the amount of regenerated NO\textsubscript{x} storage sites on the catalyst. The NO\textsubscript{x} storage capacity indicated by shaded areas “a” and “b” is denoted as the NO\textsubscript{x} storage capacity and RS-NO\textsubscript{x} storage capacity, respectively.

Figure 4 plots the NO\textsubscript{x} and RS-NO\textsubscript{x} storage capacities against the reaction temperature. The NO\textsubscript{x} storage capacity of the catalyst showed a maximum value at both 573 and 673 K, whereas the maximum RS-NO\textsubscript{x} storage capacity was observed at 673 K. For temperatures greater than 673 K, the NO\textsubscript{x} storage capacity was nearly the same as the RS-NO\textsubscript{x} storage capacity. This suggests that NO\textsubscript{x} storage sites on the catalyst are nearly completely regenerated by a 3-s RS at $>$673 K. The thermodynamic equilibrium constant for the following three chemical reactions decrease with increasing reaction temperature, indicating that the NO\textsubscript{2} partial pressure and nitrate formation from carbonate decreased with increasing temperature.

\begin{align*}
\text{NO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{NO}_2 \\
\text{BaCO}_3 + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 & \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2 \\
2\text{K}_2\text{CO}_3 + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 & \rightarrow 2\text{KNO}_2 + \text{CO}_2
\end{align*}

These calculations imply that the limitations due to thermodynamic equilibrium lead to decreases in the NO\textsubscript{2} partial pressure and the amount of Ba(NO\textsubscript{3})\textsubscript{2} and KNO\textsubscript{2} with increasing temperature. Thus, thermodynamic limitations cause a decrease in the NO\textsubscript{x} storage capacity at $>$673 K. We investigated how to improve the NO\textsubscript{x} storage capability and the nitrate stability for NSR catalysts at higher temperature by utilizing interaction between the NO\textsubscript{x} storage material and the sup-
The NO\textsubscript{2} storage capacity at 523 K in Fig. 4 is approximately 15\% less than that at 573 and 673 K. This decrease in NO\textsubscript{2} storage capacity is assumed to be caused by inadequate catalytic activity at lower reaction temperatures. Some technical papers reported that an increase in NO\textsubscript{2} partial pressure effectively enhances the NO\textsubscript{2} storage capacity at low temperature\textsuperscript{19,27,28} and many studies have investigated how to enhance NO\textsubscript{2} oxidation reactions and/or NO\textsubscript{2} formation\textsuperscript{29,30}. At reaction temperatures lower than 623 K, the NO\textsubscript{2} storage capacity on the catalyst is greater than the RS-NO\textsubscript{2} storage capacity. The ratio of the RS-NO\textsubscript{2} storage capacity to the NO\textsubscript{2} storage capacity decreases with the reaction temperature, and is 72\% at 573 K and 47\% at 523 K. This result indicates that NO\textsubscript{2} 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\textsubscript{2} is somewhat restricted at 673 K for the entire NO\textsubscript{2} storage and reduction process. Further systematic investigations revealed that the activities of the agents used to reduce stored NO\textsubscript{2} are different and decrease in the following order at <673 K: H\textsubscript{2} > CO > C\textsubscript{3}H\textsubscript{6}. Similar results were reported out by other researchers\textsuperscript{31-33}. In addition, our research revealed that some of the NO\textsubscript{2} storage sites were not regenerated even when an excess of CO or C\textsubscript{3}H\textsubscript{6} was supplied to the NSR catalysts, whereas all the NO\textsubscript{2} storage sites could be fully regenerated when adequate H\textsubscript{2} was supplied. As shown in Fig. 2, the reduction of stored NO\textsubscript{2} to N\textsubscript{2} progresses in two steps: the first is release of NO\textsubscript{2} from nitrate and the second is reduction of the released NO\textsubscript{2} to N\textsubscript{2} over a precious metal. It was confirmed that when CO or C\textsubscript{3}H\textsubscript{6} was used as the reducing agent, the release rate of stored NO\textsubscript{2} was the determining factor for the reduction of stored NO\textsubscript{2}. The promotion of H\textsubscript{2} generation activity by some 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.

### Table 1

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>RS-NO\textsubscript{2} storage amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>93 %</td>
</tr>
<tr>
<td>573</td>
<td>87 %</td>
</tr>
<tr>
<td>673</td>
<td>80 %</td>
</tr>
<tr>
<td>773</td>
<td>71 %</td>
</tr>
<tr>
<td>873</td>
<td>57 %</td>
</tr>
</tbody>
</table>

RS-NO\textsubscript{2} storage capacity of SO\textsubscript{2}-aged (○) and SO\textsubscript{2}-free-aged (●) catalysts.

---

3. Deterioration of NSR Function

Many systematic durability tests and analyses on NSR catalysts using actual or simulated exhaust gases revealed that catalyst deactivation is predominantly due to thermal damage and/or sulfur poisoning\textsuperscript{14,21,44-46}. For instance, Fig. 5 shows the RS-NO\textsubscript{2} storage capacity after durability tests under simulated oxidative and reductive exhaust gases alternated every 30 s at 873 or 973 K for 100 min. The SO\textsubscript{2} aged catalysts used in these experiments were exposed to 480 and 500 ppm SO\textsubscript{2} under alternating oxidative and reductive atmospheres, whereas the SO\textsubscript{2}-free aged catalysts were never exposed to SO\textsubscript{2}. Other components of the simulated exhaust gases for aging were 7.7\% O\textsubscript{2}, 1.43\% CO, 0.47\% H\textsubscript{2}, 0.15\% C\textsubscript{3}H\textsubscript{6}, 9.6\% CO\textsubscript{2} and 3\% H\textsubscript{2}O in N\textsubscript{2} for oxidation and 4.5\% CO, 1.5\% H\textsubscript{2}, 0.16\% C\textsubscript{3}H\textsubscript{6}, 10\% CO\textsubscript{2} and 3\% H\textsubscript{2}O in N\textsubscript{2} for reduction. The catalyst weight to reaction gas flow rate (W/F) was 2.0 mg min/cm\textsuperscript{3}. The NSR catalytic activity was evaluated according to the procedure described in Section 2, using simulated exhaust gas composed of 800 ppm NO, 6.6\% O\textsubscript{2}, 0.025\% CO, 0.008\% H\textsubscript{2}, 0.02\% C\textsubscript{3}H\textsubscript{6}, 11\% CO\textsubscript{2} and 3\% H\textsubscript{2}O in N\textsubscript{2} for NO\textsubscript{2} storage, and 11\% CO\textsubscript{2}, 5.6\% CO, 1.9\% H\textsubscript{2}, 0.11\% C\textsubscript{3}H\textsubscript{6}, 50 ppm NO and 3\% H\textsubscript{2}O in N\textsubscript{2} for stored NO\textsubscript{2} reduction. For catalysts aged at 873 K under an SO\textsubscript{2}-free atmosphere, the NO\textsubscript{2} storage capacity was approximately 80\% of that of the fresh catalyst, whereas that of the SO\textsubscript{2} aged catalyst was approximately 40\%. This result means that catalyst deactivation at this temperature was mainly caused by sulfur poisoning. In contrast, after aging at 973 K,
both catalysts had almost the same NO\(_x\) storage capacity that was approximately 40% of that of the fresh catalyst. Thus, thermal damage was the main reason for catalyst deactivation at this aging temperature. These results lead to conclusion that the influence of sulfur poisoning on NSR catalyst deterioration was predominant on aging at lower temperature.

Thermal damage involved a decrease in the specific surface area of the support, sintering of the supported precious metals, and solid-phase reaction between the NO\(_x\) storage materials and the support. These were 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 and then the NO\(_x\) storage capacity drastically decreases\(^{21,25,47~49}\) because sulfates are more stable than nitrates. It can be deduced that approximately 1 mol of sulfur is emitted from an internal combustion engine when an automobile travels a distance of 100,000 km if it is assumed that the sulfur concentration in gasoline fuel is 10 ppm and the fuel consumption of the automobile is 20 km/l. In general, NSR catalysts are doped with less than 1 mol of NO\(_x\) storage materials; this is therefore fully converted into bulk sulfates over a distance of several tens of thousand km if all of the sulfur emitted reacts with the NO\(_x\) storage materials. Sulfate formation on the storage material is a specific issue for NSR catalysts. Thus, our research focused on sulfur poisoning of NO\(_x\) storage materials and approaches to overcome this problem are discussed in the next section.

4. Improvement in Sulfur Durability

4.1. Strategy to Solve Sulfur Poisoning

Sulfur poisoning of NO\(_x\) storage materials is reversible deterioration because the sulfate formed can decompose to sulfur oxides (SO\(_x\)) or hydrogen sulfide (H\(_2\)S) when the temperature increases in reductive atmospheres\(^{25}\). If an NSR catalyst is regenerated after sulfur poisoning, its NO\(_x\) storage ability can be partially restored\(^{44,47}\). The principal approach to reduce sulfur poisoning of NSR catalysts is identifying how to accelerate sulfate decomposition with a smaller fuel consumption penalty. Our strategies to achieve this include smaller sulfate grain formation, hydrogen formation, a thin and homogeneous catalytic washcoat layer, and addition of an acidic support. These concepts have already been applied in practice using materials such as hematite\(^{50}\), Rh supported on ZrO\(_2\)\(^{25}\), a hexagonal monolithic substrate\(^{25}\) and titanium oxide (TiO\(_2\))\(^{51}\), respectively. Sulfates of smaller particle size are more easily decomposed than larger particles because surface sulfates might be more unstable than in the bulk. 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 washcoat layer reduces the diffusion distance 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 TiO\(_2\) Addition

It has been reported that the amount of sulfur deposited after durability tests decreased with 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\(_2\)O\(_3\) for practical application\(^{25}\). The theory was that sulfate on Al\(_2\)O\(_3\) would be destabilized at the TiO\(_2\)-sulfate interface.

4.3. Application of ZrO\(_2\)-TiO\(_2\) Solid Solution as NSR Support\(^{21,52}\)

One issue caused by TiO\(_2\) addition was solid-phase reaction with K\(_2\)O during durability tests. Mixed oxides formed by K\(_2\)O and TiO\(_2\) caused a decrease in 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\(_2\)O. Thus, we tried 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 finally succeeded in preparing a novel Zr-Ti solid solution we called ZT and used it as the NSR catalyst support. ZT exhibited a good balance between NO\(_x\) storage capacity and sulfur tolerance and solid-phase resistance\(^{52}\). The ZT support was synthesized by precipitation of zirconyl nitrate [Zr(NO\(_3\))\(_2\)-2H\(_2\)O] 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, Al\(_2\)O\(_3\) was not used and only K\(_2\)O was loaded as the NO\(_x\) storage material and compared with a TiO\(_2\)-supported catalyst. Hereafter, these catalysts are denoted as K/Pr-Rh/ZT and K/Pr-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\textsubscript{x} storage capacity of the sulfur-aged K/Pt-Rh/ZT catalyst was approximately three-fold greater than that of the K/Pt-Rh/TiO\textsubscript{2} catalyst. However, the amount of sulfur poisoning was slightly greater on K/Pt-Rh/ZT than on K/Pt-Rh/TiO\textsubscript{2}. To design more advanced NSR catalysts, an improvement in the sulfur resistance of ZT is required, as discussed in the subsection paragraph.

4.4. Application of Al\textsubscript{2}O\textsubscript{3}-ZT Nanocomposite for Sulfur Resistance\textsuperscript{54,55}

In the case of TiO\textsubscript{2} addition, smaller TiO\textsubscript{2} grains on the Al\textsubscript{2}O\textsubscript{3} support accelerated sulfur desorption compared to larger grains because sulfates at the interface between Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} particles are affected and destabilized by the TiO\textsubscript{2} acidity\textsuperscript{53}. A similar effect could be anticipated for ZT. It was thus expected that the key point to improving the sulfur resistance of ZT would be to increase the interface between Al\textsubscript{2}O\textsubscript{3} and ZT grains. In addition, it was clearly observed on a thin-film structured model catalyst that sulfate close to Pt particles decomposed more easily than sulfate at a distance from Pt\textsuperscript{56}, because activated reducing agents on Pt such as hydrogen atoms must spill over from Pt to the surrounding sulfate through the Pt-sulfate interface. Similar data were obtained for a powdery catalyst.

Figures 7 (a) and 7 (b) show transmission electron microscope (TEM) images of sulfur-aged catalysts with aging carried out under oxidative conditions and alternating oxidative and reductive conditions, respectively. The dotted circles indicate the location of Pt particles and the solid circles indicate the spots analyzed. The composition was analyzed using an energy-dispersive X-ray analyzer (EDX) coupled to the TEM. The S/Ba molar ratio for each spot is plotted in Fig. 7 (c) against distance from Pt. When the catalyst was aged under oxidative conditions, the S/Ba molar ratio was almost the same regardless of distance from Pt. In contrast, the ratio was proportional to distance from Pt for the catalyst aged under fluctuating oxidative and reductive conditions. From these results, it could be expected that material with a large Al\textsubscript{2}O\textsubscript{3}-ZT interface, as shown on the left in Fig. 8, improves the sulfur tolerance of the NSR catalyst. This novel nanocomposite material composed of Al\textsubscript{2}O\textsubscript{3} and ZT was named AZT. An AZT support was synthesized by precipitation of aluminum nitrate nonahydrate [Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O], zirconium oxy-nitrate dihydrate [ZrO(NO\textsubscript{3})\textsubscript{2}·2H\textsubscript{2}O] and titanium chloride (TiCl\textsubscript{4}) solution neutralized with ammonia solution, followed by drying and calcination in air. A support was prepared for comparison by physically mixing pure Al\textsubscript{2}O\textsubscript{3} and ZT, defined as physically mixed Al\textsubscript{2}O\textsubscript{3}-ZT. Both materials were composed of 50 wt% Al\textsubscript{2}O\textsubscript{3}, 35 wt% ZrO\textsubscript{2} and 15 wt% TiO\textsubscript{2}. Figures 9 (a) and 9 (b) show TEM images of the AZT and physically mixed Al\textsubscript{2}O\textsubscript{3}-ZT supports, respectively. They reveal
that \( \text{Al}_2\text{O}_3 \) and primary ZT particles in the AZT support were beside each other, whereas \( \text{Al}_2\text{O}_3 \) and ZT in physically mixed \( \text{Al}_2\text{O}_3 \)-ZT exhibited secondary particle mixing (EDX results). Therefore, it could be concluded that AZT has a nanocomposite structure of \( \text{Al}_2\text{O}_3 \) and primary ZT particles, as shown on the left of Fig. 8.

The acid and base properties of AZT and \( \text{Al}_2\text{O}_3 \)-ZT supports were evaluated using temperature-programmed \( \text{NH}_3 \) (NH\textsubscript{3}-TPD) and \( \text{CO}_2 \) (CO\textsubscript{2}-TPD) desorption. Figure 10 (a) shows profiles of \( \text{NH}_3 \) desorption with temperature. \( \text{NH}_3 \) desorption on the AZT support from 375 to 650 K was slightly less than that on the \( \text{Al}_2\text{O}_3 \)-ZT support. However, as shown in Fig. 10 (c), the total amount of \( \text{NH}_3 \) desorption per unit weight of support was almost the same for both supports. As shown in Fig. 10 (b), \( \text{CO}_2 \) desorption from AZT was substantially different to that from \( \text{Al}_2\text{O}_3 \)-ZT support. \( \text{CO}_2 \) desorption from AZT was complete at 450 K and the total amount of \( \text{CO}_2 \) desorbed was approximately one-fifth of that desorbed from \( \text{Al}_2\text{O}_3 \)-ZT (Fig. 10 (c)). A previous study\textsuperscript{52} revealed that ZT released negligible amounts of \( \text{CO}_2 \) under the same CO\textsubscript{2}-TPD conditions as used here. Thus, almost all \( \text{CO}_2 \) desorbed from AZT-ZT must be derived from \( \text{Al}_2\text{O}_3 \) particles. In contrast, \( \text{Al}_2\text{O}_3 \) particles in the AZT support have a negligible number of basic sites. Some of the Zr and/or Ti certainly formed complex oxides with \( \text{Al}_2\text{O}_3 \) during precipitation and/or calcination of the precipitated material, and basic sites on \( \text{Al}_2\text{O}_3 \) particles must be neutralized by deposited Zr and/or Ti. Further investigation is required to confirm this hypothesis. Nevertheless, it can be concluded that AZT was more acidic than \( \text{Al}_2\text{O}_3 \)-ZT and an improvement in the sulfur resistance of NSR catalysts on an AZT support can be expected.

\( \text{Ba}^+\text{-K}/\text{Pt-Rh}/\text{AZT} \) and \( \text{Ba}^+\text{-K}/\text{Pt-Rh}/\text{Al}_2\text{O}_3 \)-ZT catalysts were prepared by impregnating certain amounts of precious metals and NO\textsubscript{x} storage materials on AZT and \( \text{Al}_2\text{O}_3 \)-ZT supports, respectively. Both catalysts were exposed to an oxidative atmosphere containing \( \text{SO}_2 \) that consisted of 400 ppm \( \text{SO}_2 \), 6.6% \( \text{O}_2 \) and 3% \( \text{H}_2\text{O} \) in \( \text{N}_2 \) at 823, 873 or 923 K for 100 min. Then the catalysts were exposed 6.6% \( \text{O}_2 \) and 3% \( \text{H}_2\text{O} \) in \( \text{N}_2 \) at the same temperature as for \( \text{SO}_2 \) exposure until the \( \text{SO}_2 \) concentration in the outlet gas decreased to zero. The gas flow was then switched to a reductive atmosphere that consisted of 1.0% \( \text{C}_3\text{H}_6 \), 5.6% \( \text{CO} \), 1.9% \( \text{H}_2 \), 50 ppm \( \text{NO} \), 11% \( \text{CO}_2 \) and 3% \( \text{H}_2\text{O} \) in \( \text{N}_2 \). The amount of sulfur desorbed in 200 s after the gas flow was switched was quantified using a flame photometric detector (FPD). An example of a sulfur desorption profile is shown in Fig. 11 (a). The total sulfur desorption values are shown in Fig. 11 (b). Sulfur desorption from \( \text{Ba}^+\text{-K}/\text{Pt-Rh}/\text{AZT} \) for all temperatures investigated was greater than that from \( \text{Ba}^+\text{-K}/\text{Pt-Rh}/\text{Al}_2\text{O}_3 \)-ZT.

The RS-NO\textsubscript{x} storage capacity of sulfur-aged \( \text{Ba}^+\text{-K}/\text{Pt-Rh}/\text{AZT} \) and \( \text{Ba}^+\text{-K}/\text{Pt-Rh}/\text{Al}_2\text{O}_3 \)-ZT catalysts was evaluated. This aging and measurement of the RS-NO\textsubscript{x} storage capacity were carried out as described in Section 3. The RS-NO\textsubscript{x} storage capacity as a function of reaction temperature is summarized in Fig. 12. We
observed that the RS-NO\textsubscript{x} storage capacity of Ba–K/Pt–Rh/AZT was approximately 1.5-fold greater than that of Ba–K/Pt–Rh/Al\textsubscript{2}O\textsubscript{3}–ZT from 673 to 873 K. It can be assumed that the better RS-NO\textsubscript{x} storage capacity of sulfur-aged Ba–K/Pt–Rh/AZT can be attributed to the higher sulfur tolerance of AZT than that of the Al\textsubscript{2}O\textsubscript{3}–ZT support. AZT nanocomposite material indeed exhibited larger contact surface points between Al\textsubscript{2}O\textsubscript{3} and ZT than the physically mixed Al\textsubscript{2}O\textsubscript{3}–ZT powder, as shown in the TEM images of Fig. 9. At these contact surface points, sulfated NO\textsubscript{x} storage materials (BaSO\textsubscript{4}, K\textsubscript{2}SO\textsubscript{4}) should effectively decompose on interaction with the precious metals (Pt, Rh) and the acidic support (ZT) and then recover their NO\textsubscript{x} storage capacity. Therefore, the nanocomposite structure of AZT promoted the decomposition of K and Ba sulfates under reducing conditions.

The above observation prompted us to further improve the sulfur tolerance of NSR catalysts by enrichment of TiO\textsubscript{2} or ZrO\textsubscript{2} on the surface of the AZT support. To achieve this, Ti compound doping of the AZT surface was carried out to yield a novel material we denote as t-AZT that led to a further improvement in the sulfur tolerance of the NSR catalyst\textsuperscript{57}).

5. Synergistic Effect of NH\textsubscript{3} Storage and NH\textsubscript{3}-SCR\textsuperscript{58)}

A further advanced catalytic system for NO\textsubscript{x} removal consisting of Pd/Al\textsubscript{2}O\textsubscript{3}, Ba/Pt–Rh/Al\textsubscript{2}O\textsubscript{3} and Cu/ZSM-5 catalysts using the NSR function as core technology is discussed in this section. The originally intended functions of these catalysts were Pd/Al\textsubscript{2}O\textsubscript{3} for NO oxidation to NO\textsubscript{2}, Ba/Pt–Rh/Al\textsubscript{2}O\textsubscript{3} for NO\textsubscript{x} storage and reduction, and Cu/ZSM-5 for HC-SCR. Pelletized
Pd, Ba/Pt-Rh and Cu/Z denote Pd/Al\(_2\)O\(_3\), Ba/Pt-Rh/Al\(_2\)O\(_3\) and Cu/ZSM-5, respectively.

Fig. 13 Effect of Cu/ZSM-5 Catalyst Addition Downstream of the Pd + Ba/Pt-Rh Catalyst on NO\(_x\) Removal under Oxidative Conditions

2.4 wt\% Pd/Al\(_2\)O\(_3\), 18.3 wt\% Ba/1.3 wt\% Pt-0.13 wt\% Rh/Al\(_2\)O\(_3\) and 5 wt\% Cu/ZSM-5 (Si/Al = 40) were placed in this order in the reaction tube from upstream to downstream, denoted as the Pd + Ba/Pt-Rh + Cu/Z catalyst system. A sample for comparison consisted of Pd/Al\(_2\)O\(_3\) and Ba/Pt-Rh/Al\(_2\)O\(_3\) catalysts and is denoted as the Pd + Ba/Pt-Rh catalyst system. NO\(_x\) conversion by these catalyst systems was evaluated for oxidative (230 ppm NO, 6.5\% O\(_2\), 9.6\% CO\(_2\) and 3\% H\(_2\)O in N\(_2\)) and reductive (230 ppm NO, 0.4\% O\(_2\), 1.2\% C\(_3\)H\(_6\), 9.6\% CO\(_2\) and 3\% H\(_2\)O in N\(_2\)) simulated exhaust gases that were alternated every 3 min. Figure 13 shows the average NO\(_x\) conversion during the oxidative period as a function of the reaction temperature. NO\(_x\) conversion by Pd + Ba/Pt-Rh + Cu/Z was higher than that by Pd + Ba/Pt-Rh. NO\(_x\), HC and NH\(_3\) effluent patterns for each catalyst system at 583 K was evaluated using chemiluminescence, flame ionization, and non-dispersive infrared spectroscopy (Figs. 14 (a) and 14 (b)). During the reductive period, approximately 150-200 ppm HC and unexpected NH\(_3\) gases were detected in the outlet gas for Pd + Ba/Pt-Rh. The amount of oxidizing agent (NO + O\(_2\)) in the inlet gas was not enough to totally oxidize the reducing agent (C\(_3\)H\(_6\)), and therefore residual HC should be detected in the outlet gas. NH\(_3\) in the outlet gas must be formed on Pd/Al\(_2\)O\(_3\) and/or Ba/Pt-Rh/Al\(_2\)O\(_3\) catalysts, because NH\(_3\) was not a constituent of the inlet gas. HC and NH\(_3\) emissions from Pd + Ba/Pt-Rh + Cu/Z were much lower than those from Pd + Ba/Pt-Rh, as shown in Fig. 14 (b). Under the reductive atmosphere, there was no O\(_2\) in the outlet for Pd + Ba/Pt-Rh (data not shown). Thus it could be concluded that for the Pd + Ba/Pt-Rh + Cu/Z catalyst system, a large proportion of the HC and NH\(_3\) emissions were stored on the Cu/ZSM-5 catalyst under a reductive atmosphere. During the following oxidative period, the NO\(_x\) concentration was lower for Pd + Ba/Pt-Rh + Cu/Z than for Pd + Ba/Pt-Rh catalyst set, whereas little difference in HC and NH\(_3\) concentrations was observed between the catalyst systems. HC and NH\(_3\) stored on Cu/ZSM-5 of the Pd + Ba/Pt-Rh + Cu/Z catalyst system reacted with NO\(_x\) in the oxidative atmosphere and thus yielded better NO\(_x\) removal than that of Pd + Ba/Pt-Rh.

Further analyses of Fig. 14 revealed that catalytic re-
actions associated with NOx removal over Pd + Ba/Pt-Rh + Cu/Z could be summarized as shown in Fig. 15. During the first oxidative period in the fluctuating conditions, NO in the simulated exhaust gas was oxidized to NO2 over Pd/Al2O3 and was stored on the downstream Ba/Pt-Rh/Al2O3 catalyst. In the initial stage of the subsequent reductive period, N2 formation through SCR of the inlet NOx on Pd/Al2O3 and reduction of stored NOx on Ba/Pt-Rh/Al2O3 catalysts progressed simultaneously. During the subsequent prolonged reductive period, NH3 formed from the inlet NOx on Pd/Al2O3, NH3 formed from stored NOx on Ba/Pt-Rh/Al2O3 and NH3 was stored on Cu/ZSM-5 concomitantly. During the second and later oxidative periods, reactions on Pd/Al2O3 and Ba/Pt-Rh/Al2O3 were the same as those during the first oxidative period, and NOx reduction by stored NH3 and HC also occurred on Cu/ZSM-5. Thus, the higher NOx removal by the Pd/Al2O3, Ba/Pt-Rh/Al2O3 and Cu/ZSM-5 catalyst system compared to the Pd/Al2O3 and Ba/Pt-Rh/Al2O3 system (Fig. 13) can be attributed to a synergistic effect of NH3 storage and NH3-SCR functions on decreasing NOx storage. Catalyst systems utilizing a similar reaction mechanism to remove NOx, generated in an oxidative atmosphere under fluctuating oxidative and reductive conditions were recently reported by Nakatsuji et al.69) and Corbos et al.60).

6. Conclusions

This article has reviewed our research efforts over more than 15 years on removal of NOx emitted by lean-burn internal combustion engines using NSR catalysts. Some of the technologies identified from patient state and reaction analyzed result have contributed to the design of some practical advanced NSR catalysts.

Engine operating conditions depend on the driving situation, and thus an automotive exhaust catalyst must have excellent performance over a wide range of transient temperatures, atmosphere and gas flow rates. NSR catalysts smartly utilizes this atmosphere transient condition and principally oxidizes NO in oxidative automotive exhaust gases to NO2 and stores it as nitrates under oxidative conditions. Stored nitrates decompose and release NOx when the exhaust atmosphere changes from oxidative to reductive conditions under engine management control. The NOx emitted is finally reduced and detoxified to N2. This novel concept for NOx removal was prompted by careful monitoring of emissions and the observation NOx removal during the emission test mode was better than that expected from lean steady conditions. We believe that such an innovative discovery would never have been made in laboratory experiments or computer simulations. This highlights the importance of making observations under realistic situations to overcome the great difficulty of removing NOx under oxidative conditions.

"Pd", "Ba/Pt-Rh", "Cu/Z", "NOx(st.)", "NH3(st.)", "HC(st.)" and "Red." mean "Pd/Al2O3", "Ba/Pt-Rh/Al2O3", "Cu/ZSM-5", "stored NO species", "stored NH3 species", "stored HC species" or "Reducing agents (H2, CO or HC)", respectively.

Fig. 15 Chemical Reactions Involving N Compounds on Pd/Al2O3, Ba/Pt-Rh/Al2O3 and Cu/ZSM-5 Catalysts under Long-term Alternating Oxidative and Reductive Conditions
Since the first NSR catalyst was used in practice, we have been investigating how to improve the catalyst and identified some guiding principles for the design of more advanced NSR catalysts, as described above.

In the near future, in addition to regulation of NOx, CO and HC emissions, laws on CO2 emission or fuel consumption will be implemented in many countries. In principle, automotive catalysts cannot directly reduce CO2 emission; however, they can indirectly contribute to solving this problem via pollutant purification for fuel-efficient cars. Further research and development of NOx removal technology for lean-burn exhaust represents a promising method to increase our sustainability.

Acknowledgments

The authors are grateful to colleagues in Toyota Motor Corporation, Toyota Motor Europe, Cataler Corporation and Toyota Central R&D Labs., Inc. for their many contributions to this work.

References

52) Takahashi, N., Suda, A., Hachisuka, I., Sugiuira, M., Sobukawa,
要 旨

NOx 吸蔵還元型自動車排ガス浄化用触媒の高性能化

高橋 直樹, 今川 晴雄

(㈱)豊田中央研究所, 480-1192 愛知県愛知郡長久手町長湫横道41-1

窒素酸化物（NOx）吸蔵還元型自動車排ガス浄化用触媒は、リーンバーンエンジンから排出される一酸化窒素（NO）を二酸化窒素（NO2）へと酸化し、これをバリウムやカリウム化合物からなるNOx吸蔵材に硝酸イオンとして吸蔵する。この硝酸塩は、エンジン制御系によって作り出される還元雰囲気において、その排気ガス中に含まれる水素、一酸化炭素または炭化水素などの還元剤の反応により分解され、NOxを放出する。放出されたNOxはNOx吸蔵還元型触媒上でさらに窒素へと還元されて無害化される。世界的な自動車排ガス規制の強化に対応するためには、NOx吸蔵還元型触媒の高活性と長寿命を確保する必要がある。NOx吸蔵還元型触媒は熱劣化による貴金属の粒成長、担体比表面積の低下、およびNOx吸蔵材と担体との固相反応などによって活性点数が低下し、失活する。また、排ガス中に含まれる硫黄化合物がNOx吸蔵材に吸蔵され、これを硫酸塩へと変化させる。硫酸塩に変化したNOx吸蔵材はNOx吸蔵能を失う。本論文では、NOx吸蔵還元型触媒の耐久性改善という課題を解決するための要素技術をまとめた。また、NOx吸蔵還元機能を有する触媒とアンモニア生成吸蔵およびNOx選択還元機能を有する触媒とを融合した新しいNOx浄化システムに関しても記した。