



## Special Review

Review

# Automotive Exhaust Catalyst for Clean Air: Progress of the Three-way Catalyst and Supporting Catalyst Technologies

Hirofumi Shinjoh

Report received on Nov. 13, 2018

**■ABSTRACT■** Three-way catalysts (TWCs) for automobile exhaust purification were introduced in the late 1970s, and, in response to strengthened emission restrictions and various needs, have evolved to be the only effective and efficient method for air-quality control. Methods to address major obstacles to practical applications and to meet the further severe regulations have included: (1) effective utilization of rare metals, (2) improvement of catalyst heat resistance, and (3) introduction of lean burn countermeasures. The representative catalysts and key technologies, based on our original catalyst materials and their usage, that solve these problems and have resulted in practical applications are introduced and reviewed: (1) a Pd-only TWC has been successfully realized by use of a basic substance, and catalyst compositions that effectively utilize each noble metal have been created based on this finding, (2) the heat resistances of support and promoter materials have been enhanced, and the amounts of noble metals have been reduced by employing an optimum combination of each noble metal with a suitable support, and (3) the revolutionary NO<sub>x</sub> storage and reduction TWC for lean burn engine exhaust was successfully developed by establishing and exploiting the new concept of using a basic substance as a promoter for NO<sub>x</sub> storage.

**■KEYWORDS■** Three-way Catalyst, Exhaust Gas, Noble Metal, Heat Resistance, Sintering, NO<sub>x</sub> Reduction, NO<sub>x</sub> Storage and Reduction, Periodic Operation Effect, Anchoring Effect, Sulfur Durability

## 1. Introduction

In the early 1970s, the serious photochemical smog in Los Angeles, USA triggered severe regulations on automobile emissions, which were then also obliged against air pollution in Japan. Through much effort, including engine modifications, the catalytic system for exhaust gases had been recognized as the only efficient method to meet these regulations. The oxidation catalyst was first adopted for the removal of carbon monoxide (CO) and hydrocarbons (HC) in 1974. For the simultaneous detoxification of the three pollutant gases, CO, HC and nitrogen oxides (NO<sub>x</sub>),<sup>(1-6)</sup> a three-way catalyst (TWC) system with an oxygen sensor was put into practical use in 1977, and most gasoline-powered vehicles have since been equipped with the TWC for emission control.

Depending on the operating conditions, the composition, temperature and flow rate of the automobile exhaust varies significantly, a catalyst to purify trace amounts of harmful gas components therein with high efficiency is required under non

steady-state conditions. Moreover, a durability of at least 100000 km is necessary in accordance with the life of the automobile. From these points of view, the automotive catalysts were completely different from the conventional catalysts used in chemical factories to date.<sup>(6,7)</sup>

Even after the adoption of the TWC system, catalyst development that overcomes such challenges as strict exhaust control from the viewpoint of environmental conservation has been promoted. As shown in **Fig. 1**, the history of research and development of exhaust purification catalyst at Toyota Central Research and Development Laboratories, Inc. compiles the evolution and progress of automotive exhaust catalyst technology. After the practical use of the TWC, clarification of the reaction mechanism, and investigation of reaction and deterioration behaviors under peculiar atmospheric fluctuation have been conducted with a precious metal catalyst, whereby the basic characteristics were understood and the knowledge obtained has been used for subsequent improvement of catalyst performance. In accordance with the worldwide popularization of

automobiles and strengthening of emission regulations, we have conducted research and development on catalysts to respond to various needs, developed catalyst technologies, and produced high performance catalysts together with Toyota group companies such as Toyota Motor Corp.

In this report, following a general illustration of the automotive exhaust catalyst, its basic characteristics and the obtained findings, the efforts to improve catalyst performance against the strengthening emission regulations since the late 1980s are described. As major obstacles to practical application and to meet the strict regulations were (1) the effective utilization of rare metals, (2) improvement of the catalyst heat resistance, and (3) the introduction of lean burn countermeasures. The representative catalysts and key technologies, based on our original catalyst materials and their usage, that overcame these obstacles and

resulted in practical application are introduced and reviewed here.

## 2. Automotive Exhaust Catalyst and Its Basic Characteristics

### 2.1 Catalyst Constitution<sup>(7,8)</sup>

Automotive exhaust catalysts are composed of noble metals as active species, a support that holds the highly dispersed noble metals, and a promoter that improves catalytic performance and provides functions. A conventional monolith type TWC is illustrated in Fig. 2. The catalyst component is loaded onto a cordierite substrate ( $2MgO_2 \cdot Al_2O_3 \cdot 5SiO_2$ ) at a thickness of several 100  $\mu m$ . Pt, Rh and Pd as precious metals, and oxides such as alumina with high specific surface area and high heat resistance have been

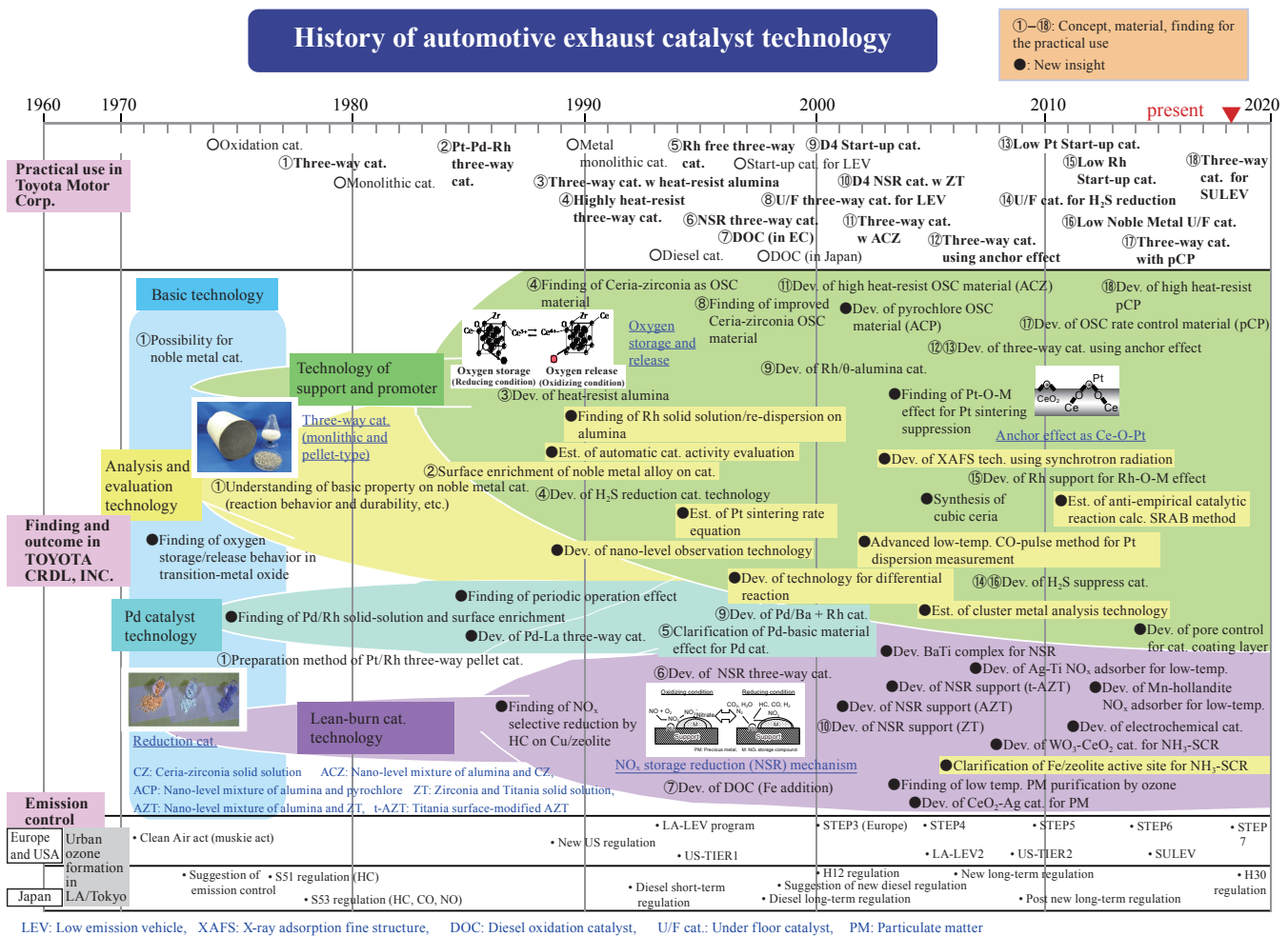


Fig. 1 The history of research and development of exhaust purification catalyst at TOYOTA CRDL, INC.

mainly used as catalyst supports. An indispensable cerium-based oxide to buffer the atmosphere of the exhaust gas, and basic materials for NO<sub>x</sub> storage are typical promoters in the catalysts. Besides these, rare earth elements, transition metal oxides and the like are used to improve catalytic activity and durability.<sup>(9-15)</sup>

### 2.2 Catalyst Performance in Fluctuating Conditions<sup>(8)</sup>

A TWC system and its characteristics for automotive exhaust purification as a function of the air/fuel ratio (A/F) are shown in Fig. 3. CO and HC are easily

oxidized in an excess oxygen atmosphere, and NO<sub>x</sub> is easily converted in a reducing atmosphere. Only in a narrow region near the chemical equivalence point can the three components all be removed at high purification ratios. At the stoichiometric A/F, the oxidizing gas and the reducing gas in the exhaust are present in chemically equivalent amounts; therefore, oxidation and reduction reactions occur on the surface of the precious metal, which is the catalytically active species without excess or deficiency, and the exhaust gases are then converted to H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub>. The TWC system uses an oxygen sensor, which provides a feedback signal to the fuel supply side to control the amount of fuel supply, constantly modifies the A/F of the engine exhaust, and obtains high purification rates for all three components (Fig. 3(c)). For this reason, automotive exhaust is an atmospheric fluctuation flow that repeats the oxidizing atmosphere and the reducing atmosphere around the chemical equivalence point.

Regarding the characteristic atmospheric fluctuation of the exhaust gas to which the exhaust purification catalyst is exposed, the atmospheric oscillations occur at a frequency of around 1 Hz, and the catalytic performance is significantly affected by

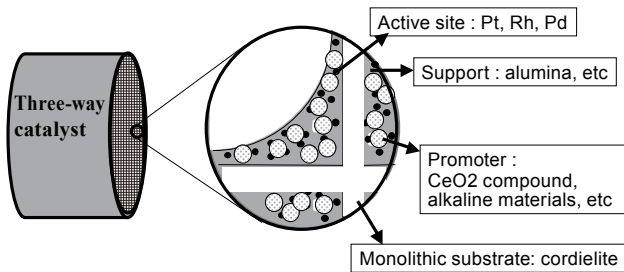


Fig. 2 Outline of three-way catalyst.

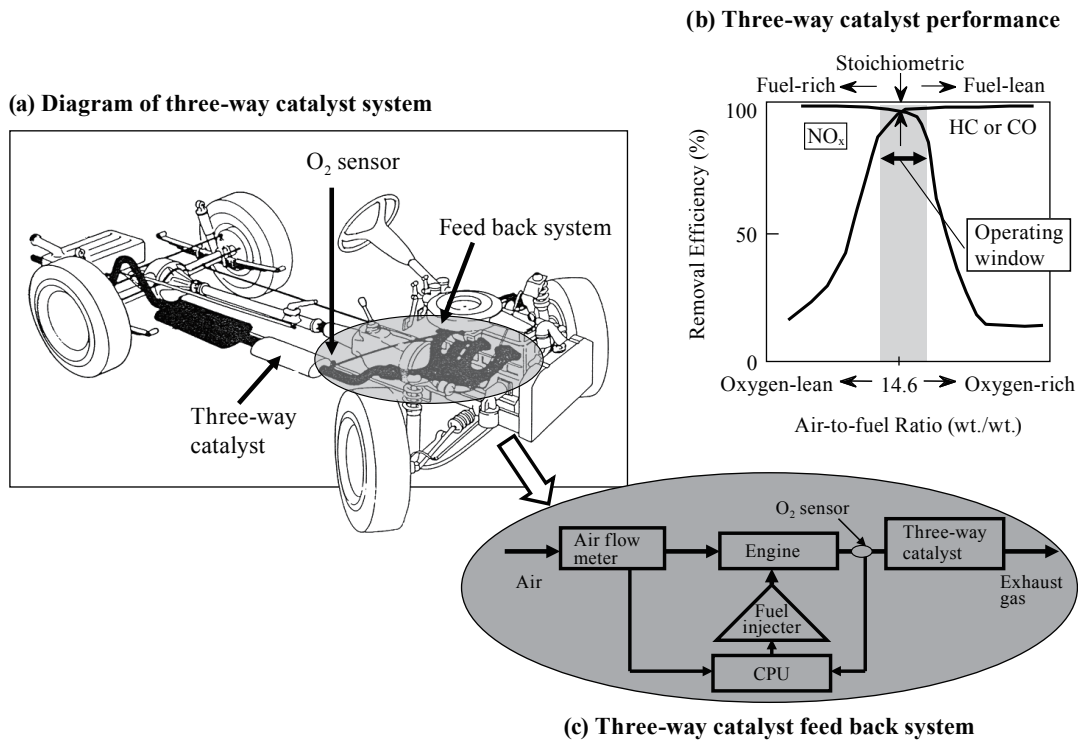
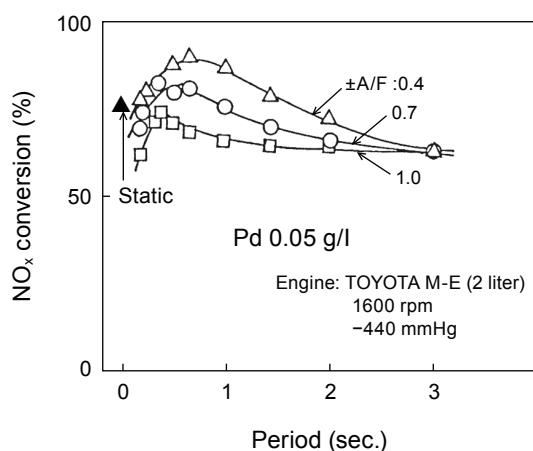


Fig. 3 Three-way catalyst system.

the noble metals species, the temperature and the atmospheric fluctuation of the exhaust gas.<sup>(3-5,16-18)</sup>

**Figure 4** shows the activity of a catalyst using Pd as the active species when the atmospheric fluctuation period and the amplitude were varied by a gasoline engine.<sup>(18)</sup> Compared to stationary conditions without fluctuation, the catalytic activity could be improved under the atmospheric fluctuation and that the activity was dependent on the fluctuation frequency and the amplitude. The phenomenon of activity improvement in the atmospheric fluctuation (periodic operation effect) is significant in a catalyst using Pt or Pd as the active species.<sup>(16)</sup> The periodic operation effect was also verified by simulated multi-component exhaust gas, as well as by a simple two-component exhaust gas.<sup>(19-22)</sup> The effect of the atmospheric fluctuation period on the activity of  $C_3H_6-O_2$  reaction over the Pt catalyst is exemplified in **Fig. 5**.<sup>(22)</sup> Compared with steady-state conditions, atmospheric fluctuation could cause higher activities, and there is an optimum period at a certain temperature. According to kinetic investigation and pattern analysis on the evolution of each gas component, the improvement of the catalytic activity from the periodical fluctuation is caused by the different adsorption capabilities between the two reactants, i.e., self-poisoning reactant molecules adsorb more strongly to the catalyst surface. Under static conditions, the catalyst surface is almost covered by the strongly adsorbed species, so that the desired reaction is suppressed. If an appropriate atmospheric fluctuation is provided, then the strongly adsorbed



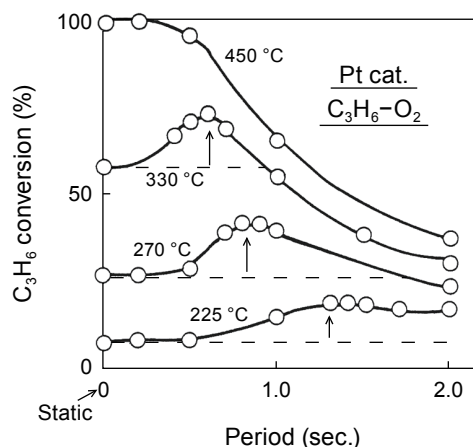
**Fig. 4**  $NO_x$  reduction behavior on Pd/alumina catalyst as a function of oscillation periods and amplitudes in an engine test.

species desorb from the catalyst surface, and the surface composition becomes suitable for promotion of the reaction. This phenomenon or promotion effect by the periodic operation occurs in every reaction on the catalyst.<sup>(21)</sup> Utilizing this phenomenon, the catalytic activity could be improved by artificially creating an optimal atmospheric fluctuation at a certain exhaust temperature.<sup>(8)</sup> On the other hand, in the case of a catalyst containing Rh, a smaller atmospheric variation generally resulted in higher catalytic activity. Rh is a particularly excellent catalyst for  $NO_x$  reduction performance and is indispensable for exhaust purification.

A ceria-based material is used for the TWC as a material to buffer the atmospheric fluctuation.<sup>(8,13,15)</sup> The ceria-based material works as an oxygen storage/release material, releases oxygen in a reducing atmosphere, absorbs oxygen in an oxidizing atmosphere, and maintains the exhaust atmosphere in the vicinity of the chemical equivalence point. The performance improvement of the oxygen storage/release materials will be described in Sec. 4.

### 2.3 Catalyst Deterioration and Noble Metal Sintering

Automotive exhaust catalysts are required to have a high purification rate for the lifetime of automobiles. However, long time exposure to the exhaust gas cause the catalyst performance to deteriorate due to heat and poisoning.<sup>(7)</sup> The temperature of the exhaust gases may



**Fig. 5** Periodic operation effect on Pt/alumina catalyst in  $C_3H_6-O_2$  reaction.

become as high as up to 1000°C under high-speed and high-load running conditions, so that the catalyst material aggregates and shrinks, whereby its catalytic performance deteriorates due to a decrease in active sites. Deterioration by poisoning is caused by the fuel-derived components of P, Zn, Ca, and SO<sub>x</sub> chemically reacting and covering the catalyst surface. Among these, catalyst deterioration at high temperatures is particularly significant, and heat resistance of the catalyst material has been improved significantly to address this problem. The detailed research and development on this challenge is described in the Sec. 4.

Here, the thermal deterioration behavior of noble metals as the catalytically active species is introduced as the basic property of the noble metal catalysts. The sintering behaviors of precious metals is dependent on not only the temperature but also on the components of the exhaust gases, and differs with the noble metal type.<sup>(23)</sup> For example, Pt and Rh sinter more under a deeper oxidizing atmosphere, whereas Pd sinters more severely under a stronger reducing atmosphere. This is related with the saturated vapor pressure of these precious metals and their oxides, i.e., the mobility of the metals and their oxides. Thus, catalyst design guidelines have been derived, for example, utilizing Pd as a catalyst for vehicles with significantly high temperatures and oxidizing atmospheres.

Two or more precious metal active species are generally used in an exhaust catalyst; however, the noble metals are easily alloyed on the catalyst. Under stoichiometric and reducing atmospheres, an alloy composition appears on the catalyst surface, while under oxidizing atmospheres, the easily oxidized metal species becomes enriched on the catalyst surface, which changes the catalytic activities significantly.<sup>(23-26)</sup> Rh is enriched on the surface in the Pt/Rh system, and Pd concentrates on the surface in the Pd/Rh system. For this reason, the Pt/Rh system was primarily used as the main catalyst component in TWCs, essentially due to the high efficiency of Rh for NO<sub>x</sub> purification.

Along with research and development of automotive exhaust catalysts, our main efforts and the challenges with respect to these issues of overcoming transient conditions such as atmospheric fluctuation and suppressing catalyst deterioration at high temperature will be described in the following Sections.

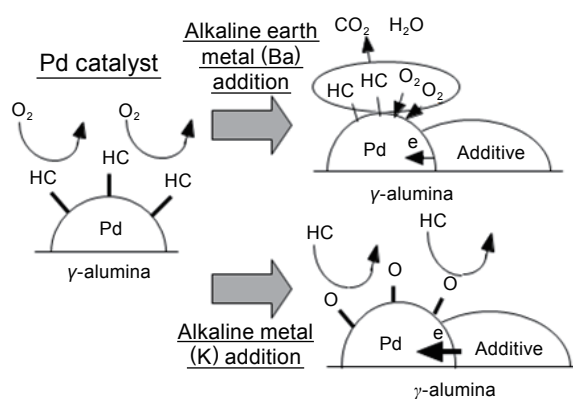
### 3. Effective Utilization of Noble Metal Resources

#### 3.1 Rh-free TWC

Noble metals used as active species are rare and expensive in terms of resources. In some cases, their supply is restrained politically; therefore, the development of a TWC without rare Rh has been highly desired. To date, Rh has been particularly effective in NO<sub>x</sub> reducing activity and is an indispensable element for a TWC.

In the period from '80 to '90, despite its relatively rich resource reserve, Pd had not been used as the main active metal for TWC due to its poor NO<sub>x</sub> reduction activity.<sup>(16,18,27-29)</sup> By kinetic analysis, such as investigation of the reaction order, HC was found to be strongly adsorbed in the exhaust, poisoning the Pd active sites and suppressing catalytic reaction.<sup>(30)</sup> In catalyst development, the addition of a basic component such as La or Ba as a promoter component was also found to suppress HC adsorption poisoning and improved the NO<sub>x</sub> activity of the Pd catalyst (**Fig. 6**).<sup>(30-35)</sup> The durability of the catalyst is also very important in considering its practical use. In particular, the addition of Ba improves the thermal durability of the catalyst because it is more difficult for Ba to react with the alumina support than La.<sup>(35)</sup> Therefore, the Pd-Ba type catalyst was put into practical use as a Rh-free TWC.<sup>(36)</sup>

From the viewpoint of controlling the reaction selectivity, the effect of adding various basic components to the Pd catalyst was investigated systematically. The addition of alkaline earth elements



**Fig. 6** Scheme of alkaline addition effect on Pd/alumina catalyst.

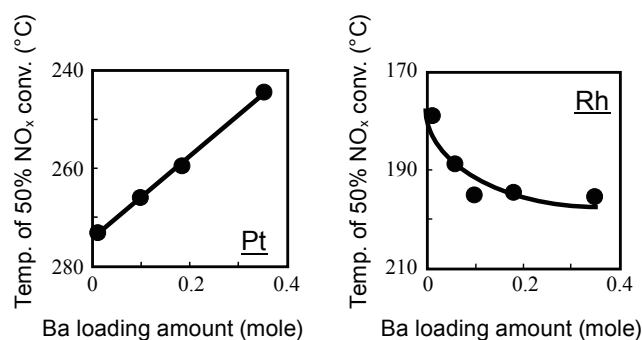


improved the catalytic activity slightly, whereas the addition of alkali metals sometimes resulted in a decrease in activity.<sup>(37)</sup> This is because electron doping with an alkaline earth metal results in moderate degree of electron donation and an abatement of HC adsorption poisoning. On the other hand, with an alkali component, particularly K and Cs, excessive electron donation occurs, which leads to oxygen adsorption poisoning on the Pd surface (Fig. 6).

### 3.2 Pd/Ba and Rh Separately Supported Catalyst

The effect of Ba addition on the other noble metal catalysts was also investigated, whereby the activity of the Pt and Pd catalysts was improved; however, the activity of the Rh catalyst declined in contrast (Fig. 7).<sup>(38)</sup> Similar to the Pd catalyst in 3.1, HC adsorption poisoning on the Pt catalyst is suppressed by electron donation from Ba addition, whereas oxygen poisoning on the Rh catalyst from Ba addition is further promoted and the catalytic activity of the Rh catalyst decreases accordingly.

These results indicated that Ba addition is a plus for the Pd catalyst, while it plays a negative role for Rh catalysts. For a TWC containing both Pd and Rh, a separate supported catalyst concept was proposed in which Ba is added with Pd, but is located away from Rh. In practical application, the catalyst was composed of two layers. After investigating the effect of the thickness of each catalyst layer of Pd/Ba and Rh, and the order of the upper and lower layers, the catalyst with a Rh upper layer and a Pd/Ba lower layer exhibited very high performance.<sup>(39,40)</sup> TWCs based on this concept have thus been widely adopted since 2000 until now.



**Fig. 7** The effect of Ba loading amount on Pt and Rh catalysts for the catalytic activity as temperature at 50% conversion of NO<sub>x</sub>.

## 4. Improvement of Heat Resistance

### 4.1 Thermal Stability of Alumina Support

The operation temperature of a catalytic converter occasionally exceeds 1000°C during high-speed cruising; therefore, thermal degradation is a significant factor for catalyst degradation. Transitional alumina support is apt to transform to  $\alpha$ -alumina, and its surface area decreases significantly under high temperature operation. The loss of the surface area causes the supported noble metal particles to agglomerate, and the catalytic activity then decreases accordingly.<sup>(41,42)</sup> It has been reported that the addition of rare earth and alkaline earth compounds is effective to suppress the  $\alpha$ -transformation of alumina.<sup>(41-44)</sup> La has a large ionic radius, and is the most effective component for thermal stability improvement. La can be easily inserted into cation defects in transitional alumina with the spinel structure. La<sup>3+</sup> with a large ionic radius inhibits the diffusion of Al<sup>3+</sup> and O<sup>2-</sup> ions, and thus prevents alumina from sintering and prevents  $\alpha$ -transformation. However, excess addition of La leads to the formation of aluminate with La; therefore, the addition of a small amount of La is very effective to significantly improve the heat resistance of TWCs.

### 4.2 Improvement of Oxygen Storage Materials and Their Heat Resistance

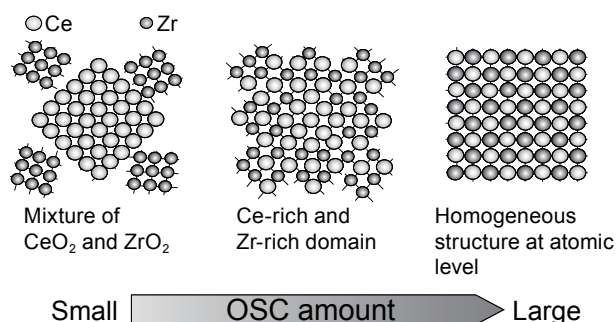
For the control of NO<sub>x</sub>, CO, HC emissions, a TWC works under an atmosphere with a fluctuating A/F ratio, while the average A/F is controlled close to the stoichiometric value. A cerium oxide compound regulates oxygen storage and release, which is the most important and significant feature of a TWC. Oxygen storage materials store an excess of oxygen in an oxidizing atmosphere and release oxygen in a reducing atmosphere. Through this oxygen storage/release, a buffer between the lean-rich fluctuations in exhaust gas compositions during vehicle operation is achieved to maintain a stoichiometric atmosphere, in which NO<sub>x</sub>, CO and HC are efficiently converted.

CeO<sub>2</sub> to maintain a cubic crystal structure and its volume changes little, even during alternate oxygen storage and release; therefore, CeO<sub>2</sub> was regarded early on as a promising material. However, the oxygen storage capacity (OSC) and thermal durability of pure

CeO<sub>2</sub> were not sufficient for practical use. The most effective method for OSC improvement is to produce a solid solution by the introduction of an element into CeO<sub>2</sub>, such as Zr with a smaller ionic diameter than the cerium ion.<sup>(41,45)</sup> The space surrounding oxygen is thus enlarged, which facilitates the reversible oxygen storage/release in the matrix. X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) analysis have further clarified that the OSC is significantly enhanced along with improvement of the homogeneity of the Ce and Zr atoms in the CeO<sub>2</sub>-ZrO<sub>2</sub> (CZ) solid solution (**Fig. 8**).<sup>(46)</sup>

Considering the reaction rates involved in oxygen storage/release, the reaction process can be divided into several steps: oxygen diffuses from the bulk to the oxide surface, oxygen diffuses from the oxide surface to the metal surface, where it reacts on the precious metal surface. Oxygen surface and bulk diffusivities correlate with the homogeneity of the Zr and Ce atom distribution in the oxide framework among samples investigated by the <sup>18</sup>O/<sup>16</sup>O isotopic exchange reaction method.<sup>(47-49)</sup>

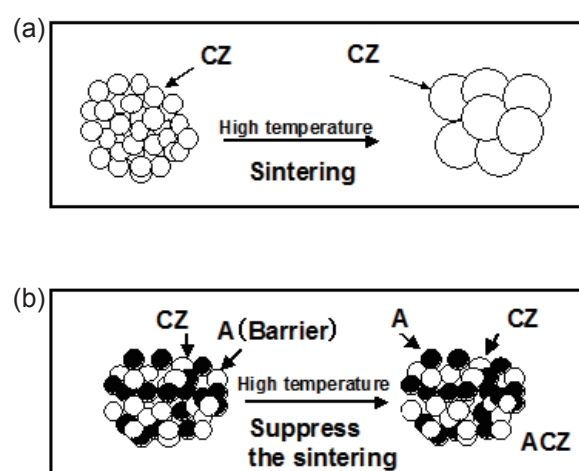
CZ has a higher thermal stability than CeO<sub>2</sub>. The heat resistance of CZ has been successfully improved by blending with nanosized alumina particles.<sup>(50-53)</sup> **Figure 9** illustrates this concept for the nanosized mixture of alumina and CZ solid solution (ACZ). Particles of the same kind are generally apt to aggregate to form larger grains, even at relatively low temperatures in air. However, if particles of the same kind are isolated by another kind of particles that do not react with the neighboring particles at high temperature, these particles do not easily aggregate



**Fig. 8** Solid state of ceria-zirconia and oxygen storage capacity (OSC).

with each other. Thus, the alumina particles inhibit the aggregation of CZ particles by acting as a diffusion barrier, even at high temperature. Catalysts containing oxygen storage materials could thus efficiently detoxify the pollutants, particularly for NO<sub>x</sub> emission control. A catalyst that employed ACZ could thus cut down NO<sub>x</sub> emissions by 20% compared with that using only CZ during a running test after a thermal aging treatment. The diffusion barrier concept has thus since become a major guideline for the high heat resistance of catalyst materials, and has been widely applied to most catalytic materials.

On the other hand, CZ becomes a pyrochlore structure by reducing treatment at high temperature, and 100% of its oxygen storage/release capacity close to theoretical value could be utilized. A unique method of high pressure molding and subsequent high temperature reduction treatment was recently used to obtain crystallized CZ with a particle size of several micrometers that had very high durability and extremely large oxygen storage/release performance. The oxygen storage/release rates are effectively controlled with this material, and the time range for maintaining a stoichiometric A/F ratio and high catalytic activity is thus extended significantly.<sup>(54)</sup> This new oxygen storage material has been put to practical use and further improvement in performance has been achieved since its adoption in vehicles in 2014.

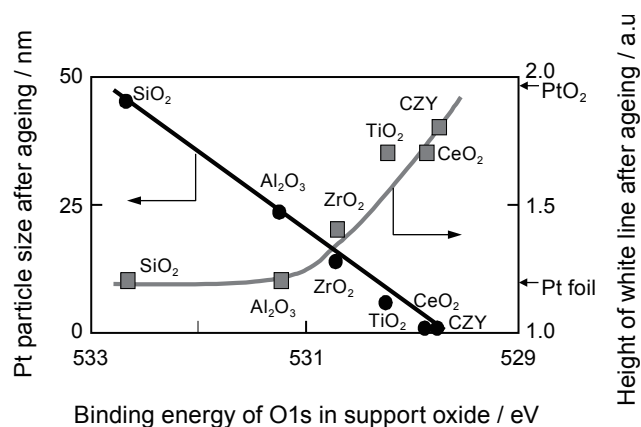


**Fig. 9** The diffusion barrier concept for ACZ compared with CZ. (a) CZ: sinter easily without any dispersal; (b) ACZ: the sintering of CZ is inhibited by Al<sub>2</sub>O<sub>3</sub> particles dispersed among CZ particles.

### 4.3 Improvement of Heat Resistance and Reduction of Precious Metal Usage<sup>(55)</sup>

Although the catalytic performance has been improved by increasing the heat resistance of the catalytic material, a fundamental solution to resolve the problem of noble metal sintering has not yet been established and has eventually resulted in significant noble metal usage in TWCs to meet the stringent emission restrictions. As a very sparse and expensive resource, it is thus necessary to reduce the use of noble metals as active sites for automotive catalysts as much as possible. The sintering of precious metals such as Pt and Rh is known to occur significantly at high temperatures and under oxidizing atmospheres.<sup>(23)</sup>

Through investigation of the sintering behavior of Pt on oxide supports, it was found that some supports could efficiently suppress Pt sintering caused by an anchoring effect on the support.<sup>(56)</sup> An atomic level X-ray absorption analysis on the effect of the support on Pt sintering was conducted under an oxidizing atmosphere, which revealed that the Pt-O-M (M: cation of oxide) bond formed on some oxide supports ( $MO_x$ ) acts as an anchor to suppress Pt sintering, and the strength of the Pt-oxide-support interaction was well correlated with the electron density of oxygen in the support oxide (**Fig. 10**). Considering the actual application with this concept of Pt-support interaction, Pt on the catalyst should be in the metallic state under a stoichiometric atmosphere as the main driving condition, and formation of Pt-oxide bonds occasionally under oxidizing conditions. To



**Fig. 10** Pt-oxide support interaction and correlation with Pt sintering in an oxidizing atmosphere.

achieve a good balance between catalytic activity and the suppression of sintering, a ceria-based oxide was found to be suitable for Pt.<sup>(57)</sup> The effect of the amount of Pt loading on Pt sintering was investigated to ascertain the appropriate amount of Pt on ceria-based oxide supports.<sup>(58)</sup> Pt sintering did not occur with a certain amount of Pt loading after an oxidizing durability aging treatment, and the catalytic activity was not deteriorated by aging. This Pt amount corresponded well with the number of Pt-O-Ce sites on the support. On the other hand, a zirconia-based oxide was verified to be an appropriate support for Rh through a similar investigation.<sup>(57)</sup>

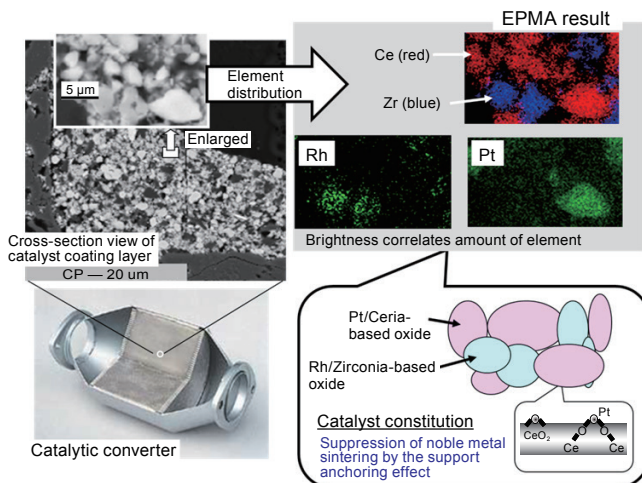
Based on these results, optimization of the combination of noble metals and supports for both Pt and Rh has led to the development of catalysts to considerably suppress deterioration of the noble metals that were put to practical use in 2005 (**Fig. 11**).<sup>(59)</sup> Thereafter, the support for Rh was further improved and a catalyst with high heat resistance was put in practical use in 2011.<sup>(54)</sup>

For details on the heat-resistant alumina, oxygen storage material and utilization of the Pt-O-M anchor effect described in this chapter, please refer to the past published R&D review reports.<sup>(55,60,61)</sup>

## 5. NO<sub>x</sub> Control for Lean-burn Engine Exhaust<sup>(8)</sup>

### 5.1 NO<sub>x</sub> Storage and Reduction Catalyst

In addition to the concern regarding the NO<sub>x</sub>, CO and HC pollutants, carbon dioxide (CO<sub>2</sub>) emission



**Fig. 11** Outline of the three-way using the anchor effect.



has attracted increasing attention, and fuel efficient lean-burn engines have been widely adopted. To improve the fuel efficiency, lean-burn engines are typically operated under an excess oxygen atmosphere. Through the use of a conventional TWC, the high oxygen excess in the lean-burn engine exhaust promotes the efficient removal of CO and HC emissions, but prohibits the conversion of NO<sub>x</sub> to N<sub>2</sub>.

NO<sub>x</sub> reduction for the exhaust from lean-burn engines is a one of the greatest challenges in environmental protection, and many researchers have strived to develop suitable catalysts in many ways. The selective catalytic reduction of NO<sub>x</sub> with HC (HC-SCR) is a desirable way to utilize non-combusted HC in exhaust gases.<sup>(62-72)</sup> Many types of catalyst, in particular Cu-zeolites and Pt loaded catalysts, exhibit HC-SCR activity and an operation window as a function of temperature. NO<sub>x</sub> reduction by HC competes with HC oxidation by O<sub>2</sub> under an excess oxygen atmosphere, and its activity and durability through a wide range of operation conditions are not adequate; therefore, HC-SCR has not been used as a main way practically for automotive pollution control.

Although it has already been stated that the atmosphere and temperature of automotive exhaust gas varies, at a transient test in a lean-burn engine experiment, a certain type of catalyst exhibited high NO<sub>x</sub> purification capability. By investigating the NO<sub>x</sub> purification behavior of various catalysts under variation of the oxidation and reduction atmospheres, high NO<sub>x</sub> purification performance could be obtained by the combination of a catalyst containing a basic substance with NO<sub>x</sub> storage capability and engine control. This led to practical application in the lean-burn engine system.

The storage of NO<sub>x</sub> under lean conditions and then reduction of the stored NO<sub>x</sub> to N<sub>2</sub> under rich conditions by controlled engine operation (**Fig. 12**), NO<sub>x</sub> storage and reduction (NSR) became a very efficient way to remove NO<sub>x</sub>. This technology is also referred as a lean NO<sub>x</sub> trap. A moderate reducing condition is created by a very short intermittent engine control. Due to the generation of a reducing atmosphere, the fuel efficiency deteriorates slightly, but NO<sub>x</sub> reduction proceeds promptly. Toyota Motor Corp. pioneered this technology and first put this NSR technology to practical use.<sup>(73-76)</sup>

As the active species, Pt promoting NO oxidation and Rh catalyzing NO<sub>x</sub> reduction are the essential

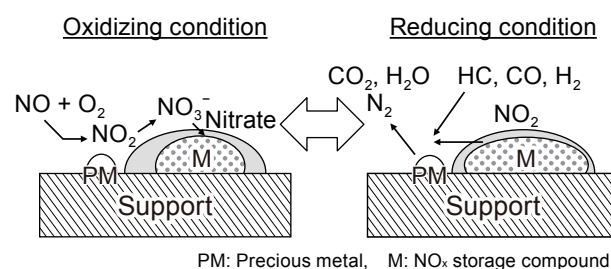
components of the NSR catalyst. The NO<sub>x</sub> storage capacity correlates with the basicity of the NO<sub>x</sub> storage material component.<sup>(75)</sup> Stronger basicity results in stronger NO<sub>x</sub> binding to the basic component and a larger amount of NO<sub>x</sub> storage. Thermally stable Ba with a high affinity for NO<sub>x</sub> is the most preferable component. K is also thermally stable at high temperature for nitrate storage, and is also used as a preferable NO<sub>x</sub> storage material.<sup>(77-79)</sup>

For NO oxidation, the effect of the support on the NSR catalyst is in the order of: SiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > TiO<sub>2</sub> > ZrO<sub>2</sub> > CeO<sub>2</sub>. This is because Pt, which is the active component of the NO oxidation activity, is easily held in the metallic state.<sup>(80)</sup> Automotive catalysts require high heat resistance and poisoning resistance for durability of 100000 km or more. As the biggest deterioration factor for an NSR catalyst, the NO<sub>x</sub> storage site is easily poisoned by SO<sub>x</sub>, and therefore requires enhancement of its durability against poisoning.

## 5.2 Improvement of Durability Against Sulfur Poisoning

SO<sub>x</sub> poisoning is a major problem for NSR catalysts due to the formation of stable sulfates under lean conditions, whereby the NSR material loses NO<sub>x</sub> storage capability. A variety of approaches, such as additives, improvement of and combination with supports and storage materials have been attempted to improve the SO<sub>x</sub> durability of NSR catalysts.

Through promotion of the decomposition and desorption of sulfates, the addition of a Fe component significantly improves the catalytic activity.<sup>(81,82)</sup> As a support material, TiO<sub>2</sub> addition enhances the durability of the NSR catalysts against SO<sub>x</sub>



**Fig. 12** NO<sub>x</sub> storage and reduction scheme on NSR catalyst.

poisoning.<sup>(83)</sup> TiO<sub>2</sub> is an acidic material, and sulfates on TiO<sub>2</sub> are less stable than that on alumina. Therefore, TiO<sub>2</sub> particles dispersed in an alumina-based catalyst promote the decomposition and removal of sulfates under reducing conditions. H<sub>2</sub> is a strong reductant for the reduction of sulfates and the Rh/ZrO<sub>2</sub> catalyst effectively promotes H<sub>2</sub> generation by the steam reforming reaction. SO<sub>x</sub> reduction and desorption were promoted by the introduced Rh/ZrO<sub>2</sub> under a reducing atmosphere; therefore, the SO<sub>x</sub> durability of the NSR catalyst was improved accordingly.<sup>(84,85)</sup> Moreover, ZrO<sub>2</sub> also plays a role to hold K as an additive for high temperature NO<sub>x</sub> performance. K is an effective basic component for NO<sub>x</sub> storage; however, it tends to react with supports such as alumina and TiO<sub>2</sub>, and easily loses its NO<sub>x</sub> storage capacity. SO<sub>x</sub> poisoning resistance was additionally improved a composite oxide of TiO<sub>2</sub> and ZrO<sub>2</sub> (ZT).<sup>(86)</sup> After SO<sub>x</sub> poisoning tests, those having a weight ratio of TiO<sub>2</sub> in ZT of 30 to 70 wt% exhibited high NO<sub>x</sub> storage ability at high temperature. The reason for this is that its solid acidity was the highest for this composition. The loss of the K component caused by solid phase reaction and sulfate formation is suppressed significantly compared with individual TiO<sub>2</sub> and ZrO<sub>2</sub> supports, so that the NSR activity is maintained effectively. Furthermore, to suppress thermal deterioration, nano-sized alumina particles are mixed with ZT to obtain AZT, where the alumina particles act as a diffusion barrier and prevent aggregation at high temperature, which was effectively demonstrated by a heat resistance test.<sup>(87-89)</sup>

In recent years, a Ba-TiO<sub>2</sub> complex as a precursor to a NO<sub>x</sub> storage material, the TiO<sub>2</sub> modified AZT support for further improvement of SO<sub>x</sub> resistance, and a low temperature NO<sub>x</sub> adsorbent for NO<sub>x</sub> discharged at engine start-up are under study.<sup>(90-94)</sup>

### 5.3 Catalyst Combination for NO<sub>x</sub> Control

The published reports indicated that an additional oxidation catalyst upstream of a NSR catalyst would effectively improve NO<sub>x</sub> storage activity through the promotion of NO<sub>2</sub> formation under an oxidizing atmosphere. However, the co-existing reductants, such as HC and CO, reduced NO<sub>2</sub> back to NO, even in an oxidizing atmosphere.<sup>(95)</sup> Therefore, this additional oxidation catalyst must be placed in front of the NSR catalyst.

Investigation of the effect of catalyst combinations has

revealed that a particular combination of Pd/alumina, NSR catalyst and Cu/zeolite in turn, exhibit very high NO<sub>x</sub> reduction activity under an oxidizing atmosphere with intermittent deep rich atmosphere operation.<sup>(96)</sup> The high NO<sub>x</sub> reduction activity with this combination of catalysts could be illustrated by the following reaction mechanism (**Table 1**): Pd catalyst upstream of the NSR catalyst improves NO<sub>x</sub> storage ability by enhancing NO<sub>2</sub> formation under an oxidizing atmosphere; the stored NO<sub>x</sub> was then easily reduced to NH<sub>3</sub> on the NSR catalyst. The generated NH<sub>3</sub> was adsorbed on Cu/zeolite downstream of the NSR catalyst and then used as a reductant to reduce NO<sub>x</sub> under the subsequent oxidizing atmosphere.

The NSR technology has also been applied for diesel engine exhaust, and has become the most reliable and attractive method for lean-burn combustion vehicles. Along with the decrease of S content in fuel and further improvement of catalyst performance, we assume that NSR catalysts will be prevailing worldwide in the near future.

## 6. Summary and Future Trends

As automotive exhaust gas purification catalysts, TWCs were first commercialized in 1977. Since then, in response to the strengthened emission restrictions and various needs, TWCs have evolved to become the only effective and efficient method for air quality control. Utmost utilization of scarce resources of precious metals, improvement of heat resistance, and countermeasures for energy efficient lean burn engines have been major challenges in the development of TWCs.

First, regarding the use of precious metals, instead of the very rare and necessary Rh for NO<sub>x</sub> reduction, Rh-free and Pd only TWCs have been successfully

**Table 1** The role of each catalyst for NO<sub>x</sub> reduction with the catalyst combination

Condition	Pd	NSR	Cu/Z
Oxidative	NO + O <sub>2</sub> → NO <sub>x</sub>	NO <sub>x</sub> → NO <sub>x</sub> (ad)*	NO <sub>x</sub> + NH <sub>3</sub> (ad)*** → N <sub>2</sub> + H <sub>2</sub> O
Reductive	NO <sub>x</sub> + Red** → NH <sub>3</sub> + H <sub>2</sub> O + CO <sub>2</sub> → N <sub>2</sub> + H <sub>2</sub> O + CO <sub>2</sub>	NO <sub>x</sub> (ad) + Red** → N <sub>2</sub> + H <sub>2</sub> O + CO <sub>2</sub> → NH <sub>3</sub> + H <sub>2</sub> O + CO <sub>2</sub>	NH <sub>3</sub> → NH <sub>3</sub> (ad)***

\*NO<sub>x</sub> adsorption \*\*Reductant (H<sub>2</sub>, HC, CO) \*\*\*NH<sub>3</sub> adsorption

realized by the use of a basic substance, and catalyst compositions effectively utilizing each noble metal have been developed based on this finding. Second, with respect to heat resistance, the heat resistances of support and promoter materials have been enhanced, and the amounts of noble metals have been significantly cut down by optimum combination of each noble metal with a suitable support. Last, by establishing and exploiting the new concept of using a basic substance as a promoter for NO<sub>x</sub> storage, a revolutionary NSR catalyst for lean burn engine exhaust was successfully developed, with Toyota group companies, such as Toyota Motor Corp. As a result of these studies, the performance of exhaust purification catalysts has reached a level several tens to hundreds of times that of the initial practical catalysts. These catalyst technologies have been commercialized and widely acknowledged academically, having received awards from a number of academic societies. From now on, further improvement of catalyst performance is expected along with further advances of the related technologies, functional materials and their use, for example, the utilization of electrochemical reactions.<sup>(97,98)</sup>

On the other hand, during the research and development of the above catalysts, high-level concepts, such as the periodic operation effect and the basic component addition effect, and new ideas and knowledge such as diffusion barrier construction, Pt-O-M bonds, and the NSR mechanism were established and applied to the exhaust purification catalyst.

Conventional motor vehicles are gradually converting to electric vehicles these days; however, internal combustion automobiles are unlikely to disappear completely in the future. The future pursuit for exhaust purification catalysts is to realize zero exhaust emissions and a significant reduction of CO<sub>2</sub> release, and further endeavors are required on the following four points:

- 1) Improvement of low temperature purification activity: along with the foreseen decrease of the engine combustion temperature, the exhaust should be treated immediately after start-up or at room temperature.
- 2) High-level particulate matter (PM) purification: removal of the solid carbon from lean burn engines.
- 3) Lean NO<sub>x</sub> control: the realization of direct catalytic NO<sub>x</sub> decomposition without using a reductant would be the ideal and ultimate goal for NO<sub>x</sub> control, although de-NO<sub>x</sub> technologies using urea and fuels, including the NSR catalyst introduced in this report, have been put into practical use for many years to date.
- 4) Precious metal-free catalysts: development of an automotive catalyst without the use of noble metals to ultimately save these scarce resources.

Through these achievements, we believe and expect that not only zero emission can be achieved, but that even a negative emission will be realized, i.e., that the air quality of the Earth's atmosphere will be improved along with car running in the future.

## References

- (1) Nakagawa, S. and Yamaguchi, T., *Jidousha-gijutsu* (in Japanese), Vol. 31, No. 7 (1977), pp. 1175-1181.
- (2) Nakagawa, S. and Tamano, A., *Jidousha-gijutsu* (in Japanese), Vol. 32, No. 11 (1978), pp. 1025-1032.
- (3) Canale, R. P., Winegarden, S. R., Carlson, C. R. and Milles, D. L., *SAE Tech. Pap. Ser.*, No. 780205 (1978).
- (4) Seiter, R. E. and Clark, R. J., *SAE Tech. Pap. Ser.*, No. 780203 (1978).
- (5) Engh, G. T. and Wallman, S., *SAE Tech. Pap. Ser.*, No. 770295 (1977).
- (6) Fujitani, Y., *Denki Kagaku oyobi Kougyou Butsuri Kagaku* (in Japanese), Vol. 57, No 10 (1989), pp. 957-960.
- (7) Ohashi, M., *Shokubai* (in Japanese), Vol. 29, No. 2 (1987), pp. 598-604.
- (8) Matsumoto, S. and Shinjoh, H., *Adv. Chem. Eng.*, Vol. 33 (2007), pp. 1-46.
- (9) Klimisch, R. L. and Taylor, K. C., *Environ. Sci. Technol.*, Vol. 7, No. 2 (1973), pp. 127-131.
- (10) Cooper, B. J. and Keck, L., *SAE Tech. Pap. Ser.*, No. 800461 (1980).
- (11) Henk, M. G., White, J. J. and Denison, G. W., *SAE Tech. Pap. Ser.*, No. 872134 (1987).
- (12) Rieck, J. S., Suarez, W. and Kubsh, J. E., *SAE Tech. Pap. Ser.*, No. 892095 (1989).
- (13) Shinjoh, H., *J. Alloys Comp.*, Vol. 408-412 (2006), pp. 1061-1064.
- (14) Trovarelli, A., *Catal. Rev. Sci. Eng.*, Vol. 38, No. 4 (1996), pp. 439-520.
- (15) Kašpar, J., Fornasiero, P. and Hickey, N., *Catal. Today*, Vol. 77, No. 4 (2003), pp. 419-449.
- (16) Muraki, H., Shinjoh, H., Sobukawa, H., Yokota, K. and Fujitani, Y., *Ind. Eng. Chem. Prod. Res. Dev.*, Vol. 24, No. 1 (1985), pp. 43-49.
- (17) Muraki, H., Yokota, K. and Fujitani, Y., *Appl. Catal.*, Vol. 48, No. 1 (1989), pp. 93-105.
- (18) Yokota, K., Muraki, H. and Fujitani, Y., *SAE Tech. Pap. Ser.*, No. 850129 (1985).

- (19) Muraki, H., Sobukawa, H. and Fujitani, Y., *Nippon Kagaku Kaishi* (in Japanese), Vol. 1985, No. 2 (1985), pp. 176-181.
- (20) Muraki, H. and Fujitani, Y., *Ind. Eng. Chem. Prod. Res. Dev.*, Vol. 25, No. 3 (1986), pp. 414-419.
- (21) Shinjoh, H., Muraki, H. and Fujitani, Y., *Stu. Surf. Sci. Catal.*, Vol. 30 (1987), pp. 187-197.
- (22) Shinjoh, H., Muraki, H. and Fujitani, Y., *Appl. Catal.*, Vol. 49, No. 2, 3, (1989), pp. 195-204.
- (23) Shinjoh, H., Muraki, H. and Fujitani, Y., *Stud. Surf. Sci. Catal.*, Vol. 71 (1991), pp. 617-628.
- (24) Muraki, H., Sobukawa, H., Kimura, M. and Isogai, A., *SAE Tech. Pap. Ser.*, No. 900610 (1990).
- (25) Chen, M., Wang, T. and Schmidt, L. D., *J. Catal.*, Vol. 60, No. 3 (1979), pp. 356-368.
- (26) Wang, T. and Schmidt, L. D., *J. Catal.*, Vol. 71, No. 2 (1981), pp. 411-422.
- (27) Muraki, H., Shinjoh, H. and Fujitani, Y., *Nippon Kagaku Kashi* (in Japanese), No. 9 (1985), pp. 1682-1688.
- (28) Summers, J. C., Williamson, W. B. and Henk, M. G., *SAE Tech. Pap. Ser.*, No. 880281 (1988).
- (29) Summers, J. C., White, J. J. and Williamson, W. B., *SAE Tech. Pap. Ser.*, No. 890794 (1989).
- (30) Muraki, H., Shinjoh, H., Sobukawa, H., Yokota, K. and Fujitani, Y., *Ind. Eng. Chem. Prod. Res. Dev.*, Vol. 25, No. 2 (1986), pp. 202-208.
- (31) Shinjoh, H., Yokota, K., Doi, H., Sugiura, M. and Matsumoto, S., *Nippon Kagaku Kaishi* (in Japanese), Vol. 1995, No. 10 (1995), pp. 779-788.
- (32) Muraki, H., Shinjoh, H. and Fujitani, Y., *Appl. Catal.*, Vol. 22, No. 2 (1986), pp. 325-335.
- (33) Muraki, H., Fukui, M., Yokota, K. and Fujitani, Y., *Nippon Kagaku Kashi* (in Japanese), Vol. 1986, No. 2 (1986), pp. 130-137.
- (34) Muraki, H., Yokota, K. and Fujitani, Y., *Appl. Catal.*, Vol. 48, No. 1 (1989), pp. 93-105.
- (35) Shinjoh, H., Suzuki, T., Takahashi, N., Yokota, K., Sugiura, M. and Matsumoto, S., *Nippon Kagaku Kaishi* (in Japanese), Vol. 1996, No. 10 (1996), pp. 433-440.
- (36) Matsuura, S., Hirai, A., Arimura, K. and Shinjoh, H., *SAE Tech. Pap. Ser.*, No. 950257 (1995).
- (37) Shinjoh, H., Isomura, N., Sobukawa, H. and Sugiura, M., *Stud. Surf. Sci. Catal.*, Vol. 116 (1998), pp. 83-91.
- (38) Shinjoh, H., Tanabe, T., Sobukawa, H. and Sugiura, M., *Top. Catal.*, Vol. 16, No. 1-4 (2001), pp. 95-99.
- (39) Shinjoh, H., Sobukawa, H. and Kanazawa, T., Patent No. 3503101 (in Japanese).
- (40) Suzuki, J., Miyoshi, N., Shinjoh, H. and Sobukawa, H., Patent No. 3798727 (in Japanese).
- (41) Miyoshi, N., Matsumoto, S., Ozawa, M. and Kimura, M., *SAE Tech. Pap. Ser.*, No. 891970 (1989).
- (42) Ozawa, M., Kimura, M. and Isogai, A., *J. Less-Common Met.*, Vol. 162, No. 2 (1990), pp. 297-308.
- (43) Oudet, F., Courtine, P. and Vejux, A., *J. Catal.*, Vol. 114, No. 1 (1988), pp. 112-120.
- (44) Ismagilov, Z. R., Shkrabina, R. A., Koryabkina, N. A., Arendarskii, D. A. and Shikina, N. V., *Stud. Surf. Sci. Catal.*, Vol. 116 (1998), pp. 507-511.
- (45) Ozawa, M., Kimura, M. and Isogai, A., *J. Alloys Compd.*, Vol. 193, No. 1-2 (1993), pp. 73-75.
- (46) Nagai, Y., Yamamoto, T., Tanaka, T., Yoshida, S., Nonaka, T., Okamoto, T., Suda, A. and Sugiura, M., *Catal. Today*, Vol. 74, No. 3-4 (2002), pp. 225-234.
- (47) Tanabe, T., Suda, A., Descorme, C., Duprez, D., Shinjoh, H. and Sugiura, M., *Stud. Surf. Sci. Catal.*, Vol. 138 (2001), pp. 135-144.
- (48) Dong, F., Suda, A., Tanabe, T., Nagai, Y., Sobukawa, H., Shinjoh, H., Sugiura, M., Descorme, C. and Duprez, D., *Catal. Today*, Vol. 90, No. 3-4 (2004), pp. 223-229.
- (49) Dong, F., Suda, A., Tanabe, T., Nagai, Y., Sobukawa, H., Shinjoh, H., Sugiura, M., Descorme, C. and Duprez, D., *Catal. Today*, Vol. 93-95 (2004), pp. 827-832.
- (50) Suzuki, T., Morikawa, A., Suda, A., Sobukawa, H., Sugiura, M., Kanazawa, T., Suzuki, J., Takada, T., *R&D Review of Toyota CRDL*, Vol. 37, No. 4 (2002), pp. 28-33.
- (51) Kanazawa, T., Suzuki, J., Takada, T., Suzuki, T., Morikawa, A., Suda, A., Sobukawa, H. and Sugiura, M., *SAE Tech. Pap. Ser.*, No. 2003-01-0811 (2003).
- (52) Morikawa, A., Suzuki, T., Kanazawa, T., Kikuta, K., Suda, A. and Shinjo, H., *Appl. Catal. B.*, Vol. 78, No. 3-4 (2008), pp. 210-221.
- (53) Morikawa, A., Kikuta, K., Suda, A. and Shinjo, H., *Appl. Catal. B.*, Vol. 88, No. 3-4 (2009), pp. 542-549.
- (54) Tanabe, T., Morikawa, A., Hatanaka, M., Takahashi, N., Nagai, Y., Sato, A., Kuno, O., Suzuki, H. and Shinjoh, H., *Catal. Today*, Vol. 184, No. 1 (2012), pp. 219-226.
- (55) Shinjoh, H., *R&D Review of Toyota CRDL*, Vol. 42, No. 1 (2011), pp. 1-8.
- (56) Nagai, Y., Hirabayashi, T., Dohmae, K., Takagi, N., Minami, T., Shinjoh, H. and Matsumoto, S., *J. Catal.*, Vol. 242, No. 1 (2006), pp. 103-109.
- (57) Shinjoh, H., Hatanaka, M., Nagai, Y., Tanabe, T., Takahashi, N., Yoshida, T. and Miyake, Y., *Top. Catal.*, Vol. 52 (2009), pp. 1967-1971.
- (58) Hatanaka, M., Takahashi, N., Tanabe, T., Nagai, Y., Dohmae, K., Aoki, Y., Yoshida, T. and Shinjoh, H., *Appl. Catal. B.*, Vol. 99, No. 1-2 (2010), pp. 336-342.
- (59) Yoshida, T., Sato, A., Suzuki, H., Tanabe, T. and Takahashi, N., *SAE Tech. Pap. Ser.*, No. 2006-01-1061 (2006).
- (60) Ozawa, M., Kimura, M., Sobukawa, H. and Yokota, K., *R&D Review of Toyota CRDL* (in Japanese), Vol. 27, No. 3 (1992), pp. 43-53.
- (61) Suda, A., Sobukawa, H., Suzuki, T., Kandori, T., Ukyo, Y. and Sugiura, M., *R&D Review of Toyota CRDL* (in Japanese), Vol. 33, No. 3 (1998), pp. 3-12.



- (62) Iwamoto, M., Yokoo, S., Sakai, K. and Kagawa, S., *J. Chem. Soc., Faraday Trans. 1*, Vol. 77 (1981), pp. 1629-1638.
- (63) Held, W., König, A., Richter, T. and Puppe, L., *SAE Tech. Pap. Ser.*, No. 900496 (1990).
- (64) Iwamoto, M., Yahiro, H., Yu-u, Y., Shundo, S. and Mizuno, N., *Shokubai* (in Japanese), Vol. 32, No. 6 (1990), pp. 430-433.
- (65) Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T. and Tabata, M., *Appl. Catal.*, Vol. 64 (1990), pp. L1-L4.
- (66) Iwamoto, M. and Hamada, H., *Catal. Today*, Vol. 10, No. 1 (1991), pp. 57-71.
- (67) Zhang, G., Yamaguchi, T., Kawakami, H. and Suzuki, T., *Appl. Catal. B.*, Vol. 1, No. 3 (1992), pp. L15-L20.
- (68) Obuchi, A., Ohi, A., Nakamura, M., Ogata, A., Mizuno, K. and Obuchi, H., *Appl. Catal. B.*, Vol. 2, No. 1 (1993), pp. 71-80.
- (69) Iwamoto, M., Yahiro, H., Shin, H.-K., Watanabe, M., Guo, J., Konno, M., Chikahisa, T. and Murayama, T., *Appl. Catal. B.*, Vol. 5, No. 1-2 (1994), pp. L1-L16.
- (70) Burch, R., Millington, P. J. and Walker, A. P., *Appl. Catal. B.*, Vol. 4, No. 1 (1994), pp. 65-94.
- (71) Burch, R. and Watling, T. C., *Catal. Lett.*, Vol. 37, No. 1-2 (1996), pp. 51-55.
- (72) Shinjoh, H., Tanabe, T., Yokota, K. and Sugiura, M., *Top. Catal.*, Vol. 30, No. 1-4 (2004), pp. 319-323.
- (73) Kato, K., Kihara, T., Asamuna, T., Gotoh, M. and Shibagaki, S., *Toyota Tech. Rev.* (in Japanese), Vol. 44, No. 2 (1994), pp. 30-35.
- (74) Miyoshi, N., Matsumoto, S., Katoh, K., Tanaka, T., Harada, J., Takahashi, N., Yokota, K., Sugiura, M. and Kasahara, K., *SAE Tech. Pap. Ser.*, No. 950809 (1995).
- (75) Takahashi, N., Shinjoh, H., Iijima, T., Suzuki, T., Yamazaki, K., Yokota, K., Suzuki, H., Miyoshi, N., Matsumoto, S., Tanizawa, T., Tanaka, T., Tateishi, S. and Kasahara, K., *Catal. Today*, Vol. 27, No. 1-2 (1996), pp. 63-69.
- (76) Shinjoh, H., Takahashi, N., Yokota, K. and Sugiura, M., *Appl. Catal. B.*, Vol. 15, No. 3-4 (1998), pp. 189-201.
- (77) Konsolakis, M. and Yentekakis, I. V., *Appl. Catal. B.*, Vol. 29, No. 2 (2001), pp. 103-113.
- (78) Toops, T. J., Smith, D. B. and Partridge, W. P., *Catal. Today*, Vol. 114, No. 1 (2006), pp. 112-124.
- (79) Takahashi, N., Matsunaga, S., Tanaka, T., Sobukawa, H. and Shinjoh, H., *Appl. Catal. B.*, Vol. 77, No. 1-2 (2007), pp. 73-78.
- (80) Takahashi, N., Dohmae, K., Sobukawa, H. and Shinjoh, H., *J. Chem. Eng. Jpn.*, Vol. 40, No. 9 (2007), pp. 741-748.
- (81) Yamazaki, K., Suzuki, T., Takahashi, N., Yokota, K. and Sugiura, M., *Appl. Catal. B.*, Vol. 30, No. 3-4 (2001), pp. 459-468.
- (82) Yamazaki, K., Takahashi, N., Shinjoh, H. and Sugiura, M., *Appl. Catal. B.*, Vol. 53, No. 1 (2004), pp. 1-12.
- (83) Matsumoto, S., *Catal. Today*, Vol. 90, No. 3-4 (2004), pp. 183-190.
- (84) Matsumoto, S., Ikeda, Y., Suzuki, H., Ogai, M. and Miyoshi, N., *Appl. Catal. B.*, Vol. 25, No. 2-3 (2000), pp. 115-124.
- (85) Hirata, H., Hachisuka, I., Ikeda, Y., Tsuji, S. and Matsumoto, S., *Top. Catal.*, Vol. 16, No. 1-4 (2001), pp. 145-149.
- (86) Takahashi, N., Suda, A., Hachisuka, I., Sugiura, M., Sobukawa, H. and Shinjoh, H., *Appl. Catal. B.*, Vol. 72, No. 1-2 (2007), pp. 187-195.
- (87) Tanaka, T., Tajima, I., Kato, Y., Nishihara, Y. and Shinjoh, H., *Appl. Catal. B.*, Vol. 102, No. 3-4 (2011), pp. 620-626.
- (88) Imagawa, H., Tanaka, T., Takahashi, N., Matsunaga, S., Suda, A. and Shinjoh, H., *J. Catal.*, Vol. 251, No. 2 (2007), pp. 315-320.
- (89) Imagawa, H., Takahashi, N., Tanaka, T., Matsunaga, S. and Shinjoh, H., *Appl. Catal. B.*, Vol. 92, No. 1-2 (2009), pp. 23-29.
- (90) Tanaka, T., Amano, K., Dohmae, K., Takahashi, N. and Shinjoh, H., *Appl. Catal. A.*, Vol. 455 (2013), pp. 16-24.
- (91) Tanaka, T., Ando, C., Hamaguchi, T. and Ikuta, Y., *Appl. Catal. A.*, Vol. 464-465 (2013), pp. 296-304.
- (92) Imagawa, H., Tanaka, T., Takahashi, N., Matsunaga, S., Suda, A. and Shinjoh, H., *Appl. Catal. B.*, Vol. 86, No. 1-2 (2009), pp. 63-68.
- (93) Tsukamoto, Y., Nishioka, H., Imai, D., Sobue, Y., Takagi, N., Tanaka, T. and Hamaguchi, T., *SAE Tech. Pap. Ser.*, No. 2012-01-0370 (2012).
- (94) Hamaguchi, T., Tanaka, T., Takahashi, N., Tsukamoto, Y., Takagi, N. and Shinjoh, H., *Appl. Catal. B.*, Vol. 193 (2016), pp. 234-239.
- (95) Takahashi, N., Yamazaki, K., Sobukawa, H. and Shinjoh, H., *J. Chem. Eng. Jpn.*, Vol. 39, No. 4 (2006), pp. 437-443.
- (96) Shinjoh, H., Takahashi, N. and Yokota, K., *Top. Catal.*, Vol. 42, No. 1-4 (2007), pp. 215-219.
- (97) Sakamoto, Y., Okumura, K., Shinjoh, H., Lepage, M. and Brosda, S., *Catal. Today*, Vol. 146, No. 3-4 (2009), pp. 299-307.
- (98) Sakamoto, Y., Kumagai, H. and Matsunaga, S., *J. Appl. Electrochem.*, Vol. 43, No. 9 (2013), pp. 967-973.

## Figs. 2 and 3

Reprinted from Adv. Chem. Eng., Vol. 33 (2007), pp. 1-46, Matsumoto, S. and Shinjoh, H., Dynamic Behavior and Characterization of Automobile Catalysts, © 2007 Elsevier, with permission from Elsevier.

## Fig. 5

Reprinted from Appl. Catal., Vol. 49 (1989), pp. 195-204, Shinjoh, H., Muraki, H. and Fujitani, Y., Periodic Operation Effects in Propane and Propylene Oxidation Over Noble Metal Catalysts, © 1989 Elsevier, with permission from Elsevier.

## Fig. 9

Reprinted from J. Alloys Compd., Vol. 408-412 (2006), pp. 1061-1064, Shinjoh, H., Rare Earth Metals for Automotive Exhaust Catalysts, © 2006 Elsevier, with permission from Elsevier.

## Fig. 10

Reprinted from J. Catal., Vol. 242, No. 1 (2006), pp. 103-109, Nagai, Y., Hirabayashi, T., Dohmae, K., Takagi, N., Minami, T., Shinjoh, H. and Matsumoto, S., Sintering Inhibition Mechanism of Platinum Supported on Ceria-based Oxide and Pt-oxide-support Interaction, © 2006 Elsevier, with permission from Elsevier.

## Table 1

Reprinted from Top. Catal., Vol. 42-43, No. 1-4 (2007), pp. 215-219, Shinjoh, H., Takahashi, N. and Yokota, K., Synergic Effect of Pd/ $\gamma$ -alumina and Cu/ZSM-5 on the Performance of NO<sub>x</sub> Storage Reduction Catalyst, © 2007 Springer Nature, with permission from Springer Nature.

**Hirofumi Shinjoh**

Research Field:

- Catalyst and Catalysis

Academic Degree: Dr.Eng.

Academic Societies:

- Catalysis Society of Japan

- The Chemical Society of Japan

- Chemical Engineering of Japan

Awards:

- Award of New Technology, The Japan Society of Mechanical Engineers, 1995

- Award of Chemical Technology, The Chemical Society of Japan, 2009

